STABLE ISOTOPE DENDROCLIMATOLOGY OF NEW ZEALAND KAURI (AGATHIS AUSTRALIS (D. DON) LINDL.) AND CEDAR (LIBOCEDRUS BIDWILLII HOOK. F.)

A thesis submitted in partial fulfilment of the requirements for the Degree of

Doctor of Philosophy in Geology

at the University of Canterbury

by T. H. Brookman

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Always appreciate good equipment in the field; Tim Stahl with the ‘nail of destiny’.
ABSTRACT

This thesis presents research that improves our understanding of the relationship between climate and tree-ring stable isotopes in New Zealand kauri (Agathis australis (D. Don) Lindl.) and cedar (Libocedrus bidwillii Hook. F). As a whole, this research creates a framework from which future investigations of stable isotope dendroclimatology can pursue at high temporal resolution across longer term temporal intervals. Such a framework is required to realize the full potential of New Zealand tree-ring records as archives of palaeoclimatic information. In the Southern Hemisphere, mid-to-high latitude terrestrial climate proxy records are sparse; the long-lived endemic conifers of New Zealand present a rare opportunity to gain valuable insight into Late-Quaternary and Holocene climatic change.

A major barrier to long stable isotope dendroclimatic proxy records has been the time-and-resource intensive nature of associated sample preparation and analytical processes. Through experimental assessment of the SBrendel α-cellulose extraction method, this research demonstrates that this simple processing method can, with some caveats, be successfully applied to resinous conifers, facilitating rapid chemical preparation of samples. Further efficiency gains are documented in through use of dual element low temperature pyrolysis of cellulose, providing carbon and oxygen stable isotope determinations on a single sample, rather than the traditionally separate analyses. These preliminary investigations into methodological efficiency enabled the ~3000 stable isotope determinations on kauri and cedar, on which the following investigations into isotopic variability, chronology quality and climate-isotope relationships are based.

Both kauri and cedar exhibit substantial intra and inter-tree isotopic variability, resulting in greater than normal sample numbers being required to isolate the common variance in composite time-series. Despite sampling 7 trees (18 cores) at one site and 8 trees (21 cores) at another, only oxygen isotope time-series reach an Expressed Population Signal score of 0.85, a common benchmark of chronology quality. Further investigations using high-resolution sequential sampling of single rings show that this variability extends to a sub-annual scale. Within single rings there are large ranges in δ\(^{13}\)C and δ\(^{18}\)O, generally corresponding with regular annual cycles of up to 4.6‰ for δ\(^{13}\)C and 8.1‰ for δ\(^{18}\)O. These data show high frequency (sub weekly) changes in δ\(^{18}\)O, demonstrating sufficiently fine resolution for event-to-seasonal scale climate/weather reconstruction. However, that potential is complicated by the lack of strong climatic correlations with isotopic cycles.

Due to their stronger common signal, δ\(^{18}\)O time series are investigated for inter-annual stable isotope dendroclimatic reconstruction from kauri and cedar. Bootstrapped correlation and multiple regression models show strong relationships between kauri and cedar δ\(^{18}\)O and relative humidity, accumulated rainfall and soil moisture deficit. The correlations are strongest for all variables during the period from Autumn prior to growth to the current growth summer. Tree-ring δ\(^{18}\)O in kauri and cedar is identified as an effective recorder of regional hydroclimate leading up to and during the Austral growth season.

While it is demonstrated that tree-ring δ\(^{18}\)O holds significant promise for inter-annual palaeoclimate reconstruction, it is equally apparent from this research that stable isotope dendroclimatology in New Zealand faces significant challenges. Foremost is gaining an improved understanding of seasonal dendrochemical cycles and their relationship with tree-physiology. Increasing the spatial and temporal coverage of tree-ring isotope records is vital to realising New Zealand’s vast potential for stable isotope dendroclimatic reconstruction.
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Brookman and Whittaker co-designed the experiment and Brookman secured research funding. Brookman conducted ~75% of FTIR analyses, ~50% oxygen stable isotope analyses and all carbon stable isotope analyses. Brookman drafted the text and figures with revisions and comments from Whittaker.

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Brookman led experimental design (with contributions from Horton, Palmer and Lorrey), secured funding and led fieldwork (aided by Palmer). Brookman prepared core material. Fenwick compiled ring-width chronology. Brookman prepared samples for analysis, modified and tested analytical equipment (with advice from Horton and Evans) and conducted all analyses. Brookman conducted data analysis and drafted the text and figures with revisions and comments principally from Horton, Lorrey, Evans and Palmer.

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Candidate contribution: (90%)  
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**Chapter 7**
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Name: Travis W Horton
Signature: [Signature]
Date: 29/11/2013
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1. INTRODUCTION

1.1 Thesis Structure

This thesis is laid out as an introduction to stable isotope dendroclimatology, with specific reference to New Zealand’s research potential, followed by a series of focussed, manuscript-style chapters which are then brought together in a research synthesis. Each manuscript is necessarily self-contained and answers a discrete set of questions. These chapters are presented such that those questions, addressed progressively, add new layers of understanding, ultimately creating an integrated research progression. The bullet points below denote this progression, chapter by chapter. The subsequent section expands on those bullet points, outlining the chapters’ integrated contributions to three broad and inter-related research goals, including a detailed abstract for each analytical chapter.

Chapter 1 – previews the thesis structure and contains abstracts for analytical chapters (3-6).

Chapter 2 – reviews the relationships between tree-ring isotopes and climate with reference to potential applications in palaeoenvironmental study within New Zealand.

Chapter 3 – investigates the effective isolation of α-cellulose from resinous woods using the Standard Brendel method, modified for small samples.

Chapter 4 – continues the description of methods employed within this research, with an introduction to dual-element low-temperature pyrolysis analysis. The resulting isotope determinations provide a detailed account of carbon and oxygen stable isotopic variability within and between New Zealand kauri (Agathis australis) and cedar (Libocedrus bidwillii).

Chapter 5 – is an evaluation of the potential for climatic reconstruction from kauri tree-ring oxygen and carbon stable isotopes on event-to-seasonal resolutions. Potential sub-annual-sampling biases are evaluated using observed and modelled data, while monthly growth models are used to investigate potential climatic drivers of seasonal isotopic patterns.

Chapter 6 – further investigates the most promising records from Chapter 4; three ~28-29 year interannual oxygen isotope time-series are compared with local climate records.

Chapter 7 – synthesises the research, evaluating its strengths and weaknesses, and makes recommendations for future stable isotope dendroclimatology in New Zealand.

1.2 Specific Research Goals

This research seeks to provide baseline information on the suitability of two New Zealand tree species
for stable isotope dendroclimatic reconstruction. To achieve this, the thesis focuses on 3 key areas, each answering a number of specific questions:

1) Adapting and improving dendrochemical research methodologies for New Zealand conifers:
   
a. Can the SBrendel α-cellulose extraction method yield cellulose of a suitable and consistent quality from highly resinous New Zealand kauri (CH 3)?

   b. Can reproducible, precise stable isotope determinations be made on α-cellulose using a dual element low temperature pyrolysis approach (CH 4)?

2) Documenting and interpreting natural isotopic variability within and between trees and its implications for chronology development:

   a. How variable are intra-tree kauri and cedar δ¹³C and δ¹⁸O values (i.e. between cores/radii)? (CH 4)

   b. How variable are inter-tree kauri and cedar δ¹³C and δ¹⁸O values within a tree stand? (CH 4)

   c. Do composite stable isotopic time-series from kauri and cedar provide robust common signals? (CH 4)

   d. Is there a clear intra-annual cycle for kauri δ¹³C and δ¹⁸O and does the isotopic mean and/or amplitude of this cycle vary between regions? (CH 5)

   e. What are the implications for sub-annual sampling strategies? (CH 5)

3) Evaluating the potential for climate-isotope correlations based on the most promising isotope time-series and modern weather data.

   a. Do kauri and cedar record similar patterns of inter-annual isotopic composition? (CH 4)

   b. Do intra-annual data achieve a resolution that could enable event-scale reconstruction using kauri? Are event-scale changes evident in the data? (CH 5)

   c. What potential does kauri have for reconstructing seasonal climate cycles? (CH 5)

   d. Do inter-annual δ¹⁸O time-series from kauri and cedar near Dunedin correlate with contemporary climate data over the 1983-2011 period (CH 6).

The progress towards each of these research goals within the thesis chapters 3-6 is outlined below (Table 1.1, section 1.3).
Introduction

1.3 Chapter Abstracts

Detailed methodological investigation was not part of the original concept behind the research presented here, which focussed on palaeoclimate reconstruction. However, it quickly became evident that to achieve robust palaeoclimate reconstructions, the refinement of processing and analytical methods to rapidly and effectively analyse tree-ring α-cellulose from New Zealand conifers was necessary.

Chapter 3: Stable isotope dendroclimatology using α-cellulose has unique potential to deliver multi-millennial-scale, sub-annually-resolved, terrestrial climate records. However, lengthy processing and analytical methods often preclude such reconstructions. Variants of the Brendel extraction method have reduced these limitations, providing fast, easy methods of isolating α-cellulose in some species. Here, we investigate application of Standard Brendel (SBrendel) variants to resinous soft-woods by treating samples of kauri (Agathis australis), ponderosa pine (Pinus ponderosa) and huon pine (Lagarostrobus franklinii), varying reaction vessel, temperature, boiling time and reagent volume. Numerous samples were visibly ‘under-processed’ and Fourier Transform infrared spectroscopic (FTIR) investigation showed absorption peaks at 1520cm\(^{-1}\) and ~1600cm\(^{-1}\) in those fibers suggesting residual lignin and retained resin respectively. Replicate analyses of all samples processed at high temperature yielded consistent δ\(^{13}\)C and δ\(^{18}\)O despite color and spectral variations. Spectra and isotopic data revealed that α-cellulose δ\(^{13}\)C can be altered during processing, most likely due to chemical contamination from insufficient acetone removal or formation of cellulose acetate. In some cases it appears that δ\(^{13}\)C can be depleted without obvious physical signs, while the most depleted samples obtained a pasty consistency. Reagent amount, temperature and extraction time all influence δ\(^{18}\)O, however, and our results demonstrate that different species may require different processing methods. FTIR prior to isotopic analysis is a fast and cost effective way to determine α-cellulose extract purity. Furthermore, a systematic isotopic test such as we present here can also determine sensitivity of isotopic values to methodological variables. Without these tests, isotopic variability introduced by the method could obscure or ‘create’ climatic signals within a data-set.
Traditionally, determination of oxygen and carbon stable isotope ratios in organic samples are separate processes. Recently, however, promising studies have determined carbon and oxygen stable isotope ratios from a single sample, lowering costs and reducing analytical time. The setup and subsequent performance of a dual element low-temperature pyrolysis system at the University of Canterbury is covered in Chapter 4 and Appendices 9 and 10. Once the capacity to effectively and efficiently process and analyse tree-ring cellulose samples was established, the logical progression was to establish a fundamental understanding of whether robust climate reconstruction could be achieved from kauri and cedar tree-ring isotopes. The stable isotopic variability within kauri and cedar are characterised at a number of different levels, and the implications for sample depth and signal strength are assessed.

Chapter 4: Tree-ring archives provide important opportunities to understand and identify perturbations in earth system processes through calendar-dated dendrochemical records of pre-historic environmental change. However, determining the natural variability in tree-ring proxy data, both within and between individual trees, is a crucial step prior to embarking on prehistoric reconstructions for a specific region. We report ~2500 low temperature pyrolysis dual carbon and oxygen stable isotopic compositions for two long-lived, endemic New Zealand species: kauri (Agathis australis) and cedar (Libocedrus bidwillii). These data provide insights into the stable isotopic variability in two dendroclimatic target species at various temporal and spatial scales: intra-tree variability within two species, inter-tree within two tree-stands and inter-annual between two species growing in the same region. Intra-tree analyses show that circumferential variability within a ring in kauri is up to 2.9‰ in δ\(^{13}\)C and 6.3‰ in δ\(^{18}\)O and 3.2‰ in δ\(^{13}\)C and 3.7‰ in δ\(^{18}\)O for cedar. These circumferential differences are larger than the variability found between trees for cedar δ\(^{13}\)C and δ\(^{18}\)O and kauri δ\(^{18}\)O. Expressed population signal (EPS) analyses of our datasets demonstrate that δ\(^{18}\)O time-series co-vary more than δ\(^{13}\)C but that even δ\(^{18}\)O records from multiple cores from 7-8 trees barely meet the EPS >0.85 criteria. δ\(^{18}\)O records are strongly and significantly correlated between species despite microclimatic differences, and a bispecies composite record shows a significant correlation with relative humidity. These results suggest that kauri and cedar stable oxygen isotope compositions are promising archives of regional environmental conditions in the dynamic climate system of the mid-latitude western South Pacific/Southern Ocean.

A potential contributor to variability within and between trees is intra-annual isotopic change. Potential errors introduced by sampling schemes are evaluated by comparing early-season and whole-ring observed data, and through the modelling of seasonal changes using high-resolution data. The use of monthly growth models facilitates investigation into the seasonal influences of climate on intra-annual isotopic patterns, with additional insight from mechanistic modelling of oxygen isotope signals. The additional influence of physiological processes in driving seasonal cycles is briefly addressed; this is an area that requires significant further research.

Chapter 5: Determining the connections between long-term climate change and anomalous weather events remains one of the major challenges to climate change science. Tree-ring records are particularly attractive stable isotope-based proxies for high frequency climate/weather events as individual rings can
be serial sub-sampled at intra-annual resolution for cross-dated calendar years. Intra-annual δ\textsuperscript{13}C and δ\textsuperscript{18}O determinations from New Zealand kauri (*Agathis australis*) are presented here and their implications for seasonal and/or event scale reconstruction are considered. Employing a simple sampling scheme, sub-weekly resolution was achieved from kauri and clear annual cycles in δ\textsuperscript{13}C and δ\textsuperscript{18}O of up to 4.6‰ for the former and 8.1‰ for the latter, were documented. There were significant differences in δ\textsuperscript{13}C and δ\textsuperscript{18}O means between early-season and whole-ring samples as a result of seasonal cycles, suggesting that sub-annual sampling schemes can be used to capture distinct seasonal periods. High-resolution serial samples showed large (~2‰) δ\textsuperscript{18}O changes between consecutive samples, suggesting high-frequency forcing of the δ\textsuperscript{18}O of tree-ring cellulose. However, despite these promising results, neither δ\textsuperscript{13}C nor δ\textsuperscript{18}O intra-annual time series were strongly correlated with recorded instrumental climate data or mechanistically modelled δ\textsuperscript{18}O, suggesting the seasonal cycle may in fact be largely non-climatic. The relative influence of climate and physiological processes is crucial to establish if high-resolution palaeotempestological or seasonal climate reconstructions are to be achieved from kauri.

*The preliminary climate relationships observed in Chapters 4 and 5 are built upon with a more detailed exploration of early-wood and whole-ring inter-annual oxygen isotope records.*

**Chapter 6:** New Zealand sits at the junction of several major Southern Hemisphere atmospheric and oceanic circulation systems. Consequently, its long lived endemic conifers represent a rare opportunity to reveal high resolution terrestrial records of Holocene and late-Quaternary circulation and climate changes from the mid- to high-latitudes of the Southern Hemisphere. This manuscript reports stable oxygen isotope compositions for early-wood and whole-ring samples from seven New Zealand kauri (*Agathis australis*) and whole-ring samples from eight New Zealand cedar (*Libocedrus bidwillii*), from sites in eastern Otago, South Island, New Zealand (~46°S). Bootstrapped correlations and multiple regression models are used to assess the direction and strength of relationships between local climatic variables, regional circulation indices and tree-ring oxygen isotope compositions. These results show that kauri and cedar are sensitive to changes in relative humidity, soil moisture deficit and rainfall amount. While the strongest correlations between the two species and climate variables occur at different times of year, they are generally characterised by a pair of peaks - one during the Autumn/Winter prior to the Austral growth season and the other peak during the Austral growth season (Spring/Summer). Accumulated antecedent and growth-season rainfall, evaporative enrichment of soil water and leaf-water combine to create a promising multi-species record of regional hydroclimate.
2. AN INTRODUCTION TO STABLE ISOTOPE DENDROCLIMATOLOGY WITH PARTICULAR REFERENCE TO NEW ZEALAND’S POTENTIAL

This chapter provides an overview of the literature about stable isotopes and dendroclimatology. Subsequent chapters draw on this information and discuss certain aspects in greater detail. Below, a review of tree-rings is presented, followed by a review of stable isotope theory and its application to palaeoenvironmental investigation. The chapter concludes with a discussion of stable isotope dendroclimatology in New Zealand with a focus on the tree species that have the greatest potential for application.

2.1 Tree Rings, Dendrochronology and Dendroclimatology

Dendrochronology is an established scientific discipline based on dating events using annual growth rings formed in trees in response to seasonal/annual climatic cycles. Its modern foundation was established by A.E. Douglass in the early 1900’s when he developed and documented the system of cross-dating, the practice of matching observed growth patterns between trees (Speer, 2010). Over the past century, dendrochronology has grown significantly, with major advances in measurement techniques, particularly with the statistical power of computers in the late 20th century (Speer, 2010).

The bulk of dendrochronology is performed on trees with annual growth rings. The first trees with discernible rings, predecessors of modern conifers, appeared during the Devonian (395-345 Ma) (Schweingruber, 1988). Since then many tree species have shown a tendency toward annual growth rings although their environmental responsiveness varies according to family, genus and species. Tropical trees, due to the relatively constant availability of heat and moisture year round, display large growth increments generally perforated by large pores and without distinct annual patterns. In contrast, many temperate species and some species from seasonally dry tropics only have several months of optimal growing conditions and form distinct tree-rings with smaller pores, based on environmental shifts which often align to seasonal or annual cycles (Schweingruber, 1988).

The annual rings of temperate species are often conceptually divided into early-wood and late-wood, the former laid down during the fast early-season growth during spring and the latter laid down as the tree approaches dormancy during autumn or early winter (Stokes and Smiley, 1968). In latewood, the walls of tracheid cells are more robust than in earlywood and their cavities are smaller; this results in more tightly spaced cells, and the increased density manifests visually as a dark band that typically represents the ‘end’ of an annual growth-ring.

The long-term seasonal shifts evident in earlywood and latewood production belie a tree’s response to its environment; trees often respond to environmental changes within a matter of minutes and while such
rapid reactions are not recorded in tree-rings, their combined signal over longer periods is preserved (Schweingruber, 1988). This complex integration of information is the signal that climate scientists attempt to decipher when interrogating the tree-ring archive for dendroclimatology. Dendroclimatology uses the tree’s systematic growth-responses to certain environmental variables that promote, or restrict growth. Annual ring-widths are compared with observed climatic data to establish which variables tree primarily responds to, and these can then be reconstructed back through time.

Traditional dendrochronology has used ring-width, cell size and cell density measurements to assess trees’ interaction with climate, generally related to temperature, moisture availability and other growth-limiting factors. The complexity of the signal in ring-width records, often incorporating a number of climatic factors, is added to by the fact that the tree’s buds, sugars and hormones, influenced by the climate of one season, respond over multiple seasons (Schweingruber, 1988). The climatic influence on growth in a given year can be gradually incorporated into the ring-width record across the subsequent ring(s) (Schweingruber, 1988).

The common environmental conditions that occur each year across broad spatial ranges influence the growth of trees, and year-to-year climate is variable. Ring width patterns from local or regional groups of trees often reflect this variability and the changeable pattern through time can be cross-dated (matched between trees). Ultimately, linking patterns from living trees to recently dead trees to trees that died long ago can provide precise, annual dates for each tree ring, with numerous chronologies around the world exceeding a thousand years in length (Friedrich et al., 2004; Boswijk et al., 2006; Stambaugh and Guyette, 2009; Loader et al., 2013a; ITRDB, 2014). The ability to precisely date events in this fashion has led to dendrochronology’s application in many fields including archaeology, palaeoclimatology, geomorphology, glaciology, volcanology, fire history and hydrology. It is far too broad a field to be thoroughly reviewed in this thesis which focuses on stable isotopes but readers can refer to Speer’s (2010) recent detailed review of dendrochronology and dendroclimatology.

2.2 Stable Isotopes in Tree-Rings as Environmental Recorders

In recent decades researchers have increasingly delved deeper into tree-ring records, moving beyond ring-width investigations to more sophisticated approaches that utilise a variety of techniques including X-ray densitometry (Polge, 1970; Schweingruber et al., 1978; Yuan et al., 2013), blue-light reflectance (Campbell et al., 2007) and the measurement of wood properties such as tracheids radial diameter and microfibril angle (Drew et al., 2012) in order to refine understanding of the links between tree-growth and environmental conditions. Increasingly, tree-ring research has incorporated studies of the chemistry of growth rings and the study of stable isotopes has become one of the fastest growing areas of dendro-science (Speer, 2010) as well as the related disciplines of plant ecology and ecophysiology (Adams and Grierson, 2001).

Stable isotopes are those that, due to the balance of protons and neutrons in their nuclei, that retain their
structure through time, rather than decaying like radioactive isotopes (Hoefs, 2004) (most prominently 14C). Provided no chemical or structural damage (diagenesis) occurs to the material selected for analysis, the ratios of stable isotopes incorporated in the material at the time of its formation can preserve an unchanged signal indefinitely (Hoefs, 2004). The interpretation of stable isotopes is based on the process of fractionation, which determines the ratios of isotopes within a material. Molecules of naturally occurring compounds exhibit subtle chemical and physical characteristics related to the strength of their chemical bonds. Molecules containing a relatively higher proportion of rarer heavy isotopes are slower to react as their chemical bonds are stronger (Hoefs, 2004). This is the fundamental basis for mass-dependent fractionation: a process during which one isotope is preferred over another, thus causing the isotopic ratio in the molecule to change as the process occurs. Common examples of mass-dependent fractionation include: crystallization, evaporation, osmosis and metabolism (Lowe and Walker, 1997). The resulting isotopic ratios can then be compared with other samples, both of which must be compared to a standard reference material of constant isotopic composition, to reveal fractionation processes.

Stable isotope ratios are typically expressed in delta-notation, which takes the form δxY, where δ means ‘relative abundance of’ and ‘Y represents the heavier, less abundant isotope (x) of the element (Y).

The research presented in this thesis focuses on the stable isotopes of carbon and oxygen; δ13C (δ18O) should be read as ‘the relative abundance of 13C (18O) compared to 12C (16O), relative to the standard and measured in ‰ (‘per mil’ or ‘parts per thousand’), as described by:

\[
\text{Eqn. 1: } \delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000,
\]

where R (Ratio) is 13C/12C or 18O/16O. Delta values throughout this thesis are expressed relative to the Vienna Pee Dee Formation Belemnitella (i.e. V-PDB) fossiliferous carbonate standard for carbon, and Vienna Standard Mean Ocean Water (V-SMOW) (Coplen et al., 1983) for oxygen.

For tree-ring cellulose, it is now reasonably well established that the stable isotope signatures in cellulose reflect a combination of environmental forcing factors. Stable isotope proxies are particularly attractive complements to traditional dendrochronology approaches as they have been shown to respond to a more limited and predictable set of environmental variables (McCarroll and Loader, 2004; 2005; see 2.2.1 and 2.2.2), resulting in significant correlations with climate in areas where ring-width records have been of limited value (Young et al., 2012). In addition, their application generally requires fewer cores to achieve a statistically robust common signal (McCarroll and Loader, 2004; 2005; Gagen et al., 2011 and references therein), measured by the Expressed Population Signal (EPS) (Wigley et al., 1984; Briffa and Jones, 1990; Chapter 4). Often as few as 4-6 cores provide an EPS >0.85 (Leavitt and Long, 1984; McCarroll and Loader, 2004; Gagen et al., 2011; Chapter 4) where 5-25 cores were generally required for ring-width chronologies (Briffa and Jones, 1990).

In addition to generally requiring fewer cores to retrieve a robust common signal than ring-widths, tree-ring isotopes at least partially overcome ring-width dendrochronology’s Achilles heel, the ‘segment length curse’ (Cook et al., 1995). This ‘curse’ is related to the fact that the maximum wavelength of recoverable
climatic information is constrained by the length of the shortest series contained within a chronology (Cook et al., 1995). Non climatic factors such as ageing, stand structure and site conditions all influence low frequency changes in ring-width chronologies and their removal through standardisation techniques, designed to focus on high frequency climatic changes, necessarily removes low frequency climatic information (Cook et al., 1995). Generally speaking, tree-ring isotopes are less sensitive to age-related low frequency changes, meaning that long chronologies can be used without standardisation, retaining low-frequency climatic information (Loader et al., 2013a; Loader et al., 2013b).

The exception to tree-ring isotopes’ relative age insensitivity is the isotope ‘juvenile effect’ (McCarroll and Loader, 2004; Leavitt, 2010; Loader et al., 2013b). While there is limited evidence for age-related effects pertaining to oxygen isotopes (Treydte et al., 2006; Leavitt, 2010), the effect has been observed in carbon isotope records from the juvenile rings of numerous species (Jansen, 1962; Grinsted and Wilson, 1979; Schleser and Jayasekera, 1985) and has been variously attributed to changes in the carbon isotope ratios of CO$_2$ as plants move up from sub-canopy to canopy emergent (Schleser and Jayasekera, 1985), changes in canopy shading (Francey and Farquhar, 1982) and/or hydraulic conductivity (McDowell et al., 2011). As yet, no consensus on the cause, or whether there is a single, unifying cause for the widespread effect, has been reached (McCarroll and Loader, 2005; Gagen et al., 2007; Leavitt, 2010). Generally speaking, however, the juvenile effect has been dealt with through the removal of ‘juvenile’ rings, constituting the early decades (20-80 years) of tree growth (Leavitt and Long, 1985; Hemming et al., 1998; Raffalli-Delerce et al., 2004; Leavitt, 2010). For kauri, however, early evidence suggests that the juvenile effect can last for over 200 years (Jansen, 1962), and consequently, care is required as chronologies are developed within New Zealand. The development of those chronologies will be based on the observed relationships between $\delta^{13}C$, $\delta^{18}O$ and environmental fractionation processes, summarised below in 2.2.1, 2.2.2 and figures 2.1 and 2.2 and explored in more detail in Chapters 4-6.

2.2.1 Oxygen Isotopes in Tree-Rings

When a tree takes up water through its roots, the water is transported up through the xylem into the leaves where evapotranspiration and physiological processes cause internal oxygen isotope fractionation. The oxygen isotope signal in a tree, therefore, reflects a combination of internal effects and external changes in the isotopic signature of the water available to the tree (i.e. the ‘source’ water). The environmental factors associated with changes in $\delta^{18}O$ can therefore be separated into two stages (Yakir, 1992):

1) factors influencing fractionation that occurs before uptake by the tree; and

2) factors influencing fractionation that occurs as part of the tree’s physiological processes.

Fractionation processes that fall within the first group can further be divided into primary and secondary groups. The primary control can be considered as the isotopic composition of the water source, generally defined by the evaporative source (e.g. tropical vs. high latitude) of water vapour that later condenses and falls as rainfall or snow. The general pattern for precipitation is that air masses of equatorial origin
carry isotopically ‘heavier’ water than air masses of high latitude origin. This occurs because the greater insolation at the equator provides more energy for the heavier H$_2^{18}$O molecules to be evaporated while in high latitudes there is a larger fractionation in favour of the lighter H$_2^{16}$O molecule during evaporation (Dansgaard, 1964; Rozanski et al., 1993; Darling et al., 2005).

Overprinting this source-region signal are secondary fractionation processes determined at or en-route to the site. The ‘temperature effect’, particularly prevalent at high latitudes, describes the preferential re-evaporation of H$_2^{18}$O from rainfall before it reaches the ground; higher temperatures mean increased re-evaporation, leading to $\delta^{18}$O increases in precipitation (Fricke et al., 1998). Similarly based on H$_2^{18}$O’s tendency to precipitate more effectively are the ‘continental’ and ‘amount’ effects. The ‘continental’ effect describes the trend for $\delta^{18}$O in an air mass to decrease with increasing distance from the moisture source, due to the preferential loss of H$_2^{18}$O in successive rainfall events (Siegenthaler, 1979). The ‘amount
effect’ describes the process by which preferential rain-out of $\text{H}_2^{18}\text{O}$ means that $\delta^{18}\text{O}$ decreases with increasing rainfall at high temperatures (Dansgaard, 1964; Rozanski et al., 1993). Both the ‘continental’ and ‘amount’ effects can be considered, along with orographically driven rain-out of $\text{H}_2^{18}\text{O}$, as part of the Rayleigh distillation effects (Sharp, 2007). Subsequent to the various precipitation fractionation effects, further fractionation of water oxygen can occur at the site prior to uptake by the tree. This primarily occurs through evaporative enrichment of surface and soil-water (see Fig. 2.1).

Once water reaches a tree, the physiological controls on $\delta^{18}\text{O}$ are largely driven by the tree’s evapotranspirative systems (Yakir, 1992; Figure 2.1). When considering tree-ring cellulose, a further fractionation needs to be considered. The $\delta^{18}\text{O}$ of stem water does not undergo fractionation during uptake, and is a mixture of groundwater and meteoric water taken up by the roots. The $\delta^{18}\text{O}$ of leaf water, on the other hand, is modified by evaporation in the leaf prior to photosynthetic production of the sucrose subsequently used to make xylem $\alpha$–cellulose (Evans and Schrag, 2004). This process results in a constant $\sim+27\%$ fractionation during production of cellulose (Epstein et al., 1977; DeNiro and Epstein, 1981). While this fractionation is complex and may vary slightly between species (Sternberg et al., 2006), it is of limited importance for dendroclimatology as it is unlikely to affect the magnitude or direction of inter and intra-annual changes in $\delta^{18}\text{O}$.

In the absence of large inter-annual changes in source water $\delta^{18}\text{O}$, inter and intra-annual tree-ring $\delta^{18}\text{O}$ changes are generally considered to be driven by evapotranspiration, and thus largely reflect shifts in a tree’s stomatal conductance and/or the vapour pressure difference between the leaf and the atmosphere (Roden et al., 2000; McCarroll and Loader, 2004; Barbour, 2007). In practical terms, this means that relative humidity, which influences both the aforementioned factors, is the major climatic control on leaf-water, and therefore, tree-ring $\delta^{18}\text{O}$.

The simplicity of that relationship, however, is deceptive; many questions relevant to the interpretation of oxygen isotopes in tree rings remain unanswered. Some are methodological and are discussed in Chapters 3 and 4, while others are related to tree physiology and are addressed, in part, in Chapter 5. For instance, the fraction of water oxygen which does not undergo isotopic re-equilibration with leaf water prior to fixation as $\alpha$–cellulose has been observed to vary with both time and species (Roden et al., 2000; Barbour et al., 2004). Furthermore, the differential/preferential use of meteoric, soil and groundwater by trees is generally unknown, as are seasonal growth patterns and inter-seasonal photosynthate use. This complex array of factors is largely why pilot studies linking isotopic data with modern meteorological data are important whenever a new species or new environmental context is being developed for longer term study.

The complexity of tree-ring $\delta^{18}\text{O}$ records are increasingly being deconvolved through the use of mechanistic models (Roden et al., 2000; Barbour et al., 2004; Cernusak et al., 2005; Cuntz et al., 2007; Saurer et al., 2012). Recent advances in the understanding of how oxygen isotope fractionations occur within leaf water and the subsequent inclusion of leaf water oxygen into tree-ring cellulose have enabled rapid progress in the mechanistic modelling and interpretation of tree-ring cellulose $\delta^{18}\text{O}$, although further
knowledge of the transfer of isotope signals from the leaf to heterotrophic tissues is still required (Gessler et al., 2013). Mechanistic models provide a means of comparing observed datasets to expected, modelled datasets based on the climatic parameters observed at a site (Evans, 2007). Early models focussed on relative humidity as the major driver of leaf-water fractionation (Roden et al., 2000) and while this remains the case, models have since been refined to include the influences of the Péclet effect (Barbour et al., 2004) (see below) and to account for temperature dependence of the diffusivity of water isotopologues (Cuntz et al., 2007; Sternberg, 2009; Waterhouse et al., 2013).

The development and improvement of mechanistic models is a field of plant physiology that can make large contributions towards advancing the field of stable isotope dendroclimatology. Barbour et al.’s (2004) model, refined to include Cuntz et al.’s (2007) temperature dependence, is applied in Chapter 5 as a tool for assessing the reliability of observed data, as well as the relative importance of climate and plant physiology to intra-annual δ¹⁸O changes in long-lived New Zealand conifers. The use of mechanistic modelling in this thesis necessitates a review of the model and its rationale here. However, a detailed improvement/refinement of mechanistic models to improve understanding of plant physiology for the species studied is beyond the scope of this thesis. The review provided here is based on a dendroclimatic ‘need-to-know’ synthesis of the elegant and detailed discussions of mechanistic models published by Barbour (2007) and Sternberg (2009). Readers interested in further detail should consult those texts or, for a more accessibly written description for the non-physiologist, McCarroll and Loader’s (2004) review.

In the broadest sense, the δ¹⁸O of cellulose is ultimately determined at three levels:

1) the δ¹⁸O of (soil) water taken up by the tree;

2) changes in the δ¹⁸O of that water due to evapotranspirative enrichment of leaf-water; and

3) the combination of leaf-water and xylem water (essentially unmodified soil water) at the site of cellulose synthesis.

The following discussion of mechanistic modelling of tree-ring cellulose δ¹⁸O focuses on levels 2 (enrichment above soil water) and 3 (cellulose synthesis).

**Enrichment of leaf-water above soil water**

The enrichment of leaf water above source water (Δ¹⁸Oₑₛ) is commonly described by a modified version of Craig and Gordon’s (1965) model for evaporative enrichment of free surface water

$$\text{Eqn. 2: } \Delta^{18}O_{es} = \epsilon_+ + \epsilon_k + (\Delta^{18}O_v - \epsilon_k) e_a/e_i$$

where \(\epsilon_k\) is the kinetic fractionation during diffusion through the stomata and leaf-boundary layer, \(\epsilon_+\) is the proportional depression of water vapour pressure by the heavier \(\text{H}_2^{18}\text{O}\) molecule and \(\Delta^{18}O_v\) is the oxygen isotope composition of atmospheric water vapour relative to source water. The relationship
is scaled by $e_a/e_i$, the ratio of ambient to intercellular vapour pressure (McCarroll and Loader, 2004; Barbour, 2007).

The proportional depression of water vapour pressure by the heavier $\text{H}_2\text{H}^{18}\text{O}$ molecule (or ‘equilibrium fractionation factor’, $\xi^+$) is dependent on leaf temperature ($T_l$) measured in K (Kelvin).

\textbf{Eqn. 3:} $\xi^+ (\text{‰}) = 2.644 - 3.206(10^3/T_l) + 1.534(10^6/T_l^2)$

The kinetic fractionation controlled by diffusion through stomata and leaf boundary layer (i.e. $\xi_k$) is dependent on stomatal ($g_s$) and boundary layer ($g_b$) conductances of water vapour.

\textbf{Eqn. 4:} $\xi_k = (32g_s^{-1} + 21g_b^{-1})/(g_s^{-1} + g_b^{-1})$

In well mixed conditions, $\Delta^{18}\text{O}_v$ is often close to $\xi^+$, meaning that $\Delta^{18}\text{O}_{es}$ is linearly dependent on $1 - e_a/e_i$. Given that $e_a/e_i$ is the ratio of ambient to intercellular vapour pressures, which is largely determined by relative humidity, if all else is equal, there should be a strong negative relationship between $\Delta^{18}\text{O}_{es}$ (and therefore, ultimately, tree-ring $\delta^{18}\text{O}$) and relative humidity (Barbour, 2007). This relationship is strengthened by the fact that $\xi_k$ is largely influenced by $g_s$ (stomatal conductance) which is also linked to relative humidity.

Equation 2 generally predicts leaf water enrichment well but numerous discrepancies between predicted and measured leaf water $\delta^{18}\text{O}$ have been observed (Barbour, 2007; Sternberg, 2009). There are numerous published explanations for these discrepancies (see Barbour, 2007 p84) that ultimately can be related to the transpiration dependent convection of unenriched water to the evaporating sites opposed by backward diffusion of the heavier isotope $\text{H}_2\text{H}^{18}\text{O}$, known as a ‘Péclet Effect’ (McCarroll and Loader, 2004; Barbour, 2007; Sternberg, 2009).

The Péclet Effect ($\rho$) is defined by the ratio of convection to diffusion

\textbf{Eqn. 5:} $\rho = (LE)/(CD)$

where $L$ is the ‘effective length’ over which the Péclet Effect is evident, $E$ is the leaf transpiration rate in mol m$^{-2}$ s$^{-1}$, $C$ is the molar density of water (55.5 x 10$^3$ mol m$^{-3}$) and $D$ is the diffusivity of $\text{H}_2^{18}\text{O}$ in water (2.66 x 10$^{-9}$ m$^2$ s$^{-1}$).

Although it provides a significant step forward in explaining discrepancies between modelled and observed leaf water $\delta^{18}\text{O}$ in tightly controlled laboratory environments, the practical relevance of the Péclet Effect in stable isotope dendroclimatology is limited. Generally, in environments where source water $\delta^{18}\text{O}$ is variable, the influence of the Péclet Effect on observed and modelled $\delta^{18}\text{O}$ is minimal (Barbour et al., 2004). Given that mean monthly $\delta^{18}\text{O}$ of rainfall measured by the International Atomic Energy Agency at Invercargill, ~150km from the sites focussed on in this thesis, varies between -8.23‰ (June) and -6.01‰ (December), with a range of -13.25 to -3.19‰ (IAEA/WMO, 2013), Consequently,
the further intricacies of calculating the Péclet Effect, including the detailed calculation of L are
considered unnecessary for this review, as their influence is likely to be minimal. See Barbour et al.
(2004) and Barbour (2007) for further discussion on the estimation of ‘effective length’ (L), the tortuous
path followed by water through the leaf to the site of evaporation.

**Cellulose synthesis**

If tree-ring cellulose oxygen was wholly derived from leaf water, relative humidity would be the primary
control on cellulose δ^{18}O due to its control of evapotranspirative enrichment of leaf water. However,
cellulose formation incorporates a mixture of leaf-water and xylem/stem water, in a ratio that varies
between species. Sucrose exported from the leaf is generally in equilibrium with leaf water (Barbour,
2007). To form cellulose, that sucrose is broken down into hexose molecules, freeing up ~20% of
oxygen to re-exchange with free water in the developing cell. A portion of those hexose molecules
do not immediately form cellulose, however, instead going through a series of repetitive, futile cycles,
facilitating further re-exchange with stem/xylem water in the cell. This process has been modelled by
Barbour and Farquhar (2000). To calculate the ‘proportion of exchangeable oxygen in cellulose formed
from simple carbohydrates’ or ‘p_{ex}’

\[ p_{ex} = 0.2 + (0.6 + 0.2/2 - y) \]

where 1-y is the proportion of hexose phosphate molecules used immediately. A number of studies have
calculated \( p_{ex} \) for different species and found a range of values including 0.31 to 0.50 (Barbour, 2007),
0.42 (Rodent et al., 2000) and ~0.40 (Cernusak et al., 2005; Gessler et al., 2009). Sternberg (2009) adopts
a \( p_{ex} \) of 0.42, originally suggested by Roden et al (2000), as standard in his recent review of mechanistic
modelling, which seems reasonable given that Cernusak et al. (2005) found that their \( p_{ex} = 0.40 \) figure
was relatively consistent between species. The latter figure is applied later (Chapter 5) in the modelling of
intra-annual δ^{18}O cycles.

As a result of oxygen-exchange with free water during cellulose formation, the leaf-water signal in
cellulose is dampened. The extent to which the resultant cellulose δ^{18}O directly reflects the mixture of
source water and relative humidity (through leaf-water oxygen) then depends on a further potential
mixing. The free water in the developing cell may not be purely unenriched source water; it often includes
phloem water which can be intermediate between leaf-water and xylem (source) water and there may be
some evaporative enrichment of xylem water in local cells (Barbour, 2007). This proportion of unenriched
source water in the developing cell is termed \( p_{x} \) by Barbour, and included in the formula for re-exchange
of oxygen atoms with local water in the sink cell:

\[ \Delta^{18}O_{cellulose} = \Delta^{18}O_{leaf-water}(1 - p_{ex}p_{x}) + \epsilon_{wc} \]

where \( \epsilon_{wc} \) is an average fractionation factor (~27‰) applied to cellulose including more than one oxygen
atom that has gone through a carbonyl group.
For cellulose in tree-rings $p_x$ has been suggested to be very close to 1, as the site of cellulose synthesis is a significant distance from the leaves, allowing phloem water to exchange fully with source/xylem water (Barbour et al., 2004; Cernusak et al., 2005; Barbour, 2007). However there is some documented variation between studies and $p_x$ remains a relative unknown, and therefore a weakness in the model (Cernusak et al., 2005; Barbour, 2007), along with the contribution of bark photosynthesis (Gessler et al., 2013).

Ultimately, the mechanistic modelling of cellulose $\delta^{18}O$ has demonstrated that relationships between climate, source-water $\delta^{18}O$ and tree-ring $\delta^{18}O$ are not necessarily direct or simple. At best, palaeoclimate reconstructions are likely to be based on sites/species where either leaf-water enrichment or source-water changes are dominant enough to provide a robust signal for reconstruction. These are likely to be environments in which source-water $\delta^{18}O$ either varies greatly, or minimally. The lack of climate data that mechanistic models rely on (and palaeoclimate studies aim to remedy) prior to instrumental recording mean that modelling across long dendrochemical time-series is not possible in many locations. However, the utility of mechanistic modelling in a dendroclimatologic context lies in the ability to better verify modern isotope-climate calibrations based on a holistic understanding of cellulose $\delta^{18}O$ rather than simple correlation with observed climate data. Without further advances in understanding of plant physiology and the models describing it, the main avenue for improvement of long dendrochemical time-series remains adopting a multi-proxy approach, using multiple isotopes within a single record, as suggested by McCarroll and Loader (2004).

### 2.2.2 Carbon Isotopes in Tree-Rings

A common partner to $\delta^{18}O$ in multi-proxy dendrochemical investigation is $\delta^{13}C$. Unlike $\delta^{18}O$, the fractionation processes that determine $\delta^{13}C$ in tree-ring cellulose are predominantly internal. While the source CO$_2$ (i.e. atmospheric) $\delta^{13}C$ can change, it is generally over long timescales that are well studied and can be calibrated for (Saurer et al., 1997; Francey et al., 1999). In certain localised situations CO$_2$ can vary on a small spatial scale, such as in thick, stratified forest canopies (Schleser and Jayasekara, 1985; van der Merwe and Medina, 1989) but given that the trees studied here are canopy or canopy emergent species, this is unlikely to be an issue.

Unfortunately, the lack of source-water-$\delta^{18}O$-like fluctuations in atmospheric CO$_2$ does not mean that $\delta^{13}C$ is simpler to interpret; the dominant drivers of carbon fractionation respond to multiple climatic influences and can change in relative importance depending on those climatic factors. Carbon dioxide is taken into the leaves through stomata, sequestering carbon isotopes within the tree through photosynthesis; the carbon isotope ratios within a tree-ring therefore reflect the carbon isotopic signature of the atmosphere, altered by a tree’s processes of stomatal conductance and photosynthetic assimilation (McCarroll and Loader, 2005). The dual control of $\delta^{13}C$ by stomatal conductance and photosynthetic rate (Figure 2.2) is due to the two stage fractionation process that occurs at/in the leaf; fractionation first occurs at the stomata, where the lighter $^{12}$CO$_2$ molecules are able to diffuse through the stomata more easily than the heavier $^{13}$CO$_2$ molecules. The fractionation due to diffusion is relatively constant at $\sim-4.4\%$ (McCarroll and Loader, 2004). The next phase of fractionation occurs during carboxylation (the
conversion of internal CO$_2$ to sugars by photosynthetic enzymes). Biological processes tend to utilise $^{12}$C in preference to $^{13}$C and this results in a similarly constant $\sim$27‰ fractionation (McCarroll and Loader, 2004). While both fractionations are relatively constant, they are additive/interactive rather than independent. The variable that changes based on climatic factors is actually the concentration of CO$_2$ in the stomatal chambers ($c_i$) relative to the ambient atmosphere ($c_a$). If the relative pressure is low then there is limited fractionation during carboxylation but if pressure is high then there is stronger fractionation. Put simply, if the rate of stomatal conductance is high (dominant), a surfeit of CO$_2$ is provided to the leaf and the pressure within the stomatal chambers is high ($c_i$ increases relative to $c_a$). The result is that the plant increases discrimination during carboxylation, resulting in lower $\delta^{13}$C. When stomatal conductance is low, less CO$_2$ is delivered to the internal chambers, resulting in low $c_i:c_a$. If photosynthetic rate is high at the same time then it dominates the relationship and uses that CO$_2$ rapidly, with a reduction in carboxylation fractionation (in other words, the plant takes what carbon it can get), resulting in higher $\delta^{13}$C (McCarroll and Pawellek, 2001; McCarroll and Loader, 2004).

**Fig. 2.2:** Carbon isotope fractionation processes and the environmental processes that influence them, from McCarroll and Loader (2004).
The total discrimination against $^{13}$C ($\Delta\%$) during the above process is generally described through the equation (Francey and Farquhar, 1982)

**Eqn. 8:** $\Delta\% = a + (b - a)(c_i/c_a)$

where $a$ is the first phase of fractionation at the stomata (i.e. $\sim -4.4\%$ discrimination against $^{13}$C), $b$ is the second, carboxylation phase of fractionation (i.e. $\sim -27\%$ discrimination against $^{13}$C).

The result of these fractionation patterns is that in environments where moisture is a limiting factor and trees close their stomata to limit water loss, stomatal conductance becomes the major controller the $c_i/c_a$ ratio and, therefore, fractionation. Consequently, $\delta^{13}$C varies principally with water-stress related variables such as relative humidity and soil moisture availability (McCarroll and Loader, 2004). If stomata are generally closed to prevent moisture loss then less CO$_2$ is available and there is less fractionation at carboxylation, meaning decreased discrimination against $^{13}$C$^{16}$O$_2$ resulting in higher $\delta^{13}$C (Farquhar et al., 1982; Francey and Farquhar, 1982).

In moist environments factors affecting photosynthetic rate such as irradiance (McCarroll and Pawellek, 2001; Walcroft et al., 2002; Young et al., 2010) and temperature (McCarroll and Loader, 2004) regulate $\delta^{13}$C. There is little limitation placed upon the plant in terms of providing CO$_2$; it isn’t pressured to retain water so its open stomata supply a surfeit of CO$_2$ for photosynthesis. Consequently, environmental conditions (warm, sunny) that increase the rate of photosynthesis lower the CO$_2$ concentration in the stomatal chambers, increasing $\delta^{13}$C while conditions that limit the photosynthetic rate mean that more CO$_2$ remains in the stomatal chambers and $\delta^{13}$C decreases (Farquhar et al., 1982; Francey and Farquhar, 1982). The relative importance/influence of stomatal conductance and photosynthetic rate are changeable with time and location so careful evaluation is needed and in some cases only a multi-proxy record will enable meaningful interpretation of $\delta^{13}$C (McCarroll and Loader, 2004; Roden and Farquhar, 2012); using $\delta^{13}$C alone to reconstruct palaeoclimate has been likened to ‘using leaky barrels to record rainfall’ (McCarroll and Pawellek, 2001, 525). In some situations $\delta^{13}$C can decouple from leaf processes due to phloem loading and transport (Gessler et al., 2009) and even with a dual-isotope approach, it is unable to unravel meaningful environmental signals from tree-rings isotope data (Roden and Farquhar, 2012).

### 2.3 The Use of $\alpha$–cellulose

The previous two sections have each made reference to the fractionation processes involved in the creation of $\alpha$–cellulose because this study focuses on that particular component of tree-rings. The reasons for that decision, and the reason why $\alpha$–cellulose is regarded as the material of choice for many stable isotopic investigations, are discussed below.

The more focussed environmental reconstructions and reduced sample numbers associated with stable isotope dendroclimatology (compared to ring-widths) are reliant on a stable, temporally specific substance for analysis. As trees grow they form rings composed of different wood constituents including cellulose
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(~50%), lignin (~30%), hemicelluloses (~15%) and resins and alcohols (Wilson and Grinsted, 1978). The exact amounts of any of these constituents vary among species, genera and families; for example conifers are generally more resinous than other trees. Some wood components are exchangeable while others are relatively stable, preserving chemical signatures from the time of their formation. This varies in scale from the constituents themselves (α-cellulose preserves time-specific signatures while resins are mobile within the tree) to individual atoms within the molecules (the O-H hydrogen, for instance, records the composition of their most recent contact with water while the C-H hydrogen does not exchange (Wilson and Grinsted, 1978)).

For most studies, particularly those targeting δ¹⁸O, tree-ring isotopic composition is determined from the α-cellulose component of the ring. α-cellulose is abundant, easily extracted and, as the structural element of wood, is specific to the time of ring-formation (McCarroll and Loader, 2004). Furthermore, α-cellulose maintains its integrity in deceased trees for prolonged periods, thus making it a more useful tool than the isotopic composition of whole-wood in sub-fossil samples (Jahren and Sternberg, 2008).

The stable isotopic compositions of whole-wood, and its individual constituents, differ for those species reported in the literature (Barbour et al., 2001; Loader et al., 2003; Verheyden et al., 2005; Battipaglia et al., 2008). The fraction of whole-wood that is α-cellulose/lignin/resin etc also varies among trees/species meaning that comparing isotopic ratios of individual isolates can be undertaken with greater confidence than comparing whole-wood values. For instance, late-wood has a higher lignin:cellulose ratio than early wood and lignin is generally more depleted in both ¹³C (Fraser et al., 1978) and ¹⁸O (Barbour et al., 2001), so whole wood analyses on an intra-ring scale might show δ¹³C and δ¹⁸O changes that are an artefact of changes in wood composition.

Of those wood constituents, the isotopic disparity between lignin and α-cellulose is the largest and most studied; it is often minor (Loader et al., 2003; Verheyden et al., 2005) for δ¹³C but varies among species and in species studied and while generally less than 1‰ (Brookman and Whittaker, 2012; Chapter 4), can be up to 3.2‰ (English et al., 2011). In contrast, the difference in δ¹⁸O values for cellulose and lignin is up to 8‰ in oak and pine (Barbour et al., 2001). Consequently, isolating α-cellulose is an effective means of negating the stable isotopic variability inherent in whole-wood.

2.4 Applications of Stable Isotopes in Tree-Rings

2.4.1 Temperature and Radiation Reconstruction

Temperature has a limited influence on fractionation at the leaf level, yet is a major controller of evaporative fractionation during precipitation events. Thus, it is not surprising that in some contexts temperature is the dominant control on tree-ring δ¹⁸O, but not in others. Recently δ¹⁸O has been used for centennial scale temperature reconstruction: Berkelhammer and Stott (2012) report decadal trends in δ¹⁸O from bristlecone pines (Pinus aristata) in the Southern Rocky Mountains that they suggest equate to ~1°C
changes in temperature. Further north, in the Canadian Arctic, Porter et al. (2013) found that temperature was the major regulator of $\delta^{18}$O in white spruce (*Picea glauca*).

In areas where it is the availability of light, or temperature, or both, that limits photosynthesis, these factors can become the dominant controls of $\delta^{13}$C. Consequently, $\delta^{13}$C, like $\delta^{18}$O, can also provide the basis for temperature reconstruction (Gagen et al., 2007). This is demonstrated by Young et al.’s (2012) recent 160 year temperature reconstruction from the United Kingdom in an area where ring-width records generally do not provide robust records of palaeoclimate. Not surprisingly, radiation and temperature often co-vary, making their effects difficult to distinguish. However, in some studies where radiation has correlated well with $\delta^{13}$C but temperature has not, it may be that temperature and radiation have diverged, suggesting cloudier conditions. In such contexts, $\delta^{13}$C may become a more effective recorder of solar radiation regimes than temperature (Young et al., 2010; Loader et al., 2013).

### 2.4.2 Drought and Rainfall Reconstructions

A major application for both tree-ring $\delta^{13}$C and $\delta^{18}$O in palaeoclimate science has been in rainfall and moisture availability reconstructions (e.g. Treydte et al., 2006; Cullen and Grierson, 2007; Leavitt et al., 2007). In areas where drought is frequent, moisture availability is generally primary major controller of $\delta^{13}$C through its regulation of stomatal conductance (McCarroll and Loader, 2004). Perhaps the most extensive application is the body of work from the arid South-West interior of the U.S. Numerous studies there have found strong, direct relationships between $\delta^{13}$C and drought indicators, particularly the Palmer Drought Severity Index (PDSI) (Leavitt and Long, 1989; Leavitt et al., 2007; Leavitt et al., 2008). That relationship has been substantiated on various time scales, with studies ranging from extremely detailed late-20th century comparisons (Leavitt et al., 2008) to longer, multi-centennial records (Leavitt et al., 2007). In that same region the presence, or absence, of drought based on $\delta^{13}$C is now also being investigated as a means of developing palaeo-rainfall records in order to evaluate the pre-instrumental strength and position of the North American Monsoon (Leavitt et al., 2011).

Through their relationships to rainfall source, amount and evaporative enrichment, changes in $\delta^{18}$O can also directly and indirectly inform drought reconstruction either independently or in conjunction with $\delta^{13}$C. Raffalli-Delerce et al. (2004) focus on $\delta^{18}$O as a measure of evaporative conditions, combined with $\delta^{13}$C’s relationship to relative humidity at their site in coastal France to create a ~120 year drought record. Kress et al. (2010) take a similar approach in their 350 year alpine drought reconstruction, using a drought index created from combined moisture ($\delta^{13}$C) and sunshine ($\delta^{18}$O) data.

Beyond searching for a particular ‘drought’ signal, rainfall regimes are a major target for tree-ring $\delta^{18}$O reconstructions. $\delta^{18}$O can relate to precipitation source region and/or rainfall amount, acting not only as a palaeo-rain gauge but also providing clues to the dominant atmospheric circulation systems responsible for rainfall patterns characterising droughts, dry seasons or monsoonal activity. In many areas ENSO is a major driver of such systems, so it is unsurprising that numerous rainfall reconstructions using $\delta^{18}$O also provide palaeo-ENSO records. Brienen et al. (2012) find primary evidence of Rayleigh distillation/
rain-out processes, resulting in a negative correlation between δ¹⁸O at their site and basin-wide rainfall and Amazon River discharge, which in turn are well correlated with ENSO indices. Zhu et al. (2012) also show a precipitation amount and ENSO relationship with δ¹⁸O from Thailand, albeit a complex one. Event-capture of particular El Niños and/or La Niñas in tropical tree rings using δ¹⁸O (Evans and Schrag, 2004) and δ¹³C and δ¹⁸O (Poussart et al., 2004) have also been published.

Other rainfall-based δ¹⁸O reconstructions reconstruct large-scale changes ranging from the East Asian monsoon in the arid interior of China (Liu et al., 2008) over ~120 years to the global hydrological cycle on a millennial scale (Treydte et al., 2006). However, not all δ¹⁸O records necessarily focus on broad-scale circulation; event-scale records are also targetable in situations where those events produce isotopically distinct precipitation. Miller et al. (2006) retrieved event-scale source/circulation from longleaf pine (*Pinus palustris*) growing on the south-east US, where tropical cyclones drop significantly ¹⁸O depleted rainfall.

While this review focuses on successful studies that reveal δ¹⁸O and δ¹³C’s utility in drought and/or rainfall reconstructions, it should be noted that a number of these studies document relationships that, while statistically significant, are of limited use for detailed climate reconstruction due to the limited climatic variance explained by δ¹⁸O. Even in situations where multiple sites and species are studied with significant resources and excellent modern precipitation δ¹⁸O data, single variable reconstruction can be elusive (Saurer et al., 2012).

**2.4.3 Forest Ecology, Plant Physiology and Genetics**

While the uses of isotopes in forest ecology, plant physiology and genetics are research fields in their own rights and none are the major focus of this thesis, they are nonetheless factors that must be taken into account due to their interaction with climatic signals in tree-ring isotopes. Each field also represents a potentially useful application of tree-ring stable isotope research in New Zealand. The contributing effects of physical processes on isotopic fractionation within a tree are an area of ongoing study. However, there is already a sound theoretical basis for the use of isotopes to evaluate forest ecology process or to compare isotopic records with ring-width records to untangle physical traumas (e.g. damage or disease) from broad climatic trends. For instance, a diseased tree may grow slowly, presenting narrow rings that from a ring-width perspective, suggest physical trauma, climatic change or a combination of the two. Carbon isotope data from the same tree may produce a similarly complex signal, as the photosynthetic and stomatal regimes, the controllers of carbon isotope fractionation, can be disrupted by disease (Benner et al., 1988; Erickson et al., 2004; Gomes-Larango et al., 2004). However, the oxygen isotope ratios within tree tissues are determined largely by the water available to the tree. Consequently, oxygen isotope ratios are less likely to be significantly affected by the disease and provide a potential distinction between disease and climate related stresses. This may allow environmental events, like an outbreak of disease within a kauri stand, to be pinpointed in the tree-ring record. The outbreak of *Armillaria* (honey fungus) in New Plymouth (Dick, 2009; Smith, 2009) or Phytophthora taxon *Agathis* in many natural kauri stands (Waipara et al., 2013) might be an appropriate study in the future.
Similarly, factors such as branch abscissions or a canopy opening may change a tree’s growth rate resulting in a ring-width record that could suggest changed climatic conditions. Such stand-level dynamics can also potentially be observed using δ\textsuperscript{13}C which has been observed to change in response to canopy shading/light availability (Buchmann et al., 1997; Walcroft et al., 2002) and canopy stratigraphy (van der Merwe and Medina, 1989). Isotopic records from the same tree may provide corroborating or contrary evidence, leading to a more informed climatic history or a more localized stand history based on environmental events. For instance, the impact of selective logging on the growth rates of remaining trees may be evident in increased ring-widths but isotopically ‘invisible’ (Saurer et al., 1997).

An aspect of forest ecology that is of particular relevance to this study and stable isotope dendroclimatology in general is the systematic change in δ\textsuperscript{13}C documented in many trees as transition from juvenile to adult. A number of causes related to forest dynamics and physiology have been suggested including reduced shading (Francey and Farquhar, 1982), less synthesis of respired canopy CO\textsubscript{2} (Schleser and Jayasekera, 1985), changes in hydraulic conductivity (McCarroll and Loader, 2004) or bark refixation of respired CO\textsubscript{2} (Cernusak et al., 2001). This juvenile effect is important to dendroclimatic studies, which must endeavour to separate biologically-driven isotope trends from climatic variability and change. The effect is discussed in more detail in relation to isotope data from this study in Appendix 8.7.

Many of the isotopic changes observed among different species have their root in genetic differences among tree species/genera/families. A growing body of Northern Hemisphere research suggests that stable isotopes, particularly carbon, can provide information on genetic variability within tree species (McCarroll and Loader, 2004) and physiological differences among species. In a New Zealand context, δ\textsuperscript{13}C has been interpreted as an indicator of genetically driven water use efficiency differences between kauri and kahikatea (Dacrycarpus dacrydioides) (Stephens et al., 1999).

While genetic variability in carbon isotopes among species has been well documented (Farquhar, 1983; Tieszen, 1991) genetic distinctions within species are a newer branch of research. Carbon isotope ratios have been used as a proxy for water use efficiency, determined by stomatal conductance, to evaluate genetic traits in maritime pine (Pinus pinaster) (Brendel et al., 2002) and black spruce (Picea mariana) (Johnsen et al., 1999). It appears that carbon isotope data can be used to select genetic lineages that have higher water use efficiency and, therefore, higher growth rates. Factors such as the altitude of origin (i.e. region of seed source) have been proposed as a determining factor of δ\textsuperscript{13}C in douglas fir (Pseudotsuga menziesii), resulting in distinct isotopic groupings of trees, based on seed source, within a single plantation (Zhang et al., 1993). A similar exercise could be applied to kauri to investigate which seed stock is performing best in plantation situations. It should be noted, however, that in some situations isotopic variability resulting from genetic variability may be absent or overwritten by a larger environmental signal (Rowell et al., 2009).

Conversely, genetics can play a key role in signals that may override climatic/environmental signals; increasingly, high resolution intra-annual are revealing that stable isotope dendrochemistry is often heavily regulated by plant physiology cycles (Helle and Schleser, 2004; Kagawa et al., 2005; Kagawa et
al., 2006b; a; Jahren and Sternberg, 2008). The primary signal is related to the storage of photosynthates by deciduous trees in order to promote growth the following spring. While this is well documented using carbon isotopes there is only brief reference to the potential for a similar effect on oxygen isotopes (Poussart et al., 2004). The level of influence such cycles have in evergreen trees, which rely less heavily on stored photosynthates (Kramer and Kozlowski, 1979; Wilson, 1984; Barbour et al., 2002), is less certain; further discussion appears along with high resolution data presented in Chapter 5.

2.5 **Stable isotope dendroclimatology in New Zealand**

New Zealand scientists were at the forefront of investigating the palaeoclimatic potential of stable isotopic investigation of tree rings (e.g. Jansen, 1962; Wilson and Grinsted, 1977). A number of early publications identified the promise of carbon (Jansen, 1962; Wilson and Grinsted, 1977; Grinsted and Wilson, 1979) and oxygen and hydrogen (Wilson and Grinsted, 1978) stable isotopes in wood components (e.g. cellulose and lignin), as well as isotopic differences between those components (Wilson and Grinsted, 1978).

Early research in New Zealand suggested that δD and δ¹³C could be used as proxies of the annual temperature cycle, based on the isotopic offset between summer (early) and winter (late) wood (Wilson and Grinsted, 1978). The idea that temperature could be reconstructed to within +/-0.1°C (Wilson and Grinsted, 1978) illustrated the huge potential of stable isotope dendrochronology but, like so many early studies, was based on a limited understanding of the complexity of the factors influencing the trees’ photosynthetic and stomatal conductance processes. Similarly, Wilson and Grinsted (1978) hypothesised that δ¹⁸O could be used to accurately document temperature and reconstruct the δ¹⁸O of atmospheric water incorporated by the tree; more than 30 years later this remains an elusive goal.

Since these early contributions, the potential for stable isotope dendroclimatology has been noted (Norton and Ogden, 1987) but there has been little further investigation of New Zealand tree species and their isotopic compositions. More recently, multiple pilot studies have been conducted but limited content has been published on native species (eg. Clarkson, 1992; Walcroft, 1994; Stephens, 1997; Poussart, 2004). The lack of long dendrochemical records, however, is in stark contrast to the progress in stable isotope ecophysiology, with multiple prominent New Zealand-based investigations into δ¹³C and δ¹⁸O in introduced *Pinus radiata* (Walcroft et al., 1997; Barbour et al., 2002; Barbour et al., 2004; Ellsworth et al., 2013). New Zealand is not unique in the general paucity of its native dendrochemical records; Australian research followed a similar pattern of early investigation (Pearman et al., 1976; Fraser et al., 1978), followed by relatively slow progress in creating long-term dendroclimatic records. As in New Zealand, the dendrochemical niche was filled by globally significant contributions to plant physiology (Farquhar et al., 1982; Francey and Farquhar, 1982; Farquhar, 1983; Farquhar and Richards, 1984; Farquhar et al., 1989). In recent years, plant physiological contributions have continued (Cernusak et al., 2005; Cuntz et al., 2007) and dendroclimatic investigation has revived (Cullen and Grierson, 2007; Sgherza et al., 2010). However, the Southern Hemisphere as a whole still lacks a robust network of stable
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isotopic dendrochronologies (McCarroll and Loader, 2004).

The lack of stable isotope dendroclimatology belies the tremendous potential for dendroclimatic research in New Zealand, which already has an extensive database of ring-width chronologies. Evidence of marked shifts in regional atmospheric circulation patterns such as El Niño-Southern Oscillation (ENSO) and the Inter-decadal Pacific Oscillation (IPO) has been observed in tree rings’ physical characteristics (Cook et al., 2006; Fowler et al., 2008a). Recent ring-width investigations (Fowler et al., 2012) of kauri have provided a 700 year record of ENSO activity, perhaps one of the best proxies from the Southern Hemisphere of that tropical phenomenon. Whether these signals are also evident in kauri isotopes merits further investigation. Kauri’s present natural range is sensitive to ENSO changes and kauri’s growth season coincides with the region’s strongest ENSO teleconnections (Fowler et al., 2012). ENSO may generate isotopically-distinct tropical and high latitude rainfall in varying amounts each year, in addition to other factors influenced by ENSO, such as the amount of rain falling in Northland and the soil water moisture balance, which may be captured by kauri tree-ring isotopes. Any of those factors may facilitate oxygen and/or carbon isotope reconstruction of globally significant climate and weather patterns.

Beyond broad circulation changes, numerous more localised factors such as temperature and relative humidity may also influence, the New Zealand kauri isotopic record and further research is needed. The complex interaction between climate and arboreal biogeochemistry means that intensive short term studies (i.e. the period of instrumental record, ~1850-present) are vital before making climatic inferences from the longer proxy records that exist in New Zealand (Fowler et al., 2004; Fowler et al., 2012). Forthcoming research by Lorrey et al. (in prep) takes the first steps towards redressing this knowledge gap form kauri’s natural range, examining a kauri time-series of up to 96 years in length from Auckland and Northland.

In recognition of the need for modern calibration studies and the potential for palaeoclimate records from New Zealand tree species, this research was conceived with the goal of multi-centennial high-resolution palaeoclimate reconstruction. It quickly became apparent, however, that there were numerous, fundamental questions that required attention before a robust record of such length could be constructed. The research focus changed accordingly, to a more ‘first-principles’ understanding of stable isotope dendroclimatology in New Zealand. While a detailed review and reconstruction of New Zealand climate and hemispheric/global teleconnections are consequently beyond the scope of this thesis, the following paragraphs characterise the motivation behind the research and, looking forward, frame the global relevance of the findings herein.

New Zealand is ideally situated for study of numerous regional, hemispheric and global climatic/atmospheric processes and conditions and their evolution through time. The main islands cover widely contrasting climatic zones from the subtropical anti-cyclonic belt in the north to high latitude temperate environments in the South, yet are dominated by circumpolar westerly atmospheric circulation (Shulmeister et al., 2004; Alloway et al., 2007; Lorrey and Bostock, in press). Of further benefit to palaeoclimatic study is the country’s axial dissection by mountain ranges, creating distinct regional
divisions in weather/climate patterns (Alloway et al., 2007; Lorrey et al., 2007).

Complex regional atmospheric circulation patterns contribute to climatic variability in New Zealand on annual to decadal timescales (Lorrey and Bostock, in press), including: changes in the intensity and positioning of the circumpolar westerly circulation (Shulmeister et al., 2004), the El Niño-Southern Oscillation (ENSO) phenomenon (Gergis et al., 2006; Lorrey et al., 2007; Ummenhofer and England, 2007), the interdecadal Pacific Oscillation (IPO) (Salinger and Mullan, 1999; Salinger et al., 2001; Lorrey et al., 2007) and the southern annular mode (SAM) (Salinger and Mullan, 1999; Renwick and Thompson, 2006; Sturman and Tapper, 2006; Ummenhofer and England, 2007). Interaction among these systems, including latitudinal changes in their respective influences (Ummenhofer and England, 2007), makes medium-to-long term climate prediction challenging. Records from tree-ring chemistry have potential to add to the promising annual archives of climatic changes from ring-width studies (Fowler et al., 2008; Fowler et al., 2012) and assess both high-resolution inter-annual variability and long-term trends using a single proxy record.

The combination of atmospheric circulation patterns that make forecasting so challenging in New Zealand also provide unique opportunities to produce detailed climate records for the mid-to-high southern latitudes which, currently, represent a major global palaeoclimate knowledge gap (Turney et al., 2006a; Turney et al., 2006b; Jansen et al., 2007; Neukom and Gergis, 2012). ENSO, IPO and SAM affect much of the Pacific but understanding of their interactions and the associated movement of air and water masses, including the occasional decoupling of oceanic and atmospheric processes (Gergis and Fowler, 2005; Gergis et al., 2006), is still evolving. ENSO alone directly affects billions of people; it impacts summer monsoonal activity in India (Kumar et al., 1999; Krishnamurthy and Goswami, 2000; Kumar et al., 2006), determines the success/failure of Pacific Ocean fishing industries on annual and multi-decadal scales (Lehodey et al., 2006) and is a major driver of drought along Australia’s fire-prone eastern coast (Williams et al., 1998; Allan, 2000). Improved understanding and forecasting of ENSO and its relationship with the IPO and SAM is essential, particularly as climate oscillations evolve in response to the current period of rapid climatic change (Rosenzweig and Hillel, 2008).

In a regional context, insights into pre-historic atmospheric circulation could have significant benefits for New Zealand’s heavily agriculturally/horticulturally based economy. Primary industry and associated manufacturing and service industries generate over 20% of GDP (Treasury, 2010). Droughts are a major concern to the pastoral and dairy industries; the 1997/1998 El Niño drought alone cost the country between $407 million (0.4% of GDP) (Gardiner, 2001 cited in; Mullan et al., 2005) and $618 million (0.9% of GDP) (Wratt, 1998), almost entirely due to primary industry losses. The immense personal hardship, focused in rural communities, is an intangible cost with very real economic and social consequences (Read, 1998). The potential for stable isotope dendroclimatology to increase understanding of the past impacts and interactions of climatic systems like ENSO, SAM and the IPO may improve current climate models, facilitating effective long term, risk analysis-based decision making which is
essential to businesses such as farming, electricity production and insurance (Mullan, 1998). Improved forecasting could benefit the New Zealand economy by between $10-100 million annually (Basher, 1996; Campbell et al., 1998), and equally important would be the social/community benefits of a successful primary sector.

Looking beyond circulatory records to a local climate scale, the ability to target hydroclimatic records using tree-ring isotopes (reviewed earlier in this Chapter and see Chapter 6) makes them an important tool for reconstructing water resource availability in key catchments (e.g. Treydte et al., 2006; Kress et al., 2010; Brienen et al., 2012). Increasingly, water resources are a source of concern and division in New Zealand communities, as the relative merits of economic and environmental agendas are discussed (Land-and-Water-Forum, 2010; Wright, 2013). At the heart of this debate lies uncertainty over the long term viability of New Zealand’s fresh-water resource due to a fundamental lack of understanding regarding the amount and sources of available water. Reconstructions of hydroclimate could play a pivotal role in setting realistic water-use limits based on long-term proxy records rather than the often brief, sparse modern data. This could be particularly crucial in East Coast catchments, many of which are suspected to be at or beyond their sustainable water-usage capacities (Land-and-Water-Forum, 2012).

While no long-term multi-centennial records of Holocene climate change/water availability arise from this research, the baseline information provided here will aid future researchers in producing long-term stable isotope dendroclimatic reconstructions from New Zealand. Those studies should lead to improved understanding of climate change on local, regional and global scales, ranging from local catchment water-availability to the oscillations of circulatory systems. The research presented in this thesis constitutes a foundational building block from which globally significant insights into climate change science can be developed.

### 2.6 New Zealand’s candidates for Stable Isotope Dendroclimatology

Fortunately, in the context of creating robust, multi-proxy climate reconstructions with broad geographic coverage, New Zealand is home to a number of long-lived tree species with excellent potential for stable isotope dendroclimatology. Most of these species have been investigated for dendrochronologic research purposes. Despite the bulk of New Zealand’s tree species being dicotyledonous hardwoods (Wardle, 2011), it is the longer lived, canopy emergent softwoods that dominate the dendrochronological record; kauri, pink pine, silver pine and both New Zealand cedars (Pahautea/Kaikawaka and Kawaka) have been extensively studied. All of these species belong to the plant order Coniferales with the pines belonging to the family Podocarpaceae, the cedars to Cupressaceae and kauri to Araucariaceae. Other conifers such as *Phyllocladus* have also been dendrochronologically investigated (Norton and Ogden, 1987; Norton and Palmer, 1992; Palmer and Ogden, 1992; Salinger et al., 1994). Studies of non-coniferous genera have been primarily limited to shorter-lived *Nothofagus* species (Norton, 1983a; b; 1984; 1985; Norton and Ogden, 1987; Norton et al., 1987).
Since early investigations, generally focussed on archaeological research (Batley, 1956; Bell and Bell, 1958), dendrochronology has bloomed in New Zealand, creating an impressive network of chronologies from multiple species. Some of the first studies used growth rate estimation rather than actual ring-counts to provide very approximate ages (Batley, 1956). Batley (1956) used more advanced/traditional methods of dendrochronology to date the removal of bark from totara by māori to create mutton-bird containers. He saw the potential for dendrochronological investigation to provide insight into a number of archaeological applications like dating the development of bark containers, axe and adze use, settlement of remote areas and population increases in forest areas. While Batley’s (1956) certainty that totara would take ‘pride of place’ in any future dendrochronological investigation has not come to pass, his optimism for dendrochronology’s ability to contribute to knowledge of New Zealand’s (pre)history has been vindicated.

Bell and Bell (1958) first noted kauri’s potential for dendrochronology whilst echoing Batley’s (1956) suggestion that totara represented an excellent dendrochronological prospect. At this early stage New Zealand dendrochronology was hampered by a lack of physiological and ecological research on New Zealand native trees; growth rates and patterns were poorly understood. Some authors considered that New Zealand provided growing conditions that were simply too equable, leading to a lack of discernible common patterns within tree stands (Golson, 1955). Similar problems continued to be encountered with poor site selection (Cameron, 1960) and sample replication resulting in limited success with cross-dating and/or climate correlations (Scott, 1972).

Towards the end of the 1970’s dendrochronology in New Zealand took large steps forward, with visits from University of Arizona Tree-Ring Laboratory academics who constructed some of the earliest comprehensively cross-dated chronologies in the country (Dunwiddie, 1979; LaMarche et al., 1979). This extensive survey which compiled 21 chronologies from 7 species and sampled numerous others kick-started local researchers, with a number of important foundation works occurring in the 1980’s and early ‘90’s including chronology development (Palmer, 1982; Ahmed and Ogden, 1985), growth increment studies (Palmer and Ogden, 1983) and early sub-fossil investigation (Ogden et al., 1992) of kauri, South Island investigations in to Nothofagus species (Norton, 1983a; 1983b; 1984; 1985; 1986) and multi-species investigations into the errors associated with partial core recovery and event-dating (Norton et al., 1987). The key to the success of this new wave of research appeared to be improved site selection combined with rigorous cross-dating, emphasised as crucial to data quality by Norton and Ogden (1987), particularly for dendroclimatology.

Four species, New Zealand kauri, cedar, pink pine (Halocarpus biformis (Hook.) Quinn) and silver pine (Manoao colensoi (Hook.) Molloy) comprise the bulk of New Zealand’s dendroclimatic reconstruction network. They are all long-lived conifers and the leading candidates for stable isotope dendroclimatology due to their longevity, the relative ease with which they can be cross-dated and their documented climatic sensitivity. Kauri and cedar, upon which this research is based, are reviewed below while pink pine and silver pine are reviewed in Appendix 8.1.
2.6.1 New Zealand Kauri (Agathis australis)

Foremost amongst New Zealand’s endemic conifers in terms of cultural significance, longevity and level of dendrochronological study is kauri. Kauri is an evergreen conifer within the family Araucariaceae, once widespread worldwide but now generally confined to the Southern Hemisphere. Nineteen Agathis species occur across over 40 degrees of latitude from South-East Asia just north of the equator to New Zealand (Kershaw and Wagstaff, 2001). Principally tropical, species are spread through Mayalsia, The Phillipines, Indonesia, northern Australia and some Pacific Islands (Fiji, east). In Australia, Araucariaceae pollen appears during the Late Cretaceous, over 70 million years ago (White, 1998), while last the remnants of the Gondwana supercontinent were still joined.

Within Australasia numerous species of Agathis exist, many called ‘kauri’. New Zealand kauri is the southern-most Araucariaceae and the only member endemic to New Zealand (Ecroyd, 1982). It thrives as a canopy emergent forest species in the warm-temperate lowland forests of the North Island (Kershaw and McGlone, 1995). Kauri forest ranges from approximately 38°S northwards (Bergin and Steward, 2004; Fowler et al., 2004), occurring as scattered trees and small stands until ~37°S, just south of Auckland (Bergin and Steward, 2004). From this point it becomes a common part of the forest assembe; the northernmost stand of kauri used in dendroecological study, Te Paki Trig (Palmer et al., 2006), occurs near Cape Reinga on the Aupouri Peninsula, New Zealand’s northernmost point at ~34.4°S. Throughout this range mature trees are generally confined to conservation areas that are at elevation on steep terrain, untouched by the widespread Kauri logging of the 19th and early 20th centuries (Boswijk, 2005; 2010) (see Appendix 8.2).

Despite its natural confinement to the North of New Zealand, plantation kauri can grow successfully across the length of New Zealand, with specimens growing as far south as Invercargill and even Stewart Island. Salmon (1996) suggests that despite these successes, there is little evidence of kauri further south than their current range in the fossil record. However, numerous authors have documented kauri fossil material in the South and lower-North Islands (Evans, 1937; Ecroyd, 1982; Mildenhall, 1985; Lee et al., 2007), ranging from Oligocene to Quaternary ages.

Kauri is a large canopy-emergent tree that, once mature, commonly reaches heights of 30-50m (Bergin and Steward, 2004). Kauri’s mass is concentrated in its trunk; they are generally straight and cylindrical for 12-25m with larger mature trees often reaching a breast-height diameter of 3-5m prior to extensive logging operations (Bergin and Steward, 2004). The largest living kauri, Tāne Mahuta in Waipoua forest, is ~4.5m in diameter, over 50m high and 244.5m$^3$ in volume (Bergin and Steward, 2004; Stewart, 2008). The largest kauri reliably measured, Kairaru, was a staggering 20.1m in circumference and rose 30.5m before branching (Halkett, 1983) to provide an estimated timber volume of 453m$^3$, over twice the size of Tāne Mahuta (Wardle, 2011). Large kauri typically grow for 600 years or more (Ahmed and Ogden, 1987) and can grow for over 2000 years (Palmer et al., 2006).

Kauri typically grows from sea level to 600m on infertile/mineral deficient soils on upper slopes and steep
ridges and spurs. Mature trees typically form small groves of 40-50 individuals rather than dominating a large area (Eckenwalder, 2009; Wardle, 2011). These mature trees act as a seed source for the next generation that invade large areas disturbed by fire or storm damage, forming dense ricker stands (Farjon, 2010).

Despite the extensive study of kauri growth rates it remains impossible to accurately estimate age from diameter, as vertical and horizontal growth rates are hugely variable (Ahmed and Ogden, 1987). This thesis includes a survey of juvenile trees in a plantation stand ~55 years old, the largest of which was 3.5 times the diameter of the smallest. Similarly, Ahmed and Ogden (1987) found that trees in the same diameter class could vary in age by up to 300 years. Growth rates also vary greatly among stands depending on environmental conditions: trees in the ~55 year old plantation surveyed in this study had diameters that Ahmed and Ogden (1987) suggest, in a natural stand, would make them 127-231. Generally younger trees have a spurt of growth which plateaus with age but some stands show the reverse trend (Ahmed and Ogden, 1987).

Kauri’s longevity, tendency to produce annual rings and straight growth habit make it a prime candidate for dendrochronological research, a fact recognised by early researchers (Dunwiddie, 1979). However, care must be taken to cross-date records. Wedging of rings, where an area of slow growth is bordered by one of accelerated growth, often occurs and both skipped and false rings have been observed in kauri (Dunwiddie, 1979; Ecroyd, 1982). To date a network of 17 modern kauri chronologies have been developed (Fowler et al., 2004) and linked to late Holocene subfossil ‘bog kauri’ and archaeological timbers to create a near 4000 year calendar dated chronology (Boswijk et al., 2006). Further subfossil material recovered from Northland dates back as far as 60,000 years before present, covering over 10,000 years of Oxygen Isotope Stage 3 (Palmer et al., 2006; Turney et al., 2010). The kauri record, despite being relatively recently developed, already rivals some of the longest Northern Hemisphere chronologies, most of which are composed from European/British oak (Schweingruber, 1988) and Fennoscandian pines (Pinus sylvestris).

While New Zealand kauri’s range is restricted, it is still an excellent candidate for palaeoclimate studies, as genetically similar trees from contrasting climatic zones are readily available. Even in kauri’s restricted range, interesting climatic gradients and patterns are evident. The climatic region kauri grows in receives moist, maritime air masses from every direction, often controlled by ENSO which results in opposing climatic characteristics for Northland (temperature, precipitation, soil moisture etc.) between El Niño and La Niña events (Gordon, 1985; Mullan, 1995; Fowler et al., 2000; Lorrey et al., 2007) and may impact kauri tree-ring biogeochemistry. Equally importantly, distinct environmental and palaeoenvironmental parameters for Northland have the potential to be reconstructed from kauri biogeochemistry, which is currently not afforded by other techniques. Investigating the potential of kauri tree ring biogeochemistry is therefore critical for helping to extend our understanding of how the environment and climate have changed past the scope of the limited instrumental record in New Zealand (Salinger and Gunn, 1975).

Kauri plays an important role in New Zealand’s Māori and European history (Appendix 8.2). While it
has limited bearing on palaeoclimate investigations it does provide context for why it is difficult to obtain permits to core kauri. A strong scientific case must be made in order to access the remaining stands of this national floral treasure and precautions taken against disease transmission (see Appendices 8.3 and 8.4).

2.6.2 New Zealand (Mountain) Cedar (*Libocedrus bidwillii*)

In contrast to *Agathis*, *Libocedrus* is a small genus with a more limited distribution. All *Libocedrus* species are evergreen trees and shrubs distinguished by their straight trunk covered in scaly red-brown to brown bark that peels in long, vertical strips and conical crown formed of short horizontal or upswept branches (Eckenwalder, 2009; Farjon, 2010). Two species, *L. bidwillii* (Mountain cedar/Pahautea/Kaikawaka) and *L. plumosa* (Kawaka), are endemic to New Zealand and three to New Caledonia. Some authors consider this the extent of *Libocedrus* (Farjon, 2010; Wardle, 2011) while others include the morphologically and geographically isolated but genetically similar, Chilean *Libocedrus uvifera* as a sixth member of the genus (Eckenwalder, 2009). *Libocedrus* fossils have been found in deposits of Mio-Pliocene age in New Zealand (Eckenwalder, 2009), suggesting the potential for long-term palaeoclimate records if suitably preserved ‘bog’ specimens are recovered but the tendency for cedar timber to decay quickly makes this unlikely. The close relationship among *Libocedrus* species in New Zealand, New Caledonia and perhaps Chile suggests potential for South Pacific/Southern Hemisphere comparisons.

*Libocedrus bidwillii* (‘cedar’ from here onwards) covers a large latitudinal range, overlapping with kauri at its northern limit in the Coromandel Range (36° 50’S) in the North Island and extending as far south as the Catlin Range (46° 30’S) in the South Island (Veblen and Stewart, 1982; Salmon, 1996). Importantly for palaeoclimate studies, it grows both east and west of the main divide in the South Island. It is most commonly found in montane and sub-alpine forests in the North (250-1200m) and from sea-level to 1200m in the South. Generally it grows in high rainfall subalpine broadleaf forests with frequent fog and short, cool summers. However it can also be found in localised high rainfall areas of the cool temperate southern beech forests (*Nothofagus* spp) and even in dry, rocky situations (Salmon, 1996). Typically, cedar prefers poorly drained peaty or strongly leached soils with impeded drainage (Wardle, 2011). Its common growth habit is a tall (~25m) slender canopy species exhibiting a cone shaped head of spreading branches and straight, bare trunk generally of up to 1m in diameter (1.25-1.5 in extreme cases), although on peaty soils at high altitude it may reach no more than a few metres in height (Salmon, 1996; Farjon, 2010; Wardle, 2011). Cedar commonly lives for over 500 years and can grow for over 700 (Xiong and Palmer, 2000a; Fenwick, 2003; Palmer and Xiong, 2004). It is a relatively slow growing tree, with average ring-width/annual growth of approximately 0.77mm (Xiong and Palmer, 2000a).

Cedar tree rings have provided local and regional temperature reconstructions via conventional dendrochronology (Xiong and Palmer, 2000a; 2000b). An extensive network of sites (23, spread over ~8° latitude and ~1000m elevation) show high levels of correlation between ring-width records. A subset of 11 covering the central-North and upper-South Islands were used for a broad-scale late-summer temperature reconstruction (Xiong and Palmer, 2000b) while a smaller subset of 5 provided a 500 year temperature record that showed local regional agreement with New Zealand speleothem records and broad regional
agreement with Tasmanian huon pine (Lagarostrobus franklinii) ring-width records (Palmer and Xiong, 2004).

$\delta^{13}C$ and $\delta^{18}O$ could potentially add to the palaeo-temperature records from cedar, given that both may be sensitive to air temperature. However, if $\delta^{13}C$ and $\delta^{18}O$ primarily respond instead to moisture-related climatic factors, this does nothing to reduce the palaeoclimate reconstruction potential; Cedar’s South Island West Coast range is one of the most La Niña sensitive areas of the country, with major increases in rainfall during La Niña years (Ummenhofer and England, 2007). Conversely, cedar’s east coast range on the South Island (including South Canterbury) receives diminished rainfall during La Niña events; a comparison between cedar stands from either side of the main divide could yield centuries of ENSO proxy data based on moisture regimes, facilitating an improved understanding of the impact of annual ENSO events and, crucially, the longer term ENSO pattern. Ultimately, it may be possible to combine a moisture (stable isotope) and temperature (ring-width) record from a single site, using a single species to create a detailed multi-proxy palaeoclimate record.

2.7 Summary

The unique ability of tree-rings to provide annual, calendar dated proxy records across time periods spanning multiple centuries to millennia makes them an attractive tool for palaeoclimate reconstruction. Recent advances in stable isotope analytical technologies make possible the addition of long dendrochemical records to traditional ring-width reconstructions. Dendrochemical records have the advantage of reconstructing a limited and relatively well understood suite of environmental variables, often adding detail to ring-width reconstructions. Questions regarding past hydroclimatic variability are particularly well matched to investigations using both $\delta^{13}C$ and $\delta^{18}O$, with the latter serving as a potentially powerful tool for reconstructing atmospheric circulation patterns. New Zealand has numerous long-lived native conifers suitable for stable isotope dendroclimatology and it sits at the junction of multiple circulatory systems of hemispheric and global importance. Consequently, there is little question that stable isotope dendroclimatology in New Zealand has great promise for addressing key knowledge gaps in Southern Hemisphere mid-latitudude palaeoclimatology.
3. EXPERIMENTAL ASSESSMENT OF THE PURITY OF α-CELLULOSE PRODUCED BY VARIATIONS OF THE BRENDEL METHOD: IMPLICATIONS FOR STABLE ISOTOPE (δ\(^{13}\)C, δ\(^{18}\)O) DENDROCLIMATOLOGY

This chapter constitutes the first major analytical research component of the thesis, in addition to providing a methodological review of dendroisotopic processing techniques. Most studies of tree-ring isotopes isolate specific wood components for analysis in order to minimise the isotopic variability associated with different wood constituents within the ring. α-cellulose, the structural foundation of wood, is the most commonly used because it is easily isolated, abundant and specific to the time of ring formation (McCarroll and Loader, 2004). The standard Brendel (SBrendel) approach, an acid digestion followed by a series of washes, was chosen for this research due to the rapid processing times and minimal equipment required. The method was well established within the stable isotope dendroclimatology literature (see Brendel et al., 2000; Evans and Schrag, 2004; Rinne et al., 2005; Anchukaitis et al., 2008). However, early processing yielded numerous samples that retained significant colouration (yellow-brown) and visible wood structure, rather than the desired white, fluffy colour/texture of pure α-cellulose. Conversations with other SBrendel users revealed that this was not an uncommon problem, although kauri appeared to be most effected. Ultimately, those discussions led to the following quantitative evaluation of the SBrendel extraction method as applied to kauri and other species. This research was conducted collaboratively with Dr Tom Whittaker of the University of New Mexico, USA. Preliminary findings were presented at the American Geophysical Union conference (Brookman et al., 2011) where feedback from Craig Brodie and Kevin Anchukaitis encouraged the expansion of the project and, ultimately, the following publication in G-cubed under the DIPPI-C working group theme.

The methodological advancement contained herein demonstrates that different species are more/less resistant to the SBrendel sample processing method. Incomplete processing can result in significant isotopic differences in sample extracts but, ultimately, minor methodological adjustments can improve processing consistency (with the caveat that over-processing may be a problem, so thorough investigation is required prior to embarking on chronology development). These findings were a crucial first step toward efficient and effective processing of kauri for stable isotope dendroclimatic investigation, minimising potential isotopic variability at the processing stage that could later obscure climate signals.
The following text is a modified (according to external thesis examiners' requirements) version of:


Modifications are primarily focussed on the interpretation of δ^{13}C results from the study. Original interpretation suggested that high- and low-temperature variants of the Brendel yielded cellulose with similar δ^{13}C. However, it appears that high-temperature extractions yield cellulose with relatively depleted δ^{13}C. While the cause is not quantitatively demonstrated, one explanation is the slight acetylation of cellulose during extraction.
3.1 Introduction

3.1.1 Stable Isotope Dendroclimatology and α-cellulose

Dendrochemical records facilitate high-temporal resolution interpretation of the magnitude, extent and causes of terrestrial environmental change. Recent years have seen a proliferation of studies investigating stable isotope signatures preserved in tree-rings (McCarroll and Loader, 2004; Leavitt, 2010) and references therein). Ratios of the stable isotopes of hydrogen (δD), carbon (δ¹³C), oxygen (δ¹⁸O) and nitrogen (δ¹⁵N) in tree-ring constituents (whole wood or extracts) have been used to reconstruct environmental variables that influence tree growth (Barbour et al., 2001; Loader et al., 2003; Bukata and Kyser, 2005; Dodd et al., 2008). The growth potential of this relatively new field of research is limited by the global distribution of living or sub-fossil (e.g. (Jahren and Sternberg, 2008)) trees suitable for study. Isotopic investigation of material obtained from a variety of genera from the tropics (Poussart et al., 2004) to high latitudes (Saurer et al., 2002; Porter et al., 2009a), sea level (Verheyden et al., 2005) to high altitude (Bale et al., 2010) and rainforest (Evans and Schrag, 2004) to semi-desert (Lipp et al., 1996; Bale et al., 2010), have revealed past environmental changes. Stable isotope research on tree-rings also has potential to inform investigations into plant physiology, paleoecology and nutrient cycles, particularly changes in the global cycles related to carbon and oxygen isotope shifts (Leavitt et al., 2010).

Tree-rings are variably composed of celluloses, lignin, waxes, lipids, oils and resins. For most dendroclimatic studies, particularly those presenting records of δ¹⁸O, tree-ring isotopic composition is determined from the α-cellulose component of the ring. The primary reason for isolating α-cellulose is that of all the components of tree-rings only α-cellulose retains both its carbon and oxygen isotopic composition from the time of formation (McCarroll and Loader, 2004). Other wood components freely exchange carbon, hydrogen and oxygen atoms with other environmental compounds over time and therefore do not necessarily record paleoclimate information from the calendar year of growth. The stable isotopic compositions of whole wood and its individual constituents differ, significantly so for δ¹⁸O (Barbour et al., 2001; Battipaglia et al., 2008) and less so for δ¹³C (Loader et al., 2003; Verheyden et al., 2005). The fraction of whole wood that is α-cellulose/lignin/resin etc. varies between trees meaning that comparing isotopic ratios of individual wood compounds can be undertaken with greater confidence than comparing whole wood values. Furthermore, unlike other wood components, α-cellulose maintains its integrity in dead trees for long periods, thus making it a more useful tool than the isotopic composition of whole wood in sub-fossil samples (Jahren and Sternberg, 2008).

α-cellulose extraction is a time-consuming, and often rate-limiting, step in many studies. In an effort to overcome this challenge, several methods have been developed to extract α-cellulose from whole wood. All of the methods include an acidic oxidizing step followed by a series of rinses (Leavitt and Danzer, 1993; Loader et al., 1997; Brendel et al., 2000; Evans and Schrag, 2004). The Jayme-Wise method (Green, 1963), and variants thereof (Loader et al., 1997; Boettger et al., 2007), require 2-5 days to process a batch of up to 100 samples and are often associated with material loss due to filtering (Brendel et al., 2000), a factor which ultimately reduces an archive’s potential temporal resolution. In contrast, the
Experimental assessment of the purity of α-cellulose

Brendel method (Brendel et al., 2000), subsequently modified for much smaller sample sizes (Evans and Schrag, 2004), yields measurable α-cellulose extracts for 90 samples or more in a single day, primarily due to its combining of solvent extraction oxidation steps.

Over extended periods, for large sample collections the efficiency increase is likely negligible, or perhaps even reversed, due to the efficiency of running multiple ‘batches’ of Leavitt-Danzer samples concurrently (Porter et al., 2009b), particularly with recent research suggesting that the initial solvent extraction may be unnecessary (Rinne et al., 2005; Boettger et al., 2007). However, this requires a streamlined, well established laboratory, generally with good technical support where the Brendel methods, particularly SBrendel (Standard Brendel), typically require only basic equipment and reagents and have the added advantage of minimising losses associated with filtering and changing of reaction vessels (Brendel et al., 2000). These factors make Brendel methods particularly attractive to non-specialist researchers/laboratories new to the field of stable isotope dendroclimatology. The nomenclature regarding variations on the original Brendel method currently groups the original method (Brendel et al., 2000) and its streamlined form for small samples (Evans and Schrag, 2004) under the title of the Standard Brendel (Gaudinski et al., 2005; Anchukaitis et al., 2008; English et al., 2011). Other iterations which include an NaOH wash and NaOH plus extra water washes are labeled the Modified Brendel (MBrendel) and Water Modified Brendel (WMBrendel) (Gaudinski et al., 2005). If, through rigorous investigation, it can be established that the SBrendel provides a consistently high-quality product for particular species, then this may be a long-term benefit to the dendrochemical community by facilitating the involvement of new laboratories in the research field.

Perhaps the only downside to the SBrendel, from our own experiences and the findings of Gaudinski et al. (2005), is that there remain uncertainties over its ability to consistently yield pure α-cellulose. Without quality control analyses on samples (e.g. FTIR and/or experimental methodological variations such as we present here), the purity of cellulose produced is suspect; for studies working at the limits of sample size and resolution confidence in the method is critical. Recent publications highlight that such problems are not isolated and have contributed to false, or at least artificially amplified, climate signals (Berkelhammer and Stott, 2008; Berkelhammer and Stott, 2011). The addition of extra chemical stages to the SBrendel as seen in the MBrendel (Gaudinski et al., 2005) or the solvent extraction step added by Dodd et al. (2008) may increase sample quality but detract from the very characteristics that distinguish SBrendel: speed, simplicity and accessibility.

3.1.2 Research Objective

This study’s primary objective is to investigate the ability of minor modifications to the SBrendel method of Evans and Schrag (2004) to deliver pure α-cellulose products from samples of long-lived, resinous tree species without significant increases in processing time or equipment and/or reagent use. Previous work suggests that with minor modification the SBrendel method can be more widely applied (Anchukaitis et al., 2008; Brookman et al., 2011). Resinous soft-woods dominate at high latitudes and altitudes and form the basis for many multi-millennial dendrochronologic archives in both Northern and
Southern hemispheres (Ferguson and Graybill, 1983; Friedrich et al., 2004; Palmer et al., 2006; Hua et al., 2009; Turney et al., 2010), necessitating the use of a consistently effective, rapid, cost-effective α-cellulose extraction for small sample sizes in developing dendrochemical archives. To investigate the purity of products from SBrendel variants we use a combination of FTIR (Fourier-Transform Infrared spectroscopy) and isotope ratio mass spectrometry on three such species: ponderosa pine (*Pinus ponderosa*), New Zealand kauri (*Agathis australis*) and huon pine (*Lagarostrobus franklinii*).

### 3.1.3 FTIR of Wood

FTIR is routinely used to investigate α-cellulose purity (Brendel et al., 2000; Rinne et al., 2005; Anchukaitis et al., 2008) as well as characteristics of whole wood (Ajuong and Breese, 1998; Pandey, 1999), biologically or mechanically altered wood (Pandey and Pitman, 2003; Schwanninger et al., 2004) and other wood constituents such as lignins and resins (Faix, 1991; Hinterstoisser and Salmén, 2000; Pandey and Pitman, 2004; Rinne et al., 2005; Anchukaitis et al., 2008). By comparing spectra of experimental products to those of whole wood and commercially produced α-cellulose isolates (e.g. Sigma-Aldrich cellulose) a simple determination of purity can be assigned based on the absence/presence of specific transmission peaks (Rinne et al., 2005). FTIR also provides an opportunity to monitor the effects on the quality of the α-cellulose product of increases in reagent to sample ratios. Anchukaitis et al. (2008) report that the SBrendel results in slight acetylation of cellulose, although the α-cellulose remains viable for δ¹⁸O analysis.

### 3.2 Material and Methods

#### 3.2.1 Sample Selection

We studied the effectiveness of SBrendel method variants using samples of resin-rich trees with potential to make significant contributions to palaeoclimate reconstruction: ponderosa pine, New Zealand kauri and huon pine. Ponderosa pines may live >400 years and have a wide geographic distribution, occurring across much of western North America. Our sample was cored from a ~100 year old specimen growing in northwest Arizona. Kauri and huon pine have more limited natural distributions; they are confined to northernmost New Zealand and southwestern Tasmania, Australia, respectively. However, individual trees can live in excess of 2000 years and the recovery of sub-fossil specimens has allowed construction of discontinuous tree-ring chronologies that extend to ~60,000 and 13,500 years before present, respectively (Hua et al., 2009; Turney et al., 2010). Furthermore, stable isotope dendroclimatology remains an almost untapped area of study in the Southern Hemisphere extra-tropics and by working with huon pine and kauri we aim to facilitate development of new records from this region. Our kauri sample comes from a fallen tree from the Upper Huia Dam region, near Auckland, New Zealand and the huon pine sample from a disk sawn from a fallen tree in western Tasmania.
3.2.2 SBrendel Processing

We obtained approximately 250mg of wood from each of the three tree species which was then shared between our laboratories at The University of Canterbury (UC) and the University of New Mexico (UNM) where a combined total of 6 powdered fractions were created. Each sample was powdered using a either a dremel tool or a saw depending on size and then homogenized through a freeze-milling process or ultrasonic disaggregation, both based on Laumer et al. (2009). For this study we used only the <355μm fraction of the generated powder (following Rinne et al. (2005)).

At each laboratory the fractions were divided into subsamples of ~20 mg plus one with mass ~10 mg. The 10mg samples remained untreated and were used to characterize the FTIR spectra and stable isotope (δ¹³C, δ¹⁸O) values of whole wood.

The ~20 mg wood samples were each divided into ~20 0.9-1.1 mg subsamples. Each batch of ~1mg subsamples was then subject to either the original small sample SBrendel method (Evans and Schrag, 2004) or one of seven variants (Table 3.1) in dedicated laboratory spaces developed by the authors. The resultant cellulose from each batch was pooled and homogenized.

### Table 3.1: Variants of the SBrendel method to be investigated as part of this project. The SBrendel method of Evans and Schrag (2004), experiment #1, describes boiling wood samples at 120°C in a 120 μL 80% acetic acid and 12 μL 70% nitric acid mixture for ~30 minutes. All experiments were repeated for each wood type at low temperature (115°C) and high temperature (120°C).

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Acetic Acid (μL)</th>
<th>Nitric Acid (μL)</th>
<th>Boiling Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>12</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>18</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>24</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>240</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>360</td>
<td>36</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>360</td>
<td>36</td>
<td>1</td>
</tr>
</tbody>
</table>

The next step of the SBrendel method is for samples to be boiled at 120°C in a nitric-acetic acid mixture. This temperature is approximately the boiling point for 70% nitric acid (120.5°C at 1 atm.;(Sigma-Aldrich, 2012)) and close to the melting point (~130°C) of many brands of polypropylene microcentrifuge tubes (e.g. VWR) which generally show signs of softening at ~125°C (personal experience and Kevin Anchukaitis, personal communication). For these experiments we trialed flip-top and screw-top microcentrifuge tubes. Each has advantages and disadvantages with respect to performance, cost and time taken to open and close. However, given the tendency for flip-top tubes to pop open during boiling.
at 120°C, often exploding the contents into the fume hood, this study investigated the influence of boiling temperature on product purity. SBrendel variants performed at UNM using flip-top vials were conducted at 115°C (rather than the 120°C suggested by the SBrendel). The 5°C temperature reduction generally prevents explosion and allows researchers to reduce costs and save time during the four rinse steps in the method. The UC samples were digested at 120°C using screw-top microcentrifuge tubes (Sarsted, 1.5ml). Samples digested at 115°C are coded LT (low temperature) while those digested at 120°C are coded HT (high temperature). Detailed, step-by-step procedures can be found in the supplementary data online (Appendix 8.8). We did not trial at temperatures greater than 120°C due to limitations of reagent boiling temperatures and microcentrifuge tube integrity. In designing the experiment we did not consider whether the effect of altitude on the boiling point of reagents may have played a role in our methods; UC experiments were conducted at near sea-level (~1.0 atm.) while the UNM campus sits at almost 1600m above sea level (0.8-0.85 atm.) where reagent boiling points are likely to be lower.

3.2.3 FTIR

Preliminary work by the authors used visual analysis to determine whether or not the cellulose extraction process resulted in a pure product. However, neither the level of purity, nor the contaminant(s) can be determined quantitatively by this method.

Subsamples of whole wood, the material produced from each experiment, and a commercial α-cellulose (Sigma Aldrich) were analyzed on a Nicolet Nexus 670 at the New MIRA FTIR facility at the University of New Mexico, using both microscope and bench transmission. The former method was preferred as it required <0.1 mg of sample and individual fibers could be selected under the microscope and analyzed separately. Multiple spectra were collected for all samples to minimize potential influence of orientation effects (Hinterstoisser et al., 2001).

Bench transmission was performed on only a sub-set of samples. Approximately ~0.25mg of desiccated sample material is pressed into a potassium bromide disk. In so doing, numerous fibers, in many orientations, are measured simultaneously, providing a ‘bulk’ spectrum of the sample, similar to the Attenuated Total Reflectance (ATR) method used in similar studies (Rinne et al., 2005; Anchukaitis et al., 2008).

3.2.4 Stable Isotope Analysis

The remainder of each sample was used for stable isotope (δ¹³C, δ¹⁸O) analysis. For each of the experiments and the whole wood, 10 subsamples were analyzed: five for δ¹³C and five for δ¹⁸O. Carbon isotope ratios were determined at the UC Stable Isotope Facility; samples of mass 255 ± 15 μg were loaded into tin capsules and combusted in a hot (1050°C) Costech 4010 EA (Elemental Analyzer) coupled with a DeltaVPlus IRMS (Isotope Ratio Mass Spectrometer) via a ConFlo III open-split continuous-flow interface. The precision of in-house and certified standard materials measured via this method during these experiments was better than 0.15 ‰ (n = 151).
Experimental assessment of the purity of α-cellulose

Oxygen isotopic analysis of experimental products was performed at the UNM Stable Isotope Laboratory. Samples of mass 255 ± 15 μg were loaded into silver capsules and pyrolyzed in the hot (1400°C) alumina:glassy carbon reactor of a TC/EA (Thermal Conversion/Elemental Analyzer). Sample gas (CO) was analyzed in a Finnigan-MAT 252 IRMS via a ConFlo III open-split continuous-flow interface. The precision of in-house and certified standard materials measured via this method during these experiments was better than 0.3‰ ($n = 107$).

3.3 Results

3.3.1 Qualitative Observations of Produced α-cellulose

There were clear color and textural differences between many of the products from experiments HT 1-8 and LT 1-8. All displayed a color gradient with cellulose getting progressively less yellow with increasing experiment number (Fig. 3.1). Kauri retained the most color; some fibers remained opaque even when wet.

Texturally, most samples were light and ‘fluffy’ as expected from α-cellulose. When scraped from the vial, particles were easily disaggregated. A few samples, however, had a ‘pasty’ consistency which meant particles clumped together. These samples also yielded distinct spectra and isotopic ratios and are discussed later (3.3.2, 3.3.4 and 3.4.1).

![Fig. 3.1: A distinct color gradient in α-cellulose processed through experiments. From left to right, Kauri experiments HT 1-8.](image)

3.3.2 FTIR

3.3.2.1 Whole wood

Ponderosa, kauri and huon yielded similar spectra, all woods displaying the same peaks ($\pm 3 \text{ cm}^{-1}$) in the fingerprint region (~900-1800 cm$^{-1}$ wavelength), which correspond to those characterized in the existing literature, summarized in [Table 3.2](#). The peaks characteristic of lignins, resins and holocellulose are
clearly evident, particularly when compared with commercial α-cellulose (Fig. 3.2). Peak intensities vary due to a combination of sample thickness, crystallographic orientation and different relative abundances of wood components.

Fig. 3.2: A spectral comparison of sigma α-cellulose (dashed blue line) with whole wood (*P. ponderosa* – solid green line) showing major differences between 1000-2000 cm⁻¹ (the fingerprint region). The peaks absent from the sigma represent the loss of resins, lignins (mostly from 1500-2000 cm⁻¹) and holo/hemi-cellulose (900-1500 cm⁻¹).

### 3.3.2.2 SBrendel Products

Using microscope transmission we were able to isolate, target and separately analyze distinct yellow fibers that, based on color, we suspected had not been fully processed. Spectra for these fibers are similar to whole wood with peaks at ~1520 cm⁻¹ and 1600 cm⁻¹, indicating presence of lignin and resin respectively ([Table 3.2](#)) (Pandey, 1999; Schwanninger et al., 2004; Anchukaitis et al., 2008).

There were more yellow fibers in the lower numbered experiments but these visible differences were not reflected in the bench transmission spectra. While changes in peak shape between microscope and bench transmission were discernible, the peaks’ positions remained constant. We are confident that the microscope transmission method provides data that are comparable with ATR and other bulk methods employed in the literature.

Most fibers viewed under the microscope were not yellow. When analyzed these fibers generally yielded spectra similar to the commercial α-cellulose, except for the SBrendel contamination peaks produced by cellulose acetylation (1235 and 1720 cm⁻¹) (Anchukaitis et al., 2008).
### Table 3.2: Diagnostic FTIR Peaks in Wood and Cellulose in the fingerprint region.

<table>
<thead>
<tr>
<th>Wave-number</th>
<th>Wood component</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>897-900</td>
<td>cellulose and hemicelluloses</td>
<td>(Pandey and Theagarajan, 1997; Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>995-1000</td>
<td>cellulose and hemicellulose</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1055</td>
<td>cellulose and hemicellulose</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1110</td>
<td>soluble cellulose acetate</td>
<td>(Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>1110-1128</td>
<td>cellulose and hemicellulose</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1160</td>
<td>cellulose and hemicellulose</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1200</td>
<td>hemicellulose</td>
<td>(Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>1245</td>
<td>soluble cellulose acetate</td>
<td>(Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>1240 &amp; 1267</td>
<td>lignin</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1265-1270</td>
<td>lignin and xylan</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1325</td>
<td>cellulose</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1328</td>
<td>cellulose and syringyl derivatives</td>
<td>(Pandey and Pitman, 2004)</td>
</tr>
<tr>
<td>1375</td>
<td>cellulose and hemicellulose</td>
<td>(Pandey and Pitman, 2004)</td>
</tr>
<tr>
<td>1430</td>
<td>cellulose crystallinity</td>
<td>(Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>1460</td>
<td>lignin</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1505-1515</td>
<td>aromatic skeletal vibration (lignin)</td>
<td>(Pandey, 1999; Schwanninger et al., 2004)</td>
</tr>
<tr>
<td>1506</td>
<td>benzene ring in lignin</td>
<td>(Pandey and Theagarajan, 1997)</td>
</tr>
<tr>
<td>1510-1740</td>
<td>H$_2$O adsorbed to cellulose-OH (long gentle peak present in all cellulose)</td>
<td>(Rinne et al., 2005)</td>
</tr>
<tr>
<td>1570</td>
<td>lignin</td>
<td>(Łojewska et al., 2005)</td>
</tr>
<tr>
<td>1593-1610</td>
<td>aromatic skeletal vibration (lignin) plus C=O stretching</td>
<td>(Pandey, 1999; Schwanninger et al., 2004)</td>
</tr>
<tr>
<td>1600</td>
<td>resin</td>
<td>(Anchukaitis et al., 2008)</td>
</tr>
<tr>
<td>1604-1732</td>
<td>resin</td>
<td>(Rinne et al., 2005)</td>
</tr>
<tr>
<td>1660</td>
<td>conjugated C=O vibration</td>
<td>(Pandey and Theagarajan, 1997; Łojewska et al., 2005)</td>
</tr>
<tr>
<td>1740</td>
<td>insoluble cellulose acetate/xylan/hemicelluloses</td>
<td>(Pandey and Theagarajan, 1997; Rinne et al., 2005; Anchukaitis et al., 2008)</td>
</tr>
</tbody>
</table>

Ponderosa and huon results from LT and HT experiments are similar, both showing minor differences between products from experiments 1 through to 7 ([Fig. 3.3a](#)). Kauri, however, displayed a consistent trend across LT experiments 1-8 in with a distinct residual lignin peak (1520 cm$^{-1}$) evident in experiment 1 and continuing, although diminishing throughout the experiments until almost indiscernible in experiments 6 and 8 ([Fig. 3.3b](#)). Significantly, this peak is present in non-yellow particles and also appears in the bench transmission spectra.

A number of samples (ponderosa HT6 and huon HT1-4, 6) produced spectra with peaks at 1458 and 1552 cm$^{-1}$ and pronounced peaks at 2855, 2871 and 2955 cm$^{-1}$ (where previously only small ‘shoulders’ were evident) that, to our knowledge, are previously undocumented ([Fig. 3.4](#)). We believe these reflect sample contamination associated with a minor methodological change, characterized by a pasty consistency which we discuss later (Section 3.4.1).
Experimental assessment of the purity of α-cellulose

Fig. 3.3: A spectral comparison of a) high temperature digestions 1(3) and 8(7) and b) low temperature digestions 1 and 8 (4).
Fig. 3.4: FTIR spectra comparing one cleanly processed huon sample (solid blue line) and one displaying contamination peaks (dotted orange line). Black vertical lines correspond to peaks at 1450, 1550, 2855, 2870 and 2955 cm$^{-1}$ introduced during processing which are not part of the 'normal' acetylation process observed in the SBrendel.

Fig. 3.5: CO$_2$ (Atomic mass 44) and CO (Atomic mass 29) yield curves from a) LT $\delta^{13}$C analyses, b) HT $\delta^{13}$C, c) LT $\delta^{18}$O and d) HT $\delta^{18}$O.
3.3.3 Isotope Analysis

3.3.3.1 Yield Curves

Yield curves (obtained by plotting sample mass against mV signal) could provide clues to whether samples are contaminated or insufficiently processed due to changes in the signal:sample mass ratio. Due to a combination of static and earthquake interference with the UC mass balance (Sartorius high precision scale) there is noise in the data (Fig. 3.5a); we are confident that this is associated with balance inconsistencies rather than varied sample yields. Ultimately, however, for α-cellulose, CO\(_2\) yield curves, except those of samples with spectra displaying the extra peaks discussed in section 3.3.2.2 which yielded much more CO\(_2\) per µg of sample, do not appear to be useful for distinguishing poorly and properly processed α-cellulose samples.

For both HT and LT experiments whole wood yielded less oxygen (CO) per µg than processed samples (Fig. 3.5c and d). Allowing for small variations in the mass-balance, the LT1 and LT8 Kauri samples essentially plotted along the same yield-curve as α-cellulose standards. HT8 also plotted with the standards but HT1 consistently yielded slightly less oxygen per µg of sample. Ultimately, for α-cellulose, yield curves provide very little information on sample purity in relation to δ\(^{18}\)O.

3.3.3.2 Delta Values

There are no patterns in δ\(^{13}\)C associated with our experimental changes within the HT and LT datasets (Fig. 3.6). α-cellulose is enriched compared to whole wood by varying amounts between species; huon by ~1‰, kauri by ~0.5 ‰ and ponderosa values are within analytical error. Between HT and LT datasets, however, it appears that huon, and to a lesser extent ponderosa, HT samples are more depleted in δ\(^{13}\)C than LT equivalents.

Samples identified as contaminated (huon HT 1-4 & HT6, ponderosa HT6) from their spectra are not shown in Fig. 3.6; all were significantly depleted compared to whole wood and uncontaminated α-cellulose (Fig. 3.7). The change in isotopic composition, in association with the increased yields, suggests a \(^{13}\)C depleted contaminant. These samples are associated with a ‘pasty’ consistency, easily distinguishable from the ‘fluffy’ consistency typical of α-cellulose. We were unable to isolate the cause of the contamination but suggest potential contributing factors in section 3.4.1, the most likely being insufficient removal (pipetting) of acetone, causing slight acetylation of cellulose.

Across the three suites of HT experiments we do not find a consistent trend in δ\(^{18}\)O with change in variable (Fig. 3.8). However, within individual suites there is minor variability, most pronounced in the ponderosa samples, which is potentially associated with the precision (0.3 ‰) of analysis or insufficient homogenization of sample material. Across the LT experiments the huon and ponderosa δ\(^{18}\)O similarly display no consistent trend. Kauri samples display a relationship between δ\(^{18}\)O and both extraction time and acid volume. Half-hour extractions produced cellulose with depleted δ\(^{18}\)O relative to the corresponding 1 hour extraction. The level of depletion decreased with increasing acid volume until experiment 7 returned δ\(^{18}\)O matching that of the 1 hour extractions (Fig. 3.8).
Experimental assessment of the purity of α-cellulose

Fig. 3.6: δ¹³C variation across the HT (left column) and LT (right column) experiments conducted on a) huon, b) ponderosa and c) kauri. Each data point is the mean of 5 replicate analyses, error bars represent the standard deviation of the replicates. Experiment # (x-axis) corresponds with the protocols described in Table 1. Missing data in HT column relate to contaminated products (Fig. 3.7) and those in LT column are due to limited sample material.
Fig. 3.7: Samples from HT experiments identified as contaminated from their spectra are represented by orange dots. Depletion of $\delta^{13}$C is clear in contaminated samples, all of which are more depleted than whole wood. $\alpha$-cellulose $\delta^{13}$C is generally enriched compared to whole wood. Experiment # (x-axis) corresponds with the protocols described in Table 3.1.
Experimental assessment of the purity of \(\alpha\)-cellulose

Fig. 3.8: \(\delta^{18}O\) variation across the HT (left column) and LT (right column) experiments conducted on a) huon, b) ponderosa and c) kauri. Each data-point is the mean of 5 replicate analyses, error bars represent the standard deviation of the replicates. Experiment \# (x-axis) corresponds with the protocols described in Table 3.1. Missing data in LT column are due to limited sample material.
3.4 Discussion

The results of this study demonstrate that the SBrendel method cannot be relied upon to consistently produce pure α-cellulose (e.g. vial HT1 in Fig. 3.1), and therefore is not a “one size fits all” method in terms of delivering pure α-cellulose products from tree-ring material. Product color, IR spectra and stable isotope data ($\delta^{13}$C, $\delta^{18}$O) all indicate that trace amounts of non-cellulosic residue remain in the product when SBrendel is used in combination with *P. ponderosa*, *L. franklinii* and *A. australis*, resin-rich softwoods.

Given the large range of isotopic compositions of individual wood components (Barbour et al., 2001) and the loss of climatic information when whole wood is analyzed compared to α-cellulose (Borella et al., 1999; Battipaglia et al., 2008), knowledge of cellulose purity or at least isotopic fidelity, are crucial. This study investigated the effects of modifying reaction temperature, reagent volume and duration of high-temperature reaction, whilst attempting to maintain the main advantages of SBrendel: its time, cost and sample-size efficiency. Our results demonstrate that:

1. Proceeding with a high (120°C) reaction temperature, as specified in the original SBrendel method, generates a purer, though still impure, product than at low (115°C) temperature for $\delta^{18}$O (see caveat regarding $\delta^{13}$C below). Original SBrendel (HT1) completely delignifies all wood types we tested whereas the delignification at low temperature is incomplete in all wood types for LT1 (Fig. 3.3), although only kauri shows a systematic influence on $\delta^{18}$O (Fig. 3.8). Based on FTIR (Fig. 3.3) and visual inspection (Fig. 3.1) resin remains in HT1 and LT products but has little isotopic effect (Fig. 3.6; Fig. 3.8). The benefit of HT1 over LT1 is balanced by the need to purchase screw-top microcentrifuge tubes (approximately US$0.09 per tube), an expensive alternative to flip-top tubes (approximately US$0.05 per tube), and the increase in total processing time incurred by the need to unscrew and re-screw vial lids on tens-to-hundreds of samples during each of the four rinse steps.

2. Boiling for an extra half an hour (total of 1 hour) typically yields a purer product for $\delta^{18}$O analysis. For kauri, the species requiring the most intensive delignification, the purity achieved when boiling at low temperature (using flip-top vials) for longer periods (LT2, 4, 6, 8) is similar to that achieved by SBrendel (HT1). Spectra reveal a very small residual lignin peak but it does not appear sufficient to affect $\delta^{18}$O. The low-temperature one-hour boil is arguably the most cost and time efficient way of modifying SBrendel due to the lower cost of flip-top tubes and the time saved opening and closing tubes during processing. However, quantitative assessment of delignification is urged.

3. Doubling and tripling reagent volume also leads to increases in product purity for low temperature extraction, with delignification and therefore $\delta^{18}$O gradually increasing. When applied at low temperature this method is the most time efficient in that boil time is kept short and flip-top vials are retained. However, the increases in purity obtained by these changes are less than can be achieved by either lengthening boil time by 30 minutes or increasing boil temperature by 5°C. The cost of extra reagent suggests this is the least cost efficient modification to the SBrendel method.
Experimental assessment of the purity of α-cellulose

(4) even amongst similar groups, in this case long-lived, resinous conifers, different species have significantly different processing requirements. Our finding that kauri was hardest to extract pure α-cellulose from does not support the suggestion that SBrendel struggles with the resins/sap in living pines (English et al., 2011). Our kauri sample was from a dead, fallen tree whilst our ponderosa (much more easily extracted) was from a living, standing tree.

We extrapolate from our observations of the products of kauri, ponderosa pine and huon pine, and the observations of English et al. (2011) that the SBrendel method will perform poorly in terms of resin extraction from samples of highly resinous woods. While we cannot isolate the exact effect of incomplete removal of resins on δ¹³C values from those of incomplete delignification, our data suggest that it is a less than 1 ‰ negative offset from pure α-cellulose, similar to previous investigations of ponderosa pine and English oak (Loader et al., 2003; English et al., 2011). Were researchers to encounter a tree with relatively large δ¹³C offsets between whole wood and α-cellulose, similar to those observed by English et al (2011) (up to 3.2‰ in Pinus edulis), it is possible that under-processing could bias δ¹³C, albeit to a lesser extent than for δ¹⁸O. In our work, improved resin removal is achieved through increased reagent volumes (refer to color gradient in [Fig. 3.1]). We did not test boiling times longer than one hour, but we suggest there is potential for this to increase resin removal. In other work pre-Brendel solvent extraction steps have also proved beneficial (e.g. Dodd et al., 2008), although this approach requires the researcher to expand the laboratory set-up to include new equipment and reagents and will lead to large increases in total cost and processing time.

At the onset of the study we also intended to observe whether there may be adverse effects due to ‘over-processing’. From visual observations of the products plus analysis of acquired FTIR and stable isotope data we find no quantitative evidence to suggest that increases in reaction time or reagent volume, or any combination of the two, led to compromised isotopic values. However, the combination of ‘contaminated’ samples (see below) and the off-set between HT and LT δ¹³C for huon and ponderosa raise the potential that acetylation of cellulose occurred and affected δ¹³C. This issue requires further investigation; this study, like that of Anchukaitis et al (2008) initially focussed on δ¹⁸O as the more likely ratio to be affected by processing. Consequently, tests were not designed to assess the affect of acetylation on δ¹³C.

A further, cautionary observation from our experiments is that while the presence of color is an indication that α-cellulose samples have not been fully processed, a lack of color cannot be used to infer purity. Much, potentially all, of the hue is associated with residual resin rather than lignin, which imparts little or no coloration. While resins contain little oxygen, particularly terpenoid resins such as those found in kauri (Langenheim, 1990), oxygen-rich residual lignin (Phillips and Goss, 1936; Adler, 1957) can strongly influence sample δ¹⁸O. The difference in δ¹⁸O values for cellulose and lignin has been shown to be approximately 8‰ in oak and pine, with whole wood values approximately 2‰ enriched compared to lignin (Barbour et al., 2001). Using our cellulose and whole wood data, and assuming that lignin δ¹⁸O values are 2‰ depleted relative to whole wood, the difference between cellulose and lignin δ¹⁸O values could be as much as 10-12‰. Given the magnitude of the difference in cellulose and lignin δ¹⁸O even
small amounts of residual lignin could affect sample δ^{18}O and therefore our ability to extract accurate paleoenvironmental information. Consequently, there are significant implications for stable isotope dendroclimatology studies. Therefore we recommend that laboratories utilizing the SBrendel method to generate α-cellulose undertake an examination of their product using FTIR in order to determine whether the variant of the SBrendel method that was employed has removed all lignin or requires minor modification. Alternatively, if FTIR is not an option, then a systematic isotopic test as presented here may suffice. Detailed analysis of CO₂ or CO yield data, often a means of assessing sample purity is not sufficient for α-cellulose purity.

### 3.4.1 Contamination Peaks

In several cases utilization of the SBrendel method yielded a ‘pasty’ product, a phenomenon also observed by Kevin Anchukaitis (personal communication). IR spectra show peaks (1458, 1550, 2855, 2871, 2955 cm⁻¹) in addition to those expected for cellulose. These peaks could result from a number of factors. As yet we, and others, have been unable to definitively isolate the cause so we present two hypotheses in the hope that an answer may be forthcoming. The cause of pasty consistency significantly impacts δ^{13}C such that carbon-related palaeoenvironmental information is unrecoverable from these samples. In contrast, the δ^{18}O of these samples appears to be unaffected.

Given the increased carbon yield curves observed, the contaminant most likely has a significant carbon component. Acetic acid, ethanol and acetone, used in the SBrendel, all contain carbon. Due to time constraints and sample settling issues a small sub-set of HT samples had minimal acetone removed after the final wash stage of the SBrendel variants. These sets of 20 sub-samples (See section 3.2.2) were pipetted into a single glass vial whilst still suspended in a small amount of acetone, in order to create the corresponding pooled, homogenous HT samples. The other, non-contaminated, sets of sub-samples had remaining acetone (minimal) evaporated in polypropylene micro-tubes (standard SBrendel procedure, see Appendix 8.8) and were then re-suspended in distilled, deionised water and homogenized in glass vials. This process resulted in very long drying and settling times (4+ days) in a 50°C oven. The last batch of sub-samples (contaminated) had only 2 days to dry before international travel so it was reasoned that small amounts of acetone would evaporate faster than water and were unlikely to leave residue, given that (significantly less) acetone is generally evaporated in a low temperature oven in the last stage of SBrendel. It seems we were mistaken and we propose that this altered acetone treatment is the most likely root of the contamination. Kevin Anchukaitis (personal communication) has also observed a relationship between the ‘pasty’ texture of contaminated samples and insufficient acetone removal. We have considered two detailed scenarios:

1) The acetone took longer to evaporate, giving it time to covalently react with the cellulose, as documented by Awadel-Karim et al. (1998). The peaks associated with the contaminated samples are characteristic of the methyl groups associated with acetonation/acetylisation of cellulose (Awadel-Karim et al., 1998).
Experimental assessment of the purity of α-cellulose

2) The insufficient removal of acetone left residue from the ethanol washes and/or acid digestion in amounts great enough to affect the isotopic composition of the sample. Further testing could show whether the retention/deposition of this residue was accentuated by the acetone evaporation occurring in glassware as opposed to the usual polypropylene.

With regard to 1), we do not believe that the experimental conditions were conducive to ‘acetonation’ of cellulose as documented by Awadel-Karim et al. (1998); those authors reacted the cellulose with acetone and acidified water under 450 psi pressure at 150°C for 2 hours. Our samples were at atmospheric pressure in a 50°C oven. However, previous researchers (Gaudinski et al., 2005; Anchukaitis et al., 2008) have shown that the SBrendel results in slight ‘acetylation’ of cellulose. While neither study documents quality issues for δ¹⁸O, Gaudinski et al (2005) note that Brendel samples have more depleted δ¹³C than other methods, similar to the results shown here (Fig. 3.6). Slight acetylation may account for the more negative δ¹³C for huon and ponderosa HT samples compared to LT, even for samples not identified as contaminated.

With regard to 2): we ran homogenized kauri powder through 3 variants of the SBrendel, one of which excluded the acetone wash altogether, another that simply evaporated the entire acetone wash rather than pipetting the bulk out and finally, a standard SBrendel. None of the samples displayed the pasty texture of the contaminated samples from our major experiments. The δ¹³C of the samples, calculated as the mean of 5 replicate analyses, was within 0.2 ‰ with all sets of replicates having standard deviation <0.2 ‰. The unwashed sample was ~0.1 ‰ depleted relative to the evaporated sample which was in turn depleted compared to the standard sample by ~0.1 ‰. However, these depletions are an order or magnitude smaller than those observed in our major experiments and do not strongly support the ‘insufficient’ washing hypothesis. This may support the suggestion that evaporation in glassware as opposed to polypropylene affects the deposition/retention of reagent residues.

At this stage we can only provide the purely qualitative advice that if a sample has a pasty/slimy consistency it may be contaminated and unsuitable for δ¹³C analysis and that the most likely cause is operator error in the form of insufficient removal of acetone. Analysis of sample yield-curves can reveal excess carbon from contaminants and could be a useful ‘double-check’ on suspected contaminated samples. Despite this, our data suggest that pasty samples remain viable for δ¹⁸O analysis.

3.4.2 Implications for Palaeoclimatic Application

Stable isotope dendroclimatological studies have gained prominence in the scientific community in recent years, recognized as a means of high resolution terrestrial palaeoclimate reconstruction. A key consideration for a number of these publications is that reconstructions, even over multi-centennial scales, are based on relatively small amplitude changes in the isotopic record (<6‰) (Hilasvuori et al., 2009; Kress et al., 2010). Even in extreme environments δ¹⁸O variability over millennial timescales can be <8‰ (Treydte et al., 2006).
Results from this study suggest that if cellulose extractions are incomplete, as they were in the case of some low temperature extractions (e.g. kauri LT1) here, inconsistency in the level of cellulose purity can introduce large isotopic uncertainties; our data show the uncertainty for kauri is up to ±1.5 ‰ for δ¹⁸O. Our data also show that the uncertainties differ between species, meaning that ±1.5 ‰ is by no means a maximum figure. As a result, a large portion of the inferred climatic signals in palaeoclimate reconstructions based on such data are questionable, particularly when considerations are given to analytical and operator error (Porter and Middlestead, 2012) and intra and inter-tree variability (Leavitt, 2010; Woodley et al., 2012). If samples from multiple radii are pooled prior to analysis the method of pooling also has implications for the influence of processing error on data quality. Pooled whole wood samples would be susceptible to greater error as any incomplete extraction would occur for all material from a given year. α-cellulose samples pooled post-extraction may reduce the influence of incomplete extraction provided the incompleteness is not systematic within/between processing runs. In either scenario, the use of natural variability quantification/reduction techniques like that of Woodley et al. (2012) may be compromised by increased analytical error, an effect compounded in scenarios where multiple annual rings are pooled to rapidly develop long chronologies (Gagen et al., 2012).

We apply the maximum ‘error’ associated with incomplete extraction using SBrendel (±1.5 ‰, based on the difference between kauri HT1 vs LT1), plus analytical error (±0.3 ‰), in our study to δ¹⁸O data from a kauri tree in southern New Zealand (Fig. 3.9) to demonstrate the potential for natural variability, be it climatic or otherwise, to be obscured by processing. In this case the entire range of variability observed within the record is ‘within error’. In moderate climates without large seasonal shifts, the impact of inadequate extraction could be critical.

The impact of inadequate processing using SBrendel has been recently demonstrated by Berkelhammer and Stott (2011). Their original publication in 2008 interpreted a significant drop in δ¹⁸O as an abrupt climatic shift related to changes in storm-track activity. However, after reviewing their data in the context of a similar study (Bale et al., 2010) the authors came to the conclusion that the δ¹⁸O shift was greatly accentuated by methodological problems; we suggest that the most likely cause was incomplete de-lignification, leading to sample δ¹⁸O significantly lower than expected from pure α-cellulose, as we observed in our LT experiments. Fortunately, in Berkelhammer and Stott’s (2011) case, the authors were diligent and honest in the quality control of their own data. Their correction is a valuable contribution in demonstrating the need for qualitative assessment of α-cellulose purity produced by SBrendel in order to avoid erroneous palaeoclimatic interpretation. It is worthy of note that the SBrendel extractions in Berkelhammer and Stott (2008) were performed at 120°C, which corresponds to HT samples in this study which showed no evidence of incomplete extraction. While we cannot isolate the cause for what appears to be incomplete extractions in others’ research, it does appear that running at 120°C does not guarantee a fully delignified cellulose product.

The interdisciplinary, collaborative research environment within which much stable isotope dendroclimatology takes place raises further issues surrounding the SBrendel method. Given the difficulty
of comparing organic material δ¹⁸O values between laboratories (Boettger et al., 2007; Brand et al., 2009), the potential variability introduced by SBrendel that we report here only adds to the uncertainty. While individual laboratories continue to use their own version of SBrendel it will be difficult to directly compare isotopic values from one study to the next. In this environment, and indeed within single laboratories, the use of Porter and Middlestead’s (2012) identical treatment quality assurance standards could provide improved comparability of data between runs/labs/species.

It may be beneficial for the current and future stable isotope dendroclimatology community to expand on this work and define acceptable protocols or best practices for certain tree-species or groups of species (e.g. resinous softwoods) such that inter-site comparisons can be achieved without undue concern for inconsistency in product purity. In the meantime, researchers should ensure that their method is quantitatively validated for their particular species.

![Graph showing δ¹⁸O variability](image)

**Fig. 3.9:** δ¹⁸O variability within averaged whole-ring sample data from 2 cores from a single young kauri tree from near Dunedin, New Zealand, over the 2000-2009 period (processed using standard SBrendel/HT1) Error bars represent the ±1.5‰ uncertainty introduced by LT digestion plus ±0.3‰ allowing for precision of high temperature pyrolysis analysis. Red dashed lines show the range of δ¹⁸O variability over the time period.
3.5 Conclusion

The SBrendel provides a fast, low-cost means of extracting α-cellulose pure enough for δ\textsuperscript{13}C and δ\textsuperscript{18}O analysis. However, its inability to routinely yield pure α-cellulose is of concern to those looking to efficiently produce high-sample-count palaeoclimate archives from tree-rings. Our findings suggest that with relatively minor alterations and appropriate testing, the SBrendel can produce analyte of sufficient quality for stable isotope dendroclimatic study. The extraction temperature can be lowered, allowing use of flip-top tubes, provided time and reagent volume are sufficient. However, all these variables must be carefully and quantitatively assessed for the particular tree species being processed as the ease of delignification varies significantly even between similar species (e.g. resinous conifers). Similarly, qualitative evidence from this study suggests that some woods can be ‘over-processed’, particularly by the HT method, resulting in lower δ\textsuperscript{13}C, perhaps due to acetylation of cellulose. Only through isotopic and spectral testing of cellulose product can researchers be confident of SBrendel results.

Visual analysis of purity can reveal if processing has been insufficient to completely remove resin but not whether α-cellulose is pure; lignin is more isotopically distinct from α-cellulose and is not always removed from samples clear of resin. Conversely, some samples still visibly resinous (i.e. yellow) are sufficiently de-lignified to provide consistent isotopic data. Ultimately, to be certain that sufficient purity is achieved, FTIR or a systematic isotopic test such as we have presented is required.
4. INTRA AND INTER-TREE STABLE CARBON AND OXYGEN ISOTOPE VARIABILITY IN LONG-LIVED NEW ZEALAND CONIFERS: IMPLICATIONS FOR PALAEOCLIMATE RECONSTRUCTION.

Having determined that resinous conifers, including kauri, could be rapidly and consistently processed to α-cellulose, the first step in establishing stable isotope dendroclimatic records from New Zealand was to characterise the level of isotopic variability within the target species. The impact of that variability on isotope chronology quality for New Zealand kauri (*Agathis australis*) and cedar (*Libocedrus bidwillii*) is outlined in the following chapter/manuscript. This chapter provides a data-based answer to a fundamental question relevant to dendrochronological research, ‘how many cores, from how many trees, are needed to create a robust record?’ This is particularly relevant for mature native kauri, for which the scientific benefits of coring must be weighed against the species’ status as a cultural and historical icon, and developing concerns surrounding the spread of ‘kauri dieback’ disease. In order to document variability between and within trees, and to establish guidelines for future research, a number of trees from a privately owned southern kauri plantation and a nearby native stand of cedar were intensively sampled. Chronology quality was assessed using Expressed Population Signal (EPS) and preliminary correlations between the two sites/species were conducted to assess the potential for using multiple species to expand the geographical coverage of New Zealand palaeoclimate reconstructions. In New Zealand, where limited investigation into the potential of native trees for stable isotope dendroclimatology has occurred, this research represents important baseline data for future studies.

During the process of creating these chronologies, further methodological development was also undertaken in an effort to expedite the analysis of large numbers of samples. Traditionally, separate analyses are required for carbon and oxygen stable isotope determinations on organics, making dual-isotope records labour intensive, time consuming and expensive. However, the emerging method of dual carbon and oxygen low temperature pyrolysis facilitates the determination of carbon and oxygen stable isotope ratios from a single sample. The method was trialled to compare its precision with traditional low temperature combustion analysis for carbon, and high temperature pyrolysis for oxygen. The promising results are briefly outlined within the following chapter/manuscript.

The methods employed in the creation and analysis of the data presented in this chapter are covered within the chapter in a manuscript-manner, providing the reader sufficient information to replicate the experiment provided further reading (references) is pursued. Further site descriptions and methodological detail, which detracted from the focus on results and analysis, are provided in Appendices 8.5-8.10. Raw data for this, and following, chapters are included in appendices 8.11-8.18.
4.1 Stable Isotope Dendroclimatology in the Southern Hemisphere

High-resolution terrestrial palaeoclimate histories are an essential resource for understanding the timing, duration, and cause of regional and global climate change events. However, few natural archives are sensitive to environmental and climatic change at sufficiently high temporal resolution (annual and finer scale) to allow investigation of both climate variability and rapid climate change. For example, recent multi-centennial climate reconstructions at annual resolution are facilitating interpretation of inter-hemispheric teleconnections in Earth’s climate system, such as El Niño Southern Oscillation (ENSO; Fowler et al., 2012). However, Southern Hemisphere and inter-hemispheric scale connections/patterns remain less well understood than their Northern counterparts due to a lack of Southern Hemisphere records (Jansen et al., 2007; Neukom and Gergis, 2012).

Numerous Northern Hemisphere stable isotope dendroclimatic reconstructions have exploited existing calendar-dated tree-ring records to establish isotope-climate relationships for reconstruction of local (Porter et al., 2009; Bale et al., 2010; Berkelhammer and Stott, 2012; Loader et al., 2013; Rinne et al., 2013) and regional climate patterns (Treydte et al., 2006; Leavitt et al., 2007; Loader et al., 2013). Similar application of isotopic techniques to long-lived Southern Hemisphere trees could increase understanding of teleconnections between hemispheres, regional circulation patterns and weather events that are now well described in the Northern Hemisphere. The use of stable isotope dendroclimatology in such studies has been based on the physiological and environmental fractionation processes that determine the stable isotopic composition of wood constituents within a tree (Reviewed in Chapter 2).

4.1.1 Key Research Questions

The previously established relationships between climate and tree-ring cellulose isotopes are investigated for two key dendroclimatic species, kauri and cedar (Agathis australis and Libocedrus bidwillii) in New Zealand. Kauri and cedar are promising for long-term climate reconstruction but few annual or sub-annual resolution dendrochemical investigations of native species have been undertaken. New Zealand’s maritime climate, influenced by a complexity of multiple atmospheric and oceanic circulation systems (Lorrey and Bostock, in press) is notoriously variable. Therefore, we set out to answer a series of fundamental questions regarding reproducibility and inherent variability both within and between composite dendrochemical time-series in order to guide future dendrochemistry studies with a palaeoclimate focus. The data, analysis, and interpretation we present were produced in an attempt to answer the following key research questions:

1) How variable are intra-tree kauri and cedar $\delta^{13}$C and $\delta^{18}$O values (i.e. between cores/radii)? Tans and Mook (1980) and Ramesh et al. (1986) were among the first to identify microclimatic and/or physiologically driven $\delta^{13}$C and $\delta^{18}$O variations both within and between trees, including radial/circumferential disparities. Isotopic variability between different radii has important implications for sampling strategies and the fidelity of climatic conditions interpreted from tree-ring records. By determining the relative magnitude of exogenous versus endogenous drivers of intra-tree isotopic
variability, our research provides important baseline knowledge relevant to robust interpretation of future longer-term dendrochemical datasets.

2) How variable are inter-tree kauri and cedar $\delta^{13}C$ and $\delta^{18}O$ values within a tree stand? Apart from Tans and Mook’s (1980) early work from the Netherlands, most studies suggest that the differences between trees are larger than those within trees (Leavitt, 2010). Establishing whether or not this is the case for kauri and cedar is crucial to understanding the relative importance of physiological, micro-environmental, local, and regional scale drivers of isotopic change.

3) Do composite stable isotopic time-series from kauri and cedar provide robust common signals? An expressed population signal (EPS) (Wigley et al., 1984; Briffa and Jones, 1990) score of 0.85 (85% common signal within a series of trees/cores) or greater is the generally accepted benchmark criterion for a strong, cohesive dendrochronological or dendrochemical record. To date, research has suggested that stable isotope dendroclimatology is often able to retrieve a strong common signal from as few as 4-6 trees (McCarroll and Loader, 2004; Leavitt, 2010; Gagen et al., 2011). In comparison, common signals from ring-width studies often require records constructed from approximately 5-25 trees (Briffa and Jones, 1990). If true for kauri and cedar, this could be particularly useful in settings where tree numbers are limited, such as is the case for the kauri sub-fossil archives (see Boswijk et al., 2006; Palmer et al., 2006; Turney et al., 2010).

4) Do kauri and cedar record similar patterns of inter-annual isotopic composition? In the context of regional climate reconstruction, it is important to understand whether different species can be used to reconstruct changes in similar environmental variables. Published research shows mixed responses to this question (see Leavitt, 2010 and references therein). Given the different, but overlapping, natural ranges of kauri and cedar, answering this question will help to maximise the potential contribution of New Zealand dendroisotopic archives to paleoclimate research in the middle southern latitudes. While full-scale climatic reconstruction is beyond the scope of this manuscript, preliminary investigation of climatic relationships with any strong common records between kauri and cedar is warranted to assess palaeoclimate potential.

Answers to these questions will facilitate future tree-ring research by constraining the number of trees and cores likely required to create a statistically robust record from tree-ring isotopes. Ultimately, this information can be used to inform targeted reconstructions of local and regional climate using cedar and kauri. Our data also add a Southern Hemisphere perspective to the growing pool of literature dealing with the absolute and relative amounts of variability observed in inter and intra-tree dendrochemical studies.

4.1.2 Analytical progress for stable isotope dendroclimatology

To provide a solid platform for the future climatic investigation using kauri and cedar, we address the key questions posed relating to reproducibility within the record using data acquired through the dual element low-temperature pyrolysis analytical technique. While the concept and analytical design for dual-element
pyrolysis of cellulose has been reported in the literature (Werner et al., 1996), the potential for glassy carbon contribution to CO (Leuenberger and Filot, 2007) and the incomplete conversion of cellulose to CO at low temperatures (Loader and Buhay, 1999), have remained a possible concern. While the potential for time and resource savings through dual C and O determination is well known (Saurer et al., 1998; Kornexl et al., 1999; Nakatsuka et al., 2004; Knöller et al., 2005), the approach has only recently been applied to long-term reconstructions (Young et al., 2011; Woodley et al., 2012b). We present a brief summary of our reproducibility trials with the low-temperature pyrolysis method below.

4.2 Materials and Methods

4.2.1 Site description and dendrochronological methods

Samples for this study were collected in the vicinity of Dunedin on the South Island of New Zealand. The Dunedin Kauri (DK) site (45.833 S, 170.3614 E; Fig. 4.1) is situated on the north-eastern margin of the Taieri Plain, at ~46m above sea level (asl). The area’s climate is typical of coastal Otago, with warm summers and cool winters and relatively uniform rainfall throughout the year (Sturman and Tapper, 2006; Fig. 4.1). Invermay, ~5km from the DK site, receives ~730mm of annual rainfall and has a mean annual temperature of ~10.3°C (NIWA, 2011). Approximately 70 of the 110-112 kauri originally planted at the site between 1954 and 1957 remain (Unknown, 1964). The DK trees are one of the southernmost substantial plantations of this naturally sub-tropical species (Brookman et al. accepted; Appendix 8.7). Thirteen trees ranging from 28-40cm diameter at breast height (DBH) were sampled comprising a total sample set of 37 cores.

In contrast to the DK plantation, the Mt Cargill Cedar (MtC) site (45.808 S, 170.5664 E) (Fig. 4.1) is a mature natural stand in remnant native forest. Less than 20 km from DK, it has an existing >500-year chronology (LaMarche et al., 1979), suggesting potential for a long palaeoclimate reconstruction. The site is closer to the coast and at higher elevation (~500-550m asl) than DK and while it fits the same regional climate description it is cooler and wetter due to its higher altitude setting (Fig. 4.1). Sullivan’s Dam (~3.5km west at 300m asl), receives ~1220mm of annual rainfall, and Swampy Summit (~6km west at 700m asl) has a mean annual temperature of ~7.3°C (NIWA, 2011). Twenty-four trees, ranging from 37 to 77cm DBH were sampled comprising a total sample set of 67 cores.

Cores were taken with 400mm long, 5.15 mm diameter increment borers. Two to three cores were taken from each tree, separated by at least 90° around the tree circumference where practical. The cores were visually cross-dated using a binocular microscope, and ring-widths were measured with a Velmex measuring stage. COFECHA software (Holmes, 1983) was used to check visual cross-dating. DK cores had a mean length of 45 years, a mean series inter-correlation of 0.56 and average mean sensitivity of 0.211. MtC series had a mean length of 238 years, a mean series intercorrelation of 0.66 and average mean sensitivity of 0.219. See appendices 8.5 - 8.7 for more methodological, site and chronology details for DK and MtC.
Fig. 4.1: Shaded relief digital elevation model of the Dunedin region showing the two sample collection sites studied (Dunedin Kauri – DK; Mount Cargill Cedar – MtC). Average monthly temperature and precipitation amount are presented as climographs based on data collected by the National Institute of Water and Atmospheric research (NIWA) at nearby sites (from west to east) Invermay, Swampy Summit and Sullivan’s Dam (red stars). DK climograph is composed of monthly temperature and rainfall averages from Invermay (1943-1977). MtC climograph is a composite of Swampy Summit temperature (2008-2013) and Sullivan’s Dam rainfall (1980-2012). Inset map of New Zealand’s South Island is shown for reference.
4.2.2 Sample preparation

Only cores that achieved highly significant ring-width correlation with site master records ($p < 0.01$) during cross-dating were selected for isotope analysis. Cores were sampled with a straight-bladed scalpel under an illuminated magnifying glass. DK rings (excluding high resolution samples) and a sub-set of wide MtC rings were divided into three sub-samples: a ‘whole-ring’ (WR) sub-sample, an ‘early-season’ (ESW) sub-sample taken from the first ~50% of the ring and a ‘late-season’ sub-sample composed of the later 50% of an individual ring, which was stored for archival purposes. The division into early and late-season was designed to enable future study of seasonal (spring vs summer/autumn) climatic responses from this dataset. Kauri has a documented tendency to form most of its annual ring during a period of rapid growth during Austral Spring, including as much as 50% of total annual growth during October and November (Fowler et al., 2005; Wunder et al., 2013). We consider variability and common signal in both WR and ESW records here but refrain from an in-depth comparison of the two, which will be presented separately.

Samples were processed in order to isolate the α-cellulose wood component, using the ‘High Temperature 3x SBrendel’ procedure described in Brookman and Whittaker (2012), modified from Evans and Schrag (2004) and Brendel et al. (2000). Whole-wood sample sizes were ~4.5mg for DK and <4.5mg for MtC. Samples were then re-suspended in distilled, de-ionised water, chilled to ~4°C in a refrigerator and fragmented using an ultrasonic probe (as in Laumer et al., 2009) to aid homogenisation. Processed samples were then placed in a 50°C oven for ~3-4 days until dry.

Dried α-cellulose samples were massed into silver foil capsules (either 5x3.5mm or 4x3.2mm, OEA laboratories), in order to avoid the larger δ¹⁸O ‘blank’ associated with tin capsules (Wang et al., 2008). Massed DK samples were generally 250 ± 25 µg while MtC samples were 125 ± 10 µg, with the latter being smaller due to limitations on sample material from narrower rings. Capsules were folded and transferred to a vacuum desiccator for a minimum of 2 days with the pump running continuously. Samples were then transferred into a 100 place Costech zero-blank autosampler with an isolation valve and purged in a stream of ultra-high purity helium (UHP He) for 10 minutes. Following purging, the isolation valve to the reactor of the Costech 4010 Elemental Analyser (EA) was opened and samples were left in the He stream for a minimum of 3 hours prior to starting the analytical sequence. This allowed backgrounds to stabilise and facilitated the removal of any atmospheric H₂O adsorbed to the silver during the rapid transfer of samples from the dessicator to the autosampler.

4.2.3 Dual element low temperature pyrolysis

Dual carbon and oxygen stable isotopic compositions of α-cellulose extracts were determined using continuous flow LT pyrolysis in the Stable Isotope Facility at the University of Canterbury, Department of Geological Sciences. Sample carbon and oxygen were converted to CO in an ~100ml/minute helium stream at 1080°C in a Costech 4010 ECS operated in oxygen mode and purified using in-line water and carbon dioxide traps as well as a 1m 5Å mol sieve gas chromatography column (at 110°C).
Intra and inter-tree stable carbon and oxygen isotope ratios were determined on eluted CO (via a ‘ConFlo II’) using a Delta V Plus Isotope Ratio Mass Spectrometer running Isodat 2.5. Each analytical sequence started and ended with ~6-10 reference material analyses. An additional 3 reference materials were analysed approximately every 10 samples of processed α-cellulose. The mean internal precision of the Delta V Plus mass spectrometer (calculated from CO reference gas standard on-off tests performed immediately prior to analytical sequences) is better than 0.07‰ for carbon and 0.12‰ for oxygen. The mean external precision (i.e. reproducibility) for the UC dual element low temperature pyrolysis system is better than 0.10‰ for carbon and 0.30‰ for oxygen, based on over 1500 reference material analyses during this study, using predominantly α-cellulose in the form of in-house Sigma (SAC) and IAEA CH-3 (CH3), and 170 replicate analyses of sample unknowns [Table 4.1].

Within-run precision is reported as the standard deviation about the mean of drift corrected standards within that run. Reported long-term analytical precision is calculated from the standard deviation of all reference standards run throughout this project. The data cover two major analytical ‘periods’, labelled DK and MtC as samples from those sites comprised the bulk of the two periods respectively. A third, distinct sample dataset with replicates, Dunedin Kauri High Resolution (DK HR, the results from which are used here purely in the discussion of analytical precision/reproducibility) was run during the MtC analytical period and its replicates are distinguished while its standards are incorporated in the MtC period. All data were corrected to the V-PDB for δ¹³C and V-SMOW for δ¹⁸O international standards using a 1-point normalisation (i.e. an additive correction) based on the SAC (δ¹³C: -25.44, δ¹⁸O: 32.4) and IAEA CH-3 (δ¹³C: -24.724‰, δ¹⁸O: 32.6‰) reference materials analysed in each Isodat sequence.

Those reference materials were also used to check and correct for instrument drift within each run; drift was corrected through linear regression. δ¹³C reference values for SAC and δ¹⁸O for SAC and CH3 were originally determined across multiple analytical series using certified reference materials with conventional EA combustion and TC/EA HT pyrolysis.

A 2-point normalisation (i.e. a ‘stretch and shift’ or ‘mean and variance bias’ correction) would have been preferred due to the potential compression of δ¹³C variance during LT pyrolysis (Young et al., 2011; Evans et al., in prep), which potentially compromises the accuracy of δ¹³C determinations. However, this requires more isotopically distinct standards than SAC and IAEA-CH-3. Similarly, the accuracy of δ¹⁸O determinations is hampered by the well reported lack of a certified reference material (CRM) for organic δ¹⁸O (Saurer et al., 1998; Boettger et al., 2007; Brand et al., 2009). Ultimately, stable isotope time series from either element can facilitate palaeoclimate reconstruction based on inter-annual changes provided samples are identically treated within a single processing and analytical system.

4.2.4 Data Quality Control

Establishing a quantitative and objective process for handling outliers created by analytical or sample processing errors is an important step in assessing data quality. To identify statistical outliers a ‘box and whisker’ probability density estimation was applied. For δ¹³C samples, this was conducted after applying a linear correction for atmospheric depletion due to fossil-fuel use (McCarroll and Loader, 2004, pp. 787-
Outliers were defined as those results more than 1.5 times the interquartile range above the third quartile or below the first quartile (See Appendix 8.10).

After removing analytical outliers, three data quality control experiments were undertaken: First, the relative precision/reproducibility of the two major analytical periods (DK, MTC) was investigated by comparing the variance of SAC and CH3 δ\textsubscript{13}C and δ\textsubscript{18}O across the two periods, using an F-test to show whether the variances were significantly different (H\textsubscript{0}: σDK=σMTC, dfDK, dfMTC). Second, the relative precisions of reference standards were investigated across the entire research period using the same approach (H\textsubscript{0}: σSAC=σCH3, dfSAC, dfCH3). This test established a baseline for the third experiment: a comparison of reference standard precision with the precision (and by inference, the sample homogeneity) of replicate analyses of our sample unknown α-cellulose extracts. Paired t-tests allowing for unequal variances (Welch’s t-test) were used to test whether the mean precisions obtained for DK, DKHR and MtC replicates were significantly different relative to one another, or to the mean within-run precisions of SAC and CH3.

4.2.5 Circumferential and Inter-Tree Analyses

To characterise the isotopic variability between cores from the same tree (i.e. intra-tree variability or circumferential variability) and cores from different trees in the same stand (i.e. inter-tree variability) we present the ranges and mean intra and inter-tree isotopic differences. This allows us to make progress towards determining the relative importance of endogenous (e.g. physiological) and exogenous (e.g. hydroclimatic) isotopic drivers. As was the case for the intra-annual data analysis, Root-Mean-Square (RMS) error was used to characterise the reproducibility of δ\textsubscript{13}C and δ\textsubscript{18}O from cores around a tree.

4.2.6 Determining Expressed Population Signal

The level of common variance amongst the series was then tested using the expressed population signal (EPS) statistic (Wigley et al., 1984; Briffa and Jones, 1990), a common statistical measure of signal versus noise within a stand of trees, using ‘detrender’ (Campelo et al., 2012) package in ‘R’ (R-Core-Team, 2012). EPS calculations included each core as an individual series so that EPS scores reflect ‘effective correlation’ (REFF), a measure that accounts for singal coherence within a tree (RWT) by including each core as a separate time series, as well as the signal coherence between-trees (RBT) (Briffa and Jones, 1990).

After determining EPS values for our composite records, we sought to establish an approximate theoretical minimum number of trees required for a coherent signal, using the widely accepted benchmark of EPS >0.85 (McCarroll and Loader, 2004). We ran a cross-correlation between our ‘outlier-stripped’ time-series and their respective site master chronologies (compiled from the mean of all cores apart from that being tested) in order to identify any cores that correlated poorly, presumably due to non-climatic endogenous influences. Time-series that failed to meet the Pearson’s product-moment \( p = 0.05 \) significance level (one-tailed) were stripped from the site chronology and resulted in ‘improved’
chronologies which were then re-analysed using EPS. A similar ‘stripping’ technique using EPS has already demonstrated modest improvements for kauri ring-width chronologies (Fowler and Boswijk, 2003). Both ‘improved’ and entire series are discussed in sections 4.3.4 and 4.4.3 to evaluate their relative EPS scores and subsequent implications for sampling strategies and palaeoenvironmental reconstruction potential. Climate correlations are only run on entire series, as it was deemed inappropriate to rely on the qualitative improvement process without further experimentation and justification.

As part of our EPS investigation, in an effort to understand how data transformation and correction affects EPS results, we determined multiple sets of EPS scores for isotope and ring-width records (Table 4.3). For δ\textsubscript{13}C this was run on raw data, atmospherically corrected data (labelled ‘Atmos’) and for DK δ\textsubscript{13}C, which had a residual decreasing trend after atmospheric correction, data detrended using linear regression (labelled ‘Detrended’). This residual trend may be related to a non-climatic ‘juvenile effect’, the suggested causes for which are still debated (McCarroll and Loader, 2005; Loader et al., 2007). The ‘juvenile’ effect in relation to DK samples is discussed in more detail in Chapter 2 and Appendix 8.7. EPS was also calculated for each record at multiple stages of ‘quality control’. For stable isotope records these are the ‘whole record’, the ‘outlier stripped’ record based on the quantitative removal of individual outliers (see section 4.2.4) and the ‘improved’ records (see section 4.2.4). Ring-width records were not ‘outlier stripped’ as the process was introduced to remove data created by flawed stable isotope analyses (contaminated α-cellulose, poor sample drop into the reactor etc.).

4.2.7 Common Signal Between Kauri and Cedar – Palaeoclimate Potential

In order to explore the palaeoclimate potential for using kauri and cedar as a regional climate reconstruction proxy, we created a cross-correlation matrix to assess which records between the two species/sites are significantly correlated. Then strongest inter-species/site record was then used to create a bispecies composite record to calibrate against local climate data extracted from NIWA’s virtual climate station network (NIWA, 2011). In order to create the bispecies composite, the MtC and DK master time-series were normalised to an internal scale of variability by subtracting the series’ mean from each annual value and dividing by the series’ standard deviation. This facilitated combination of the two records by creating a common scale, as their amplitudes of inter-annual change and mean values raw isotope values are significantly different (see section 4.3.5). A bootstrapped correlation (with 1000 resamples) was then run between the bispecies composite and climate data using DENDROCLIM 2002 software (Biondi and Waikul, 2004).

4.3 Results

4.3.1 Standard and Replicate Precision in Dual Element Low Temperature Pyrolysis

We present a detailed break-down of reference standard and sample data from low-temperature pyrolysis demonstrating the system’s precision (Table 4.1).
Table 4.1: Standard and replicate precision calculated as the mean of within-run precision (standard deviation of reference material analyses) from a number of analytical periods. Data from Brookman & Whittaker (2012) are not part of this study but are included here for comparison of precision between 'traditional' methods of δ¹³C and δ¹⁸O analysis and LT pyrolysis.

<table>
<thead>
<tr>
<th>Method</th>
<th># of Analyses</th>
<th># of Runs</th>
<th>Mean δ¹³C of all samples</th>
<th>δ¹³C StDev of all samples</th>
<th>δ¹³C StErr of all sample mean</th>
<th>Mean δ¹³C Run Precision ± SE (‰)</th>
<th>δ¹³C Run Precision Range (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC*</td>
<td>29</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.15 ± 0.06</td>
<td>0.01 - 0.52</td>
</tr>
<tr>
<td>Jahren*</td>
<td>27</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.28 ± 0.03</td>
<td>0.20 - 0.35</td>
</tr>
<tr>
<td>Replicates:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Dual CO, DK | 102 (25) | | | | | | ...
| Dual CO, MtC | 51 (18) | | | | | | ...
| Dual CO, DK Hi Res | 18 (6) | | | | | | ...

Highlights:

- SAC*: In-house standards at the University of New Mexico.
Intra and inter-tree stable carbon and oxygen

The mean precision achieved for reference materials across the two major sample/standard sets (DK and MTC) on the UC system were 0.10‰ or better for δ\(^{13}\)C from IAEA CH-3 and 0.09‰ or better from SAC. IAEA CH-3’s precision for δ\(^{18}\)O was 0.28‰ or better while SAC’s was 0.34‰ or better. CH3’s δ\(^{18}\)O precision was significantly (\(F_{759,670} = 1.41, p < 0.01\)) better than SAC while SAC’s very slightly (in a practical sense) better δ\(^{13}\)C precision was also statistically significant (\(F_{670,759} = 1.28, p < 0.01\)). Between the two major analytical periods there were small but statistically significant changes in reference standard precision. δ\(^{13}\)C precision was ~0.01‰ better during the MTC period, a statistically significant improvement for CH3 (\(F_{353,316} = 1.43, p < 0.05\)) while δ\(^{18}\)O precision was ~0.2-0.4‰ worse during the MTC period, a statistically significant decline for both SAC (\(F_{368,390} = 1.31, p < 0.05\)) and CH3 (\(F_{316,353} = 1.22, p < 0.05\)).

For sample replicates, a comparison of mean precisions show that MTC and DKHR samples were not significantly different from the SAC and CH-3 standards run alongside them (\(p > 0.05\), Welch’s t-test). The mean precision of DK replicates, however, was significantly lower other replicates (\(p < 0.05\), Welch’s t-test) and reference materials (\(p << 0.001\), Welch’s t-test).

4.3.2 Intra-Tree Variability

Maximum intra-tree differences in δ\(^{13}\)C were between 2.8 and 3.3‰ for both DK and MTC, with mean intra-tree differences ca. 0.7-1.1‰. δ\(^{18}\)O differences for DK were 6.0-6.3‰ at their largest and 1.3-1.5‰ on average. In contrast, the maximum MTC δ\(^{18}\)O differences were smaller (2.9-3.7‰) than kauri, as were the mean inter-core differences (0.6-0.8‰) (Table 4.2a).

Across the 29 year record, RMS error ranged from 0.0 to 1.5‰ for MTC δ\(^{13}\)C and 0.0-1.8‰ for MTC δ\(^{18}\)O. DK RMS errors, over 28 years, were similar for δ\(^{13}\)C (0.0-1.5‰) but higher for δ\(^{18}\)O (0.0-2.9‰). The grand-mean of series’ RMS errors showed a higher level of reproducibility for δ\(^{18}\)O (0.4‰) compared with δ\(^{13}\)C (0.5-0.6‰) in MTC, but the opposite for DK which had a δ\(^{18}\)O grand-mean of (0.8‰) compared with δ\(^{13}\)C (0.4-0.5‰).

The patterns of intra-tree variability were diverse and too numerous to include here individually, but selected examples for cedar are illustrated in Fig. 4.2. Some trees yielded three cores with well correlated changes throughout the record but with constant off-sets in isotope values (Fig. 4.2a). Other trees exhibited convergent/divergent patterns where two cores were consistently separated with values from a third core ‘bridging’ the two cores at some point (Fig. 4.2b). In some cases, trees yielded three cores that were essentially well correlated within a tight range of raw values, with the occasional abrupt departure on one or more radii (Fig. 4.2c).
4.3.3 Inter-Tree Variability

Inter-tree differences for MtC were smaller than intra-tree, with maxima of between 2.0-2.9‰ for $\delta^{13}C$ and 2.0-2.3‰ for $\delta^{18}O$, with means all <1.0‰. In contrast, DK $\delta^{13}C$ inter-tree differences were slightly larger than intra-tree for both maxima (3.9-4.4‰) and mean (1.2‰). $\delta^{18}O$ inter-tree differences for DK, on the other hand, were smaller than their respective intra-tree records with maximum differences of 4.6-5.8‰ and means of 1.1-1.4‰.

The range of annual RMS errors for each inter-tree series was smaller than for intra-tree. Inter-tree time series’ mean RMS errors were similar to intra-tree for MtC but DK inter-tree series RMS errors were all larger than intra-tree. Inter-tree RMS errors for DK are generally more than double those for MtC and this increased variance about the mean is partnered with a greater amplitude in inter-annual isotope changes and the range of values covered by the time series (Fig. 4.3).

Table 4.2: Maximum and mean isotopic differences calculated for MtC and DK on a) an intra-tree (ie. circumferential) scale including RMS error calculations indicating reproducibility of $\delta$-values around a tree and b) an inter-tree scale including RMS error calculations indicating reproducibility of $\delta$-values between trees within a stand.

<table>
<thead>
<tr>
<th>a.</th>
<th>Period</th>
<th>Trees (cores)</th>
<th>Single Year Max Difference Between Cores</th>
<th>Single Year Mean Difference Between Cores</th>
<th>Range of RMS error between cores</th>
<th>Mean RMS error between cores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta^{13}C$ (‰)</td>
<td>$\delta^{18}O$ (‰)</td>
<td>$\delta^{13}C$ (‰)</td>
<td>$\delta^{18}O$ (‰)</td>
</tr>
<tr>
<td>MtC</td>
<td>ESW</td>
<td>1983-2011</td>
<td>3 (6)</td>
<td>2.8</td>
<td>2.9</td>
<td>1.1</td>
</tr>
<tr>
<td>MtC</td>
<td>WR</td>
<td>1983-2011</td>
<td>8 (21)</td>
<td>3.2</td>
<td>3.7</td>
<td>0.8</td>
</tr>
<tr>
<td>DK</td>
<td>ESW</td>
<td>1983-2010</td>
<td>7 (18)</td>
<td>3.3</td>
<td>6.0</td>
<td>0.7</td>
</tr>
<tr>
<td>DK</td>
<td>WR</td>
<td>1983-2009</td>
<td>7 (18)</td>
<td>2.9</td>
<td>6.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b.</th>
<th>Period</th>
<th>Trees (cores)</th>
<th>Single Year Max Difference Between Trees</th>
<th>Single Year Mean Difference Between Trees</th>
<th>Range of RMS error between trees</th>
<th>Mean RMS error between trees</th>
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<td></td>
<td></td>
<td>$\delta^{13}C$ (‰)</td>
<td>$\delta^{18}O$ (‰)</td>
<td>$\delta^{13}C$ (‰)</td>
<td>$\delta^{18}O$ (‰)</td>
</tr>
<tr>
<td>MtC</td>
<td>ESW</td>
<td>1983-2011</td>
<td>3 (6)</td>
<td>2.0</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>MtC</td>
<td>WR</td>
<td>1983-2011</td>
<td>8 (21)</td>
<td>2.9</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>DK</td>
<td>ESW</td>
<td>1983-2010</td>
<td>7 (18)</td>
<td>4.4</td>
<td>4.6</td>
<td>1.2</td>
</tr>
<tr>
<td>DK</td>
<td>WR</td>
<td>1983-2009</td>
<td>7 (18)</td>
<td>3.9</td>
<td>5.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Fig. 4.2: The effect of intra-tree/circumferential variability on reproducibility of tree-ring time series: 3 core (i.e. tree) mean whole-ring isotope series plotted alongside individual core series and the associated RMS error a) MtC16 (δ¹³C), b) MtC12 (δ¹³C) and c) MtC12 (δ¹⁸O). a) consistently offset intra-tree δ¹³C; b) diverging and converging intra-tree δ¹³C; c) relatively coherent intra-tree δ¹⁸O records with occasional abrupt departures.
Fig. 4.3: The effect of inter-tree/circumferential variability on reproducibility of tree-ring time series: compiled tree means (i.e. mean of 2-3 radii) whole-ring and early season isotope series (colour) plotted alongside composite series means (bold, black) and its associated RMS error a) MtC δ¹³C, b) DK δ¹³C, c) MtC δ¹⁸O and DK δ¹⁸O.
4.3.4 EPS in Kauri and Cedar

The effects of various data treatments (atmospheric detrending, outlier stripping and chronology ‘improvement’) on the level of common signal for isotope time-series was investigated by comparing EPS scores for multiple records at different steps of the data analysis. In the DK records it was readily apparent that EPS decreased with each level of detrending that occurred, as a large trend common to most cores (i.e. decreasing $\delta^{13}C$) was removed (see Table 4.3).

Even prior to detrending, $\delta^{18}O$ series’ EPS scores are considerably higher than $\delta^{13}C$ scores and remain so following both individual outlier stripping and correlation significance based core ‘improvement’ (Table 4.3). Yet, the only DK isotope record to reach the 0.85 EPS threshold is ESW $\delta^{18}O$, which was improved from 0.80 to 0.85 by individual outlier stripping and maintained an EPS of 0.85 after ‘improvement’ stripped 8 cores from the record. Other isotope series showed mixed responses to individual outlier stripping and improvement. Generally for DK, ring-width EPS is higher than detrended isotope series’ EPS with the exception of the ESW $\delta^{18}O$ record. Despite the lower analytical precision of these data, the DK early-season $\delta^{18}O$ record demonstrates that it is possible to attain a cohesive and common isotopic signal from a relatively small number (7) of trees.

In contrast to the DK record, the MtC record provides an opportunity to assess EPS processing on dendrochemical records with less intra and inter-tree variability. Based on the improved MtC chronologies, the stable isotope dendrochemical whole-ring time series have EPS scores comparable to ring-width (0.88) for both $\delta^{13}C$ and $\delta^{18}O$, utilising 1-3 fewer trees (1-7 fewer cores) than originally sampled. $\delta^{18}O$ surpasses the 0.85 threshold using 7 trees, while $\delta^{13}C$ falls just short (0.84) based on only 5 trees. In the absence of the chronology improvement process, using all cores (21) from all trees (8), the $\delta^{18}O$ record’s EPS was comparable to that of ring-width but dropped when outliers were removed (Section 4.2.4). As with DK, however, $\delta^{18}O$ records had higher EPS scores than $\delta^{13}C$.

4.3.5 Regional Similarities Between Kauri and Cedar

Kauri and cedar show different ranges of $\delta^{13}C$ and $\delta^{18}O$ values, as well as different amplitudes of signal. DK $\delta^{13}C$ values range from -25.5 to -19.9‰, covering a 5.5‰ range around a mean of -22.8‰. In comparison, MtC’s mean $\delta^{13}C$ of -20.8‰ is significantly ($p < 0.01$, Welch’s t-test) more enriched and values cover a smaller range (3.3‰), from -23.3 to -19.0‰. In contrast, MtC are less enriched in $\delta^{18}O$ with values covering a 4.4‰ range from 28.0-32.4‰ with a mean of 30.0‰. DK has a significantly ($p < 0.01$, Welch’s t-test) more enriched mean of 31.9‰ with values ranging 8.0‰ from 28.8 to 36.8‰. These relationships are visually characterised by a cross-plot of MtC and DK $\delta$-values from corresponding years of early-season and whole-ring master series (Fig. 4.4).

While the range of MtC’s $\delta$-values about its master series are lower, both in absolute terms and in terms of variance (see RMS scores in Table 4.3), the record is also characterised by smaller inter-annual changes than DK. The mean inter-annual change in master series for MtC is 0.21‰ for $\delta^{13}C$ and 0.35‰ for $\delta^{18}O$, compared with 0.33‰ and 0.70‰ for DK. These differences are statistically significant ($p < 0.01$, Welch’s t-test).
Table 4.3: EPS values for MtC and DK ring-width (not detrended) and isotope series at each stage of data treatment.

<table>
<thead>
<tr>
<th>Whole Record</th>
<th>Individual Outliers Stripped</th>
<th>Improved Record</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trees/Cores</strong></td>
<td><strong>EPS</strong></td>
<td><strong>Trees/Cores</strong></td>
</tr>
<tr>
<td><strong>Record</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Improved Record</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Whole Record</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For EPS to be calculated from the (already stripped) record, a concentration, or outliers removed in the early portion of the record, meaning that years 1983-1989 did not have full length of record.

**Welch’s**

**Table 4.3:** EPS values for MtC and DK ring-width (not detrended) and isotope series at each stage of data treatment.

<table>
<thead>
<tr>
<th>Whole Record</th>
<th>Individual Outliers Stripped</th>
<th>Improved Record</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trees/Cores</strong></td>
<td><strong>EPS</strong></td>
<td><strong>Trees/Cores</strong></td>
</tr>
<tr>
<td><strong>Record</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Improved Record</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Whole Record</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For EPS to be calculated from the (already stripped) record, a concentration, or outliers removed in the early portion of the record, meaning that years 1983-1989 did not have full length of record.

**This (already stripped) record was reduced to 1 core by the stripping process, making EPS redundant.**

---

**Dunedin Kauri:**

<table>
<thead>
<tr>
<th>DK Ring-Wide</th>
<th>EPS</th>
<th>DK Ring-Wide</th>
<th>EPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MtC δ₁₈O (ESW)</td>
<td>0.95</td>
<td>MtC δ₁₃C (ESW)</td>
<td>0.95</td>
</tr>
<tr>
<td>MtC δ₁₈O (Detrended)</td>
<td>0.79</td>
<td>MtC δ₁₃C (ESW)</td>
<td>0.79</td>
</tr>
<tr>
<td>MtC δ₁₈O (Atmos)</td>
<td>0.80</td>
<td>MtC δ₁₃C (Detrended)</td>
<td>0.57</td>
</tr>
<tr>
<td>MtC δ₁₈O (Detrended)</td>
<td>0.50</td>
<td>MtC δ₁₃C (ESW)</td>
<td>0.85</td>
</tr>
<tr>
<td>MtC δ₁₈O (Atmos)</td>
<td>0.62</td>
<td>MtC δ₁₃C (Detrended)</td>
<td>0.49</td>
</tr>
</tbody>
</table>

* this (already small) record was reduced to 1 core by the stripping process, making EPS redundant.

**1990-2008**

- these records were reduced in length due to a concentration of outliers removed in the early portion of the record, meaning that years 1983-1989 didn't have a full length of record.
Intra and inter-tree stable carbon and oxygen

t-test) for both records.

Despite their different ranges of values and amplitudes of signal, Pearson’s Product Moment Correlations show that outlier-stripped oxygen records from the two sites are all significantly correlated ($p < 0.05$, Welch’s t-test, Table 4.4, Fig. 4.5). Significant ($p < 0.05$) inter-site correlation does not occur for $\delta^{13}$C records but for DK there are numerous significant ($p < 0.05$) within-site correlations between $\delta^{13}$C and $\delta^{18}$O records. For MtC there is a single significant ($p < 0.01$) correlation between $\delta^{13}$C and $\delta^{18}$O.

Raw ring widths between the two sites are not significantly correlated ($p > 0.05$). DK ring-width is correlated ($p < 0.05$) with DK whole-ring isotope series and MtC whole-ring $\delta^{18}$O while MtC ring-width significantly ($p < 0.05$) correlates with solely MtC isotope series (early-season $\delta^{18}$O and whole-ring $\delta^{13}$C).

Whole-ring $\delta^{18}$O from DK and MtC were selected to create a composite bispecies record as they displayed the highest inter-site correlation. RMS errors for the bispecies record were low, with the maximum RMS error only 0.33 and mean just 0.08. A bootstrapped correlation between the bispecies record and relative humidity (generally the major local climatic driver of $\delta^{18}$O changes in tree-rings based on the literature) showed a strong (-0.63) and highly significant ($p < 0.01$) relationship for the prior (t-1) May (Fig. 4.6).

Fig. 4.4: Cross plot of WR and ESW $\delta^{13}$C and $\delta^{18}$O master (‘outlier stripped’) series for DK and MtC showing the larger range of DK (x) values compared to MtC (y) as well as the consistent off-set of values between the two sites/species. Both EW and WR $\delta^{18}$O relationships are statistically significant ($p < 0.01$) but the WR linear relationship is clearly stronger.
Fig. 4.5: Whole-ring master records (‘outlier stripped’) for DK and MtC δ^{13}C and δ^{18}O, showing clear site/species differences in absolute ranges as well as similar inter-annual patterns through time (with the exception of MtC δ^{13}C) (See Table 4.4 for r-values).

Fig. 4.6: Bispecies (DK kauri + MtC cedar) composite δ^{18}O record (red, solid line) compared with previous May (t-1) relative humidity (black, dotted line). Note the relative humidity axis is reversed to help visualise the negative correlation. Error bars for δ^{18}O indicate the RMS error of the bispecies composite mean.
Table 4.4: Pearson’s product-moment correlation matrix with p-values (in brackets) for all outlier stripped isotope series.

<table>
<thead>
<tr>
<th></th>
<th>MtC ESW</th>
<th>MtC ESW</th>
<th>MtC WR</th>
<th>MtC WR</th>
<th>DK ESW</th>
<th>DK ESW</th>
<th>DK WR</th>
<th>DK WR</th>
<th>DK R-W</th>
<th>MtC R-W</th>
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<tbody>
<tr>
<td>δ¹³C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtC ESW</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ¹⁸O</td>
<td>0.18</td>
<td>(0.36)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>MtC WR</td>
<td>0.35</td>
<td>0.53</td>
<td>(0.07)</td>
<td>(&lt;0.01)</td>
<td>0.18</td>
<td>0.73</td>
<td>0.30</td>
<td></td>
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</tr>
<tr>
<td>δ¹³C</td>
<td>(0.36)</td>
<td>(&lt;0.01)</td>
<td>(0.12)</td>
<td></td>
<td>(0.07)</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>DK ESW</td>
<td>0.04</td>
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<td>0.00</td>
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<td></td>
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<td>δ¹³C</td>
<td>(0.83)</td>
<td>(0.14)</td>
<td>(&gt;0.99)</td>
<td>(0.14)</td>
<td>(0.18)</td>
<td>(0.08)</td>
<td>(0.01)</td>
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<tr>
<td>DK ESW</td>
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<td>0.53</td>
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<td>0.59</td>
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<tr>
<td>δ¹⁸O</td>
<td>(0.18)</td>
<td>(&lt;0.01)</td>
<td>(0.02)</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
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<tr>
<td>DK WR</td>
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<td>0.27</td>
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<td></td>
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<tr>
<td>δ¹³C</td>
<td>(0.32)</td>
<td>(0.18)</td>
<td>(0.98)</td>
<td>(0.01)</td>
<td>(&lt;0.01)</td>
<td>(0.01)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>DK WR</td>
<td>0.26</td>
<td>0.48</td>
<td>-0.03</td>
<td>0.64</td>
<td>0.47</td>
<td>0.60</td>
<td>0.75</td>
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<tr>
<td>δ¹⁸O</td>
<td>(0.18)</td>
<td>(0.01)</td>
<td>(0.89)</td>
<td>(&lt;0.01)</td>
<td>(0.01)</td>
<td>(&lt;0.01)</td>
<td>(&lt;0.01)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DK</td>
<td>0.26</td>
<td>0.38</td>
<td>-0.08</td>
<td>0.40</td>
<td>0.21</td>
<td>0.37</td>
<td>0.43</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-W</td>
<td>(0.21)</td>
<td>(0.06)</td>
<td>(0.68)</td>
<td>(0.04)</td>
<td>(0.30)</td>
<td>(0.07)</td>
<td>(0.03)</td>
<td>(&lt;0.01)</td>
<td></td>
<td></td>
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<tr>
<td>MtC</td>
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<td>0.43</td>
<td>0.44</td>
<td>0.11</td>
<td>-0.10</td>
<td>0.11</td>
<td>-0.13</td>
<td>-0.17</td>
<td>0.08</td>
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</tr>
<tr>
<td>R-W</td>
<td>(0.47)</td>
<td>(0.02)</td>
<td>(0.02)</td>
<td>(0.56)</td>
<td>(0.62)</td>
<td>0.56</td>
<td>(0.51)</td>
<td>(0.41)</td>
<td>(0.71)</td>
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</tr>
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</table>

4.4 Discussion

4.4.1 Standard and Replicate Precision in Dual Element Low Temperature Pyrolysis

The standard and sample data generated across the DK and MtC analytical periods suggest that the dual element low temperature pyrolysis system achieves precision (standard deviation about the mean of reference standard analyses) comparable to the traditional, separate, on-line combustion and high temperature pyrolysis techniques when using commercial or certified α-cellulose standards (i.e. ~0.1‰ for δ¹³C and ~0.3‰ for δ¹⁸O, see Table 4.1). The MtC and DKHR sample replicates analysed during this research were also able to achieve these precisions. DK sample replicates, however, exhibited significantly lower mean precision for both δ¹³C and δ¹⁸O and we suggest three possible reasons for these anomalous results below:

1) The growth rate (i.e. ring width) of the DK samples was relatively large because a) kauri has wider rings is than cedar and b) juvenile kauri typically grow faster than mature trees. As a consequence, samples cut out of the kauri cores for isotopic processing were generally larger than MtC samples. It is possible that homogenisation and fragmentation of extracted α-cellulose may not have been sufficient on larger DK samples.

2) Potentially compounding the influence of insufficient homogenisation, isotopic heterogeneity in the DK samples parallel to the growth axis (i.e. seasonal variability) is relatively large (up to 4.6‰ for δ¹³C and ~0.3‰ for δ¹⁸O in kauri, compared with 1.9‰ and 3.6‰ for cedar δ¹³C and δ¹⁸O; Chapter 5). This
suggests that any deficiencies in homogenisation of DK samples could result in much more isotopically
distinct sub-samples being taken for analysis compared to MtC or DK HR samples. In other words, an
isotopic ‘nugget effect’ (i.e. sample heterogeneity) (Hofmann, 2011) could occur where the intra-annual
variability in the tree-ring can dominate the result for what was intended to be an aggregated signal for a
longer period.

3) Both of the above interpretations, may be exacerbated by kauri’s resilience to α-cellulose extraction.
The bulk of DK samples were extracted before Brookman and Whittaker (2012) showed that kauri
is particularly difficult to process and that in some situations there are potentially no visual clues of
impurity. The lower quality of the DK data show the value of early quality control investigations such
as Fourier Transform Infrared Spectroscopy (Rinne et al., 2005; Anchukaitis et al., 2008; Brookman and
Whittaker, 2012) and ongoing laboratory processing quality monitoring schemes as outlined by Porter and
Middlestead (2012). Replicate analyses of extracted α-cellulose, where sample size permits, are also a key
measure of sample, as opposed to system, precision/reproducibility.

EPS calculations in section 4.3.4 show that despite their lower analytical precision, DK isotope records
co-vary with each-other and comparison with MtC records (see section 4.3.5) show some strong
correlations. This suggests that common climatic forcing mechanisms for δ\(^{18}\)O may not be obscured by
the analytical/processing short-comings. Ultimately the low replicate precision for DK samples (~ 0.26‰
for δ\(^{13}\)C and ~0.64‰ for δ\(^{18}\)O) is still an order of magnitude lower than the observed natural intra and
inter-tree variability.

4.4.2 Comparing Intra and Inter-Tree Variability and Their Implications for Sampling Strategy

The magnitude of circumferential/radial variability observed in DK and MtC isotope records finds few
comparisons in the literature (Leavitt, 2010 and references therein) other than (for δ\(^{13}\)C alone) the early
work of Tans and Mook (1980). Maximum circumferential differences in δ\(^{13}\)C (Table 4.2a) from both
MtC and DK samples are approximately double the range of most studies (~0.5-1.5‰, see Leavitt,
2010, Table 4.1). They are more similar to Tans and Mook’s early (1980) findings of up to 4.5‰ in oak
(Quercus rubra and Q. robur) and beech (Fagus sylvatica) from the Netherlands. While there are fewer
studies on circumferential δ\(^{18}\)O variability, our results again show a greater range (2-3 times) than the 0.5-
2.0‰ suggested by Leavitt’s (2010) review of previous studies.

Several studies demonstrate that, for their respective species, circumferential (intra-tree) δ\(^{13}\)C and δ\(^{18}\)O
differences are smaller than the differences between trees (see McCarroll and Loader, 2004 and references
therein; Leavitt, 2010). Our results show the opposite pattern. For MtC, intra-tree δ\(^{13}\)C and δ\(^{18}\)O
differences, both maximum and mean, are equal to or greater than those between trees. DK inter-tree δ\(^{13}\)C
variability exceeds the intra-tree variability slightly but δ\(^{18}\)O intra-tree variability is larger than inter-tree
(Table 4.2).

Multiple explanations are considered for the observed pattern of intra-tree versus inter-tree variability.
First, there could be a sample size effect. The bulk of the data presented in Table 4.2 is based on individual, annual analyses of 18-21 cores from 7-8 trees (i.e. approx 3 radii per tree), which we believe is an unusually large combination of temporal resolution and number of trees/radii previously unattained. If sample size were the major contributing factor in our findings, however, we might also expect to see similarly ‘greater than normal’ inter-tree variability compared with previous studies. While our results (Table 4.2b) show inter-tree variability at the upper end or slightly over Leavitt’s (2010) proposed norms (1-3‰ δ\(^{13}\)C and 1-4‰ δ\(^{18}\)O), proportionally these slight increases do not align with the intra-tree variability increases to 2-3 times ‘normal’ levels.

Extreme circumferential variability (up to 3.3‰ δ\(^{13}\)C and 6.3‰ δ\(^{18}\)O) in DK could be a result of tree-age (youth) but this explanation seems less tenable considering MtC samples are from a mature, natural stand and still exhibit high circumferential variability (up to 3.2‰ for δ\(^{13}\)C and 3.7‰ for δ\(^{18}\)O).

Tans and Mook (1982) suggest that the similarly high levels of intra-tree δ\(^{13}\)C variability they observed in oak and beech in the Netherlands could be due to microscale influences such as nutrient and water availability to different areas of trees’ root systems. Without further research, the idea that differences in uptake between lateral roots results in differences in incorporation of water and nutrients into sapwood seems tenuous, given that δ\(^{13}\)C is determined in the canopy, based on photosynthesis of atmospheric CO\(_2\). It seems more likely that shading might alter the CO\(_2\) assimilation rate of portions of a tree’s foliage (Francey and Farquhar, 1982) which could also manifest itself as a consistent off-set in δ\(^{13}\)C (Fig. 4.2a), or a sudden and persistent shift in δ\(^{13}\)C along one radius due to canopy opening as a result of windfall (e.g. MtC12.1, Fig. 4.2b). However, uneven canopy shading is certainly not unique to our sites, so while it may explain some of the larger than normal intra-tree variability seen at MtC and DK, it seems unlikely to be the sole cause.

Similarly, explanations focussed on resource availability fail to explain the more variable intra-tree δ\(^{18}\)O records. While authors have suggested that δ\(^{18}\)O differences between species, and presumably trees of different ages, may result from access to different aquifers due to different root depths (Marshall and Monserud, 2006), this seems unlikely in the egalitarian plantation stand at DK and at MtC does not explain records like MtC12 (Fig. 4.2b,c) which is generally coherent in δ\(^{18}\)O, with occasional abrupt departures (MtC 12.3 in 1990). Ramesh et al. (1986, pp 803) offer an explanation for circumferential variability that addresses both δ\(^{13}\)C and δ\(^{18}\)O discrepancies: a ‘lateral redistribution or asymmetrical production of a growth-regulating hormone, a growth inhibitor or an auxin-destroying enzyme’ that would result in active growth at some points around the trunk but not others at any given time. Alternatively, Kagawa et al. (2005) suggest that seasonal changes in phloem transport can result in circumferential δ\(^{13}\)C variability which could also affect δ\(^{18}\)O; δ\(^{18}\)O is ultimately determined at the leaf and fixed in sucrose, which is transported by the phloem to the stem and used to produce cellulose (Barbour et al., 2002). Detailed physiological investigations, such as those being conducted by Macinnis-Ng et al (2013), may provide insight into the relevance of Kagawa et al’s (2005) suggestion to kauri.

While we cannot isolate the cause of the intra-tree variability, we can ascertain that it has, alongside
inter-tree variability, important implications for palaeoclimatic reconstructions. The circumferential RMS errors seen at the inter-annual level are large (~±0.5 for δ¹³C and ~±0.4-0.8 for δ¹⁸O), suggesting that sampling schemes with limited intra-tree replication may not achieve coherent/representative dendrochemical records. Even where multiple cores can be taken from trees, inter-tree RMS errors remain large for 7-8 trees (~±0.4-1.0 for δ¹³C and ~±0.4-1.1 for δ¹⁸O), suggesting at least that number of trees are required to provide robust estimates for a mean isotope series. This is of particular concern for records based on archaeological and sub-fossil assemblages with limited sample depth.

The data presented here reveal significant and unexpected challenges that must be more fully understood before such palaeoclimate research should be undertaken in earnest. A similar trial using an alternative method of α-cellulose extraction would be valuable, to isolate any processing errors from natural isotopic variability. Similar research, with similarly large sample depths, should be performed on mature, native stands of both kauri and cedar elsewhere in New Zealand. By expanding the geographic scope it may be determined how anomalous, or common, the circumferential and inter-tree variability results presented in this study truly are.

4.4.3 EPS in Kauri and Cedar

One of the driving motivations behind this research was to assess whether predominantly Northern Hemisphere-based estimates of the number of trees and/or cores per tree required for a robust common signal would hold true to New Zealand’s endemic species in their maritime environment. Estimates of sample depth should be reasonably well known prior to embarking on analytically intensive long-term investigations of palaeoclimatic and palaeoenvironmental conditions if the research is to succeed. In the New Zealand context, such knowledge is all the more important given the potential utilisation of sub-fossil ‘bog kauri’ (Boswijk et al., 2006; Palmer et al., 2006) and the relatively rare occurrence of long-lived native tree stands throughout the country.

Despite the large intra and inter-tree variability documented above in cedar and kauri, the combination of DK and MtC data suggests that for kauri and cedar in New Zealand 7-8 trees (with 2-3 cores per tree) can provide δ¹⁸O time series that meet or approach the 0.85 EPS threshold (Table 4.3). However, δ¹³C appears less consistent; the only record that approached an EPS of 0.85 was improved by the removal of poorly correlated series. The removal of 3 trees and 7 cores from that record (MtC WR δ¹³C) suggests that while there is a common, presumably climatic, signal embedded in MtC δ¹³C, it is obscured by endogenous factors. A similar finding has been reported by Raffali-Delerce et al. (2004) for oak from coastal France. The lack of a strong common signal in δ¹³C was also evident in the DK δ¹³C ESW and WR records, from which removing 3 trees and 13-14 cores was still insufficient to achieve an EPS greater than 0.55. Without ‘improvement’, all EPS scores for detrended δ¹³C records were <0.63. The influence of a juvenile effect on inter-annual isotope time-series is an unknown quantity here and may explain some of the low EPS scores for DK trees. It does not, however, apply to the similarly variable MtC trees; an alternative explanation for both sites’ δ¹³C time-series is that they were affected by acetylation of cellulose during processing (Chapter 3), resulting in method-related depletion of δ¹³C in some samples.
Intra and inter-tree stable carbon and oxygen

Table 4.5: Compilation of published dendrochemical δ¹³C and δ¹⁸O records using EPS

<table>
<thead>
<tr>
<th>Study</th>
<th>Species</th>
<th>Total Trees/Cores</th>
<th>Time Period</th>
<th>EPS Score(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holzkämper et al. 2012</td>
<td>Alaskan White Spruce (Picea glauca)</td>
<td>7*</td>
<td>1938-2003</td>
<td>&gt;0.85</td>
</tr>
<tr>
<td>McCarroll and Pawellek, 1998</td>
<td>Scots Pine (Pinus sylvestris)</td>
<td>5 (x5 sites)**</td>
<td>1954-1994</td>
<td>0.89-0.95</td>
</tr>
<tr>
<td>McCarroll and Pawellek, 2006</td>
<td>Scots Pine (Pinus sylvestris)</td>
<td>5-20 (5 sites) **</td>
<td>1961-1995</td>
<td>0.95-0.98</td>
</tr>
<tr>
<td>Porter et al. 2009</td>
<td>Alaskan White Spruce (Picea glauca)</td>
<td>3/3*</td>
<td>1850-2003</td>
<td>0.40-0.85</td>
</tr>
<tr>
<td>Robertson et al. 1997</td>
<td>Oak (Quercus robur) (Finland)</td>
<td>2-3*</td>
<td>1895-1994</td>
<td>&gt;0.85</td>
</tr>
<tr>
<td>Robertson et al. 1997</td>
<td>Oak (Quercus robur) (England)</td>
<td>4-8*</td>
<td>1895-1994</td>
<td>&gt;0.85</td>
</tr>
<tr>
<td>Sgherza et al. 2010</td>
<td>Callitris Pine (C. preissii, C. canescens, C. columellaris)</td>
<td>4 (x4 sites)</td>
<td>Various within 1880-2005</td>
<td>0.59-0.88</td>
</tr>
<tr>
<td>Doucet et al. 2012</td>
<td>Picea rubens, Fagus grandifolia, Pinus strobus, Thuja occidentalis</td>
<td>3/3*</td>
<td>1880-2007</td>
<td>0.8-0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Study</th>
<th>Species</th>
<th>Total Trees/Cores</th>
<th>Time Period</th>
<th>EPS Score(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brienen et al. 2012</td>
<td>Cedrela odorata (Bolivia)</td>
<td>8/8</td>
<td>1900-2000</td>
<td>0.97</td>
</tr>
<tr>
<td>Holzkämper et al. 2012</td>
<td>Alaskan White Spruce (Picea glauca)</td>
<td>5*</td>
<td>1938-2003</td>
<td>&gt;0.85</td>
</tr>
<tr>
<td>Porter et al. 2009</td>
<td>Alaskan White Spruce (Picea glauca)</td>
<td>3/3*</td>
<td>1850-2003</td>
<td>0.75-0.94</td>
</tr>
<tr>
<td>Porter et al. 2013</td>
<td>Alaskan White Spruce (Picea glauca)</td>
<td>3/3*</td>
<td>1780-2003</td>
<td>0.74-0.96</td>
</tr>
<tr>
<td>Doucet et al. 2012</td>
<td>Picea rubens, Fagus grandifolia, Pinus strobus, Thuja occidentalis</td>
<td>3/3*</td>
<td>1880-2007</td>
<td>0.7-0.9</td>
</tr>
</tbody>
</table>

*These studies utilised multiple cores per tree, but pooled the material prior to analyses, creating a 3 tree/core record as far as the EPS statistic is concerned.

**These studies did not specify whether multiple radii were pooled or analysed separately

This study reported how many trees from within the whole record were required to achieve an EPS score >0.85, not an EPS score for the number of trees actually sampled.

The decision to ‘improve’ master series by removing poorly correlated cores from a record was based on: 1) the presumption that endogenous factors may be obscuring an underlying climatic signal, and 2) a desire to find a theoretical minimum number of trees required for a coherent record. The process ultimately provided only small improvements; while improved records from 5-7 trees yielded acceptable EPS scores, from a practical perspective, the initial field sampling to create those improved records is likely to require 2-3 cores from 10 or more trees.

While the improved EPS score for WR δ¹³C shows that EPS scores approaching 0.85 can theoretically be achieved from as few as 5 cedar, this result stands alone amongst our isotope series. Numerous records in this study failed to achieve an EPS of 0.85 despite sampling 2-3 cores from 7-8 trees. While previous
dendrochemical studies have generally achieved EPS scores >0.85 from smaller samples (Table 4.5), the bulk of the literature also documents much lower intra-tree variability than documented in the trees we studied; thus, the high intra-tree variability seems the most likely cause of the relatively low EPS scores achieved. Our EPS results (Table 4.3) show that for kauri and cedar, isotopes could theoretically provide similar and more coherent (i.e. higher EPS) series from fewer trees than ring-width reconstructions. However, this would require the coincidental sampling of a sub-set of cores chosen here by the ‘improvement’ of a much larger series, meaning there is no real reduction in sample numbers. For kauri ring-widths 10 trees, each with 2 or more cores, are generally sufficient to reach an EPS of 0.85, with some sites achieving it with 7-8 trees (Fowler and Boswijk, 2003). Cedar can also achieve ring-width EPS scores >0.85 from as few 7 trees, although generally 9 or more are required (Xiong and Palmer, 2000a). Given that only two of the unimproved records presented here approach (MtC δ\textsubscript{18}O WR) and reach (DK δ\textsubscript{18}O ESW) EPS scores of 0.85 from 8 and 7 trees respectively, our findings do not support an argument in favour of stable isotope dendroclimatology over dendrochronology for New Zealand kauri and cedar based on reduced sample-size.

We suggest that analysing multiple cores from more than 10 trees in the same detail presented here would make any stable isotope dendroclimatic reconstruction prohibitively time-consuming over longer time-periods, even with dual-element analyses. Consequently, for kauri and cedar we recommend initial coring of 10-15 trees with 2-3 cores per tree; based on the literature (Fowler and Boswijk, 2003; Palmer and Xiong, 2004) this should provide ample well cross-dated material for ring-width study, from which material can be selected for stable isotopic study of ≤10 trees (~20 cores). Where more trees are required or particularly long records necessitate large sample numbers, the pooling of radii prior to analysis (as in Porter et al., 2009; Porter et al., 2013) could provide a single sample that synthesises intra-annual variability and reduces analytical workload (Leavitt and Long, 1984). The splitting (i.e. analysis of individual radii) of those samples at 5 or 10 year intervals would allow researchers to calculate time-series error estimates (Woodley et al., 2012a).

### 4.4.4 Regional Similarities Between Kauri and Cedar

Despite the generally low EPS scores for kauri and cedar isotope records there are a number of significant correlations (\( p < 0.05 \)) between isotope records both within and between MtC and DK (Table 4.4, Fig. 4.4, Fig. 4.5). In fact, all MtC and DK δ\textsubscript{18}O records (ESW and WR) are significantly (\( p < 0.05 \)) correlated suggesting that a common driver of the δ\textsubscript{18}O signal recorded at both sites is probable. The whole-ring δ\textsubscript{18}O records are strongly correlated (\( r = 0.64, \ p << 0.01 \)) suggesting that these may provide the best record of regional climate.

However, the inter-species/site correlations observed for δ\textsubscript{18}O do not extend to δ\textsubscript{13}C. The only significant correlation for MtC δ\textsubscript{13}C is between whole-ring carbon and ring-width. In contrast, for DK there are strong correlations (\( r > 0.50, \ p < 0.01 \)) between δ\textsubscript{13}C and δ\textsubscript{18}O, suggesting that in these trees further there may in fact be a common driver for both elements and that δ\textsubscript{13}C records may also be useful in climate reconstruction despite generally low EPS scores. It is tentatively suggested that despite some relatively
Intra and inter-tree stable carbon and oxygen

low EPS values (<0.85) for DK WR δ¹⁸O/WR δ¹³C/ESW δ¹³C and MtC ESW δ¹⁸O, significant correlations with records that yield higher EPS scores (DK ESW δ¹⁸O and MtC WR δ¹⁸O) suggest they are preserving a similar pattern of inter-annual variability.

Where significant inter-site correlations exist between numerous DK and MtC isotope records and all intra-site DK isotope records and MtC δ¹⁸O records, no inter-site correlation exists between ring-width records and few correlations are observed between ring widths and their respective sites’ isotope records (Table 4.4). The generally lower number and magnitude of intra-site correlations between ring-widths and isotope records and, particularly, the lack of any correlation between ring-width records for sites with strongly correlated δ¹⁸O records suggests that the stable isotope time-series have potential to add significant regional climate reconstruction value as a complementary approach to ring-width records.

Kauri and cedar, at different sites within the same region provide strongly and significantly correlated \( (r = 0.64, p << 0.01) \) whole ring δ¹⁸O records (Table 4.4, Fig. 4.5). Given the various microclimatic differences between the two sites (Section 4.2.1, Fig. 4.1) and the fact that one stand is a young plantation and the other is a mature native remnant, a regional climate driver seems the most logical explanation for the correlation. The coherent response from the two species suggests that they could potentially be used in tandem where they overlap or to expand regional climate reconstructions beyond the natural range of each in isolation.

This potential is reinforced by our preliminary investigation of the bispecies composite δ¹⁸O record’s correlation with relative humidity (Fig. 4.6). The significant negative correlation between relative humidity and cellulose δ¹⁸O suggests that local water was enriched through evaporation during periods of low humidity. This could occur either in the leaf or prior to the tree’s uptake of the water; the fact that the correlation is with the May prior to growth suggests the latter, as a growth season leaf-water enrichment signal would be incorporated into cellulose in a matter of weeks (Barbour et al., 2002; Gessler et al., 2009). An alternative is that the signal reflects a strong contribution to the current growth year’s isotopic signal from carbohydrate stored late in the previous growth season to stimulate spring growth. Either scenario requires further, detailed investigation but equally, either suggests that kauri and cedar, either separately or together, have potential as a palaeoclimate archive.

### 4.5 Conclusions

Our study of kauri and cedar tree-ring carbon and oxygen stable isotopic composition sets the groundwork for future investigation of two key long-lived native tree species in New Zealand’s highly variable maritime climate. The work here contributes to the relatively small pool of Southern Hemisphere stable isotope dendroclimatic literature by addressing the four key research questions posed earlier (see section 4.1.2).

1) We document large radial (i.e. intra-tree) variability in of up to 2.9‰ in δ¹³C and 6.3‰ in δ¹⁸O in kauri
and 3.2‰ in δ¹³C and 3.7‰ in δ¹⁸O for cedar. Intra-tree variability is 2-3 times that observed in studies of most other species. The role of the juvenile effect and cellulose acetylation, due to SBrendel processing, in these variable results are both unknown and require further investigation.

2) We also observe higher levels of inter-tree variability than many studies, but not to the same extent as intra-tree variability. This finding is significant when considered alongside the first finding: our data show that, contrary to previous published studies, intra-tree variability often exceeds inter-tree variability.

3) Most likely due to the high intra and inter-tree variability observed, kauri and cedar require significantly more trees to achieve EPS values of 0.85 compared to most species previously studied using stable isotopes. δ¹⁸O records from 7-8 trees (2-3 cores per tree) achieve or approach EPS scores of 0.85 but δ¹³C generally achieves much lower EPS scores. For future New Zealand-based research we suggest that coring a minimum of ~10-15 trees (2-3 cores per tree) and then sampling 7-10 of those trees (< 20 cores) for stable isotope analysis appears to be the minimum threshold for robust dendroclimatic records from kauri and cedar.

4) Finally, our data show strong δ¹⁸O correlations between two sites/species, including a significant correlation with relative humidity. While a more detailed investigation is required to validate this preliminary study, these data suggest potential for regional climate reconstruction using composite kauri and cedar records, a particularly important finding given kauri’s restricted natural range. Weaker inter-site/species correlations for ring-width and δ¹³C records likely reflect the complex contribution of various micro-scale endogenous factors and microclimatic differences to those records, potentially exacerbated by a juvenile effect for the DK trees. These findings make dual element isotopic analysis an attractive and potentially powerful approach for differentiating endogenous from exogenous controls on tree ring chemistry.
5. ANNUAL CYCLES IN STABLE ISOTOPES FROM NEW ZEALAND KAURI (AGATHIS AUSTRALIS): IMPLICATIONS FOR SEASONAL AND EVENT-SCALE CLIMATE RECONSTRUCTION.

The large isotopic differences observed within and between trees in Chapter 5 resulted in isotope records with lower EPS scores than most published studies, despite the relatively large number of kauri and cedar analysed. In order to ascertain whether this variability was in fact natural, as opposed to an artefact of sampling or analytical processes, further investigation into isotopic variability was required. The major concern was that the sampling strategies employed (i.e. separating whole-ring and early-season wood) may have contributed to the observed variability, potentially obscuring common climatic signals within and between trees. To address this issue, a number of wide kauri rings from the DK site were sampled at the highest resolution possible with simple tools. The aim was to investigate the extent to which seasonal variability is synthesised within an annual sample and whether that variability was random or followed seasonal/annual patterns that might affect or inform sub-annual sampling strategies.

An exciting benefit of this high-resolution investigation was the opportunity it created to assess whether annual isotopic cycles were driven by climatic/meteorological drivers, and the consequent implications for seasonal, or even event-scale, climate reconstructions. Not only did this represent a tantalising advance in climate reconstruction resolution, but it also helped to inform lower frequency, inter-annual, climate reconstructions by highlighting key high-frequency climatic drivers of changes in cellulose δ¹³C and δ¹⁸O. The focus on event-scale potential was expanded by the inclusion of samples from within kauri’s natural range, taken from growth years corresponding to significant ex-tropical cyclone events. The two datasets also facilitated comparison of the (in)consistency of kauri’s climatic response across a range of tree ages and climatic settings. All of the above investigations add to the foundations for future research established in the Chapter 5.

The initial optimism surrounding the potential for seasonal and even-scale reconstruction from annual isotopic cycles was ultimately frustrated by limited correlations with monthly climate. In an attempt to achieve a more holistic understanding of the data than simple isotope-climate correlations, mechanistic modelling of δ¹⁸O was employed, integrating the best available information on local climate and kauri physiology. Rather than explaining the variability observed in kauri inter-annual records, this modelling highlighted the gaps in understanding of annual tree-ring isotope cycles and physiological processes, identifying further key future research areas.
5.1 Introduction

High-resolution terrestrial palaeoclimate records are essential for improving understanding of the timing, duration, and cause of both regional and global climate change events. Increasingly, pre-historic records of extreme weather events are sought to assess the potential impact of climate change on severe weather (Bernstein et al., 2007); a number of weather events including droughts, extreme rainfall, and for some areas, ex-tropical cyclones (IPCC, 2012), appear to be increasing in frequency as a result of current changes in climate. Tree-rings have long been regarded as one of the premier sources of such records, as they offer calendar dated records at annual resolution with quantifiable uncertainty (McCarroll and Loader, 2004). In addition to long long-term, high-resolution stable isotope reconstructions of local (Porter et al., 2009; Bale et al., 2010; Berkelhammer and Stott, 2012; Loader et al., 2013; Rinne et al., 2013) and regional climate patterns (Treydte et al., 2006; Leavitt et al., 2007; Loader et al., 2013), stable isotope dendroclimatology has created additional opportunities to pursue seasonal and even event-based climate reconstruction (Barbour et al., 2002; Miller et al., 2006; Li et al., 2011).

High-resolution tree-ring isotope studies also inform researchers about sampling strategies ahead of undertaking longer inter-annual climate studies (e.g. early-wood vs whole-ring vs late wood). This phase of experimentation is important to understanding the amplitude and pattern of intra-annual variability being synthesised in annual samples and whether sub-annual division (e.g. isotopic analysis of late wood only (McCarroll and Pawellek, 1998; McCarroll and Loader, 2004)) may help separate climatic and physiological drivers of intra-annual isotopic changes (Kagawa et al., 2006a).

To assess records of these climatically driven fractionations, suitable tree species are required. In the New Zealand context, kauri (Agathis australis) is a leading candidate for stable isotope dendroclimatology. Not only is kauri long lived and climatically sensitive, as reviewed in Chapter 2, in the context of extreme weather reconstruction, kauri’s natural range in the north of New Zealand places it well for ex-tropical cyclone (ETC) reconstruction (Lorréy et al., 2013). Preliminary studies of kauri stable isotopes show potential for high-resolution seasonal cycles (Poussart, 2004). To provide a basis for intra-annual palaeoenvironmental reconstructions and to better inform sub-annual sampling schemes, intra-annual stable isotopic changes and linkages to climate variability are investigated here.

5.1.1 Key Research Focii

The research presented here is intended to achieve four primary objectives: first, to establish whether clear annual/seasonal isotopic cycles are evident in kauri and characterise them; second, to evaluate the implications of intra-annual cycles for inter-annual sampling schemes; third, to establish whether sufficiently fine resolution can be achieved for event-scale weather reconstruction; and finally, whether annual/seasonal cycles are driven by corresponding changes in climate.

1. Is there a clear intra-annual cycle for kauri δ¹³C and δ¹⁸O and does the isotopic mean and/or amplitude of this cycle vary between regions? Seasonal cycles in stable isotopic composition are known to occur
Annual cycles in stable isotopes from New

for a number of species, including both deciduous and evergreen trees, and across a wide range of environments (e.g. Evans and Schrag, 2004; Helle and Schleser, 2004; Poussart et al., 2004; Jahren and Sternberg, 2008). Preliminary investigation of a single ancient kauri sample from Oxygen Isotope Stage 3 suggests that similar cycles existed in kauri that grew prior to the LGM (Poussart, 2004) but no data exist to characterise modern kauri.

2. What are the implications for sub-annual sampling strategies? Such characterisation is particularly important given that the amplitude and pattern of seasonal isotope variability may have repercussions for sampling strategies and isotope chronology construction practices based on early-wood or late-wood. Kauri is reportedly an ENSO proxy due to its dominant spring growth flush (30-50% of annual growth (Fowler et al., 2005)) that coincides with the timing of strongest ENSO teleconnection to New Zealand (Wunder et al., 2013). Previous work has applied this seasonal growth response to sampling strategies, separating the first 50% of the ring (early-season wood) from the whole ring (Lorrey et al., in prep; Brookman et al., submitted). However, while a spring-dominant signal could be expected based on the established growth timing, other factors including plant physiological processes (Barbour et al., 2002; Helle and Schleser, 2004; Kagawa et al., 2006a) may influence the intra-annual isotopic cycle independent of climate. A clearer understanding of these processes, and how they relate to changes in sampling position need to be established in order to determine the optimum sampling strategy for reconstructing inter-annual changes in climate.

3. Do intra-annual data achieve a resolution that could enable event-scale reconstruction using kauri? Are event-scale changes evident in the data? Recent dendrometer-band studies of kauri’s growth (Fowler et al., 2005; Wunder et al., 2013) provide a template from which a simple growth (wood deposition) model can be developed. Intra-annual isotope samples can be ‘binned’ into monthly or finer groups to facilitate a comparison with meteorological data (aggregated on synoptic, or weekly scales and longer climatic timescales). The application of this approach may also indicate what sampling resolution can be achieved for different parts of the growth season and whether there is potential for event-scale reconstruction.

4. What potential does kauri have for reconstructing seasonal climate cycles? Based on the climate-isotope relationships established in the literature described above, this investigation focuses on correlating stable isotope signatures with temperature, relative humidity, rainfall, soil moisture deficit and solar radiation. For δ¹⁸O the first three variables are likely to determine localised fractionation of δ¹⁸O either through evaporative enrichment of rainfall and/or soil water or evapotranspirative enrichment of leaf water. Climatic cycles rather than primary rainfall δ¹⁸O signatures related to source region and/or circulation patterns are focussed on because the limited evidence available for NZ indicates small and annually variable seasonal changes in rainfall δ¹⁸O (Taylor, 1990; Blackstock et al., 2011; Blackstock et al., 2012; IAEA/WMO, 2013; Fig. 5.1). The same factors plus soil moisture deficit and solar radiation are also the most likely to control photosynthetic rate and stomatal conductance, and the balance between the two, thus determining δ¹³C (McCarroll and Loader, 2004).
5.2 Methods and Materials

5.2.1 Site descriptions

The primary series of samples for this study were collected from the DK site (See Chapter 4 and Appendix 8.7). The fast growing plantation trees were targeted for seasonal analysis as their rings were, on average, approximately three times wider than mature kauri. The seasonal climatic stress associated with their southern location was seen as a potential source of enhanced climatic responsivity (Stokes and Smiley, 1968; Schweingruber, 1988). Kauri grew well south of its current range during the Pleistocene (Ecroyd, 1982; Mildenhall, 1985) but is thought to have been gradually restricted by successive glacial cycles (Steward and Beveridge, 2010).

A second series of cores are included here to provide comparison from mature trees within kauri’s natural growth range. These cores were originally taken for preliminary investigation into kauri’s potential as a recorder of ex-tropical cyclone events from an area of established native forest at the Lower Huia site (LH, 36.972604°S, 174.566846°E, 70m asl), in the southern Waitakere Ranges to the west of Auckland (Fig. 5.1). LH’s climate is characterised by warm, humid summers and mild winters with a winter rainfall maximum (Sturman and Tapper, 2006; Fig. 5.1). The results presented here are from 6 cores, taken from 6 trees ranging from 103-165cm DBH. The cores cover the growth seasons incorporating several major ex-tropical cyclone events (Lorrey et al., 2013): Sina in March 1980 (1979 growth-ring), Bola in March 1988 (1987 growth-ring) and Ivy in March 2004 (2003 growth-ring). The data are used here for comparison with DK rather than for ex-tropical cyclone reconstruction. See Chapter 5 and Lorrey et al. (submitted) for coring and dendrochronology details of DK and LH respectively.

5.2.2 Sample preparation and analysis

Cross-dated kauri increment cores were sliced with a straight-bladed scalpel under an illuminated magnifying glass. For coarse scale, seasonal intra-annual investigation, DK rings were divided into a ‘whole-ring’ (WR), and an ‘early-season’ (ESW) sub-sample taken from the first ~50% of the annual ring. The paired early-season wood (ESW) and whole ring (WR) data span a 28-year (1983-2010) record of over 500 samples for $\delta^{13}$C and $\delta^{18}$O (7 trees, 18 cores).

High-resolution samples from DK (DKHR) were sliced perpendicular to the growth axis into ~1mg wafers, resulting in a record composed of 358 samples taken from 4 DK cores (2 pairs from 2 trees) spanning a 4-year interval (1979-1982). The number of samples per ring ranges 17 to 32. LH rings were sliced in a similar fashion into 10 equal samples per ring. The lower resolution was dictated by the much narrower rings from mature trees.

Samples were processed to isolate $\alpha$-cellulose, disaggregated, re-dried and then massed and desiccated, following the process described in Chapter 4. The analytical process for DK high resolution samples (continuous flow dual carbon and oxygen low temperature pyrolysis) also followed the method outlined
Annual cycles in stable isotopes from New Zealand

**Fig. 5.1:** Shaded relief of New Zealand with inset details of DK (-45.833°S, 170.361°E) and LH (-36.972°S, 174.566°E) surrounds and local climatologies. Red stars indicate the positions of the climate stations used to compile the average climographs (middle panel) for DK (Invermay and Invermay 2, 1942-1985) and LH (Auckland Aero, 1962-2010) (NIWA, 2011). The bottom panel is monthly average precipitation δ¹⁸O measured for Invercargill (1961-2008, ~170km WSW of DK) and Kaitaia (1962-1994, ~240km NNW of LH) (IAEA/WMO, 2013). The compiled record from Invermay and Invermay 2 was only created after it was ascertained that the monthly mean values for the 2 records in the overlapping period were not significantly different. Nonetheless, slight heterogeneities may exist.
in Chapter 4 while LH samples underwent as similar analysis at the University of Maryland. The external analytical precision (1σ) on 100µg cellulose samples for LH samples run at Maryland were 0.13-0.21‰ for carbon and 0.31-0.37‰ for oxygen (Lorrey et al., in prep, See Chapter 4 for DK precision). All data were corrected to the V-PDB scale for δ\(^{13}\)C and V-SMOW scale for δ\(^{18}\)O using a 1-point normalisation (i.e. an additive correction) for samples run at UC and a 2 point normalisation (i.e. a ‘stretch and shift’ or ‘mean and variance bias’ correction) for samples run at UMD.

Direct comparison of δ\(^{18}\)O determinations from different laboratories, even with very similar analytical systems, is hampered by the well reported lack of a certified reference material and the hydroscopic nature of α-cellulose (CRM) (Saurer et al., 1998; Boettger et al., 2007; Brand et al., 2009). Inter-laboratory comparisons of δ\(^{18}\)O were made with this knowledge in mind and in-house standards from UC and UMD were run in both laboratories. UMD SAC (δ\(^{18}\)O = 30.0 ± 0.2‰) analysed at UC and UC SAC (δ\(^{18}\)O = 32.4 ± 0.3‰) analysed at UMD were both within analytical error (± 0.3‰) of the original laboratory’s reference value.

5.2.3 Intra-Annual Series Compositing

To facilitate comparison with monthly climate data and modelling of seasonal cycles, it is necessary to put cores sampled at different resolutions on common timescales. First, in order to facilitate comparison of isotopic patterns among DK rings through wavelet analysis and sinusoidal modelling, the intra-annual time-series for each ring was linearly interpolated at increments of 0.0588 (i.e. 1/17th) of a ring, corresponding to the minimum original sampling resolution. This facilitated the creation of a composite intra-annual time-series, based on ring-fraction sample position that could be used to assess intra-annual sampling schemes.

Second, in order to convert the original, unevenly sampled intra-annual time series to a common monthly timescale to facilitate comparison with climate data, original time-series were ‘binned’ according to a ring-fraction growth models. This process also provided an estimate of how sampling resolution varied throughout the year. The model assumed that each ~1mg sample was an even spatial unit within the ring, similar to the linear interpolation of growth used by Evans and Schrag (2004) and others (Poussart et al., 2004; Poussart and Schrag, 2005; Anchukaitis and Evans, 2010). Each sample was subsequently assigned to a growth month based on its location within the ring, according to depositional models based on the monthly growth curves developed for kauri by Fowler et al. (2005) and Wunder et al. (2013) from dendrometer-band studies. The first depositional model, based on Fowler et al.’s (2005) growth curve (DK\(_F\) when applied to DK), comprised from trees ranging from 0.3-1.1m in diameter, was applied to both DK and LH datasets. A revised depositional model (DK\(_W\)) was later used to remodel DK (Fig. 5.2) using Wunder et al.’s (2013) juvenile-specific (DBH < 40cm) growth-data and a temperature-truncated growth season, based on DK Virtual Climate Station (NIWA, 2011) data compared with required minimum mean-minimum (8°C) and minimum mean-maximum (17°C) monthly temperatures required for kauri growth (Wunder et al., 2013). The monthly resolved composite time series were then used to investigate correlations with monthly climate.
Annual cycles in stable isotopes from New

The binning and linear interpolation processes are approximations of past events with associated errors (see Fowler et al., 2005; Wunder et al., 2013 for estimates of growth associated variability). Growth rates vary naturally between and within trees through time. To acknowledge that variability and the fact that binning and interpolation of time-series to create composites smooths some of the higher-frequency variability in the original data, the Root-Mean-Square (RMS) error of the monthly-binned composite time series are calculated and presented.

5.2.4 Analysing annual cycles and their sub-annual sampling implications

To quantitatively establish whether annual and/or seasonal periodicities exist within the 4-year DK time-series spectral analysis was undertaken using Torrence and Compo’s (1998; n.d.) interactive wavelet tool. This analysis was conducted on the normalised linearly interpolated 4 core composite in order to focus on intra-annual cycles rather than inter-annual variability. Normalisation subtracts the mean of a set of intraannual samples from each individual sample and divides the result by the standard deviation of the sample set, producing a time series with a y axis centred on 0, facilitating comparison of trees with different mean isotope values and between intra-annual changes with similar patterns but different amplitudes. A similar exercise was not conducted for LH due to the data spanning non-consecutive years and being composed from various trees.

The potential for a coarse sub-annual sampling scheme (i.e. ESW vs late wood or WR) to avoid inadvertently sampling contrasting portions of any sub-annual cycles was then addressed in two ways. First, a sinusoidal model was fitted to normalised and raw linearly interpolated composite DK $\delta^{13}$C and $\delta^{18}$O time-series using the PAST software package (version 2.17c, Hammer et al., 2001). The first sinusoid was fitted with a period of 1, based on the hypothesis that isotope data, whether driven by climate or physiology or some combination of the two, would follow an annual cycle. The second sinusoid was fitted using a ‘blind’ spectral analysis (Hammer, 2012), which found the best fit second sinusoid; any second sinusoids with periods $>1$ were discarded as the study is focussed on intra-annual cycles. The Akaike Information Criterion (AIC) score, a measure of the goodness of fit of a statistical model that includes a penalty for the number of parameters, was used to prevent over-fitting of the model (i.e. explanation of variability purely by introducing a large number of parameters) (Hammer, 2012).

The sinusoidal models were used to create a theoretical dataset for comparison with the actual results obtained from paired ESW and WR analyses of DK samples. Each modelled annual cycle was split and the modelled values for the ESW portion and annual whole calculated.
The second source of irregular sampling within an annual cycle is likely to be operator error in consistently sampling at the same point within a ring. In order simulate an operator error effect 2 sampling scenarios based on DKHR data were created, in which the sampler under-estimated and took only 40% of the ring and over-estimated and took 60%. The individual high-resolution $\delta^{13}$C and $\delta^{18}$O values for the first 40% and 60% of each ring were averaged to provide an indication of what $\delta^{13}$C and $\delta^{18}$O a single, homogenous ESW sample taken at that point would have yielded. Paired t-tests were used to assess whether mean isotope values were significantly different, followed by Pearson’s Product-Moment correlation to observe whether they were consistently off-set.

5.2.5 Investigation of Climate Cycles

In order to assess the influence of climate on tree-ring isotopes at a monthly scale, the monthly binned composite isotope time-series from DK were compared with monthly climate variables taken from the NIWA VCSN using Pearson Product-Moment correlation. The VCSN was used because local climate station records are fragmented over the 1970-present time period. The same process was followed for LH, using climate data for Auckland Airport which are considered the most complete within the region (Lorrey et al., in prep).

Correlations were first conducted assuming near-instantaneous recording of climate by tree-ring isotopes as, while isotopic pulse labelling of trees shows that carbon can move within the tree for over a year (Kagawa et al., 2005; Kagawa et al., 2006b; a), it is likely that the bulk of C and O distinctly labelled by climatic events are recorded in cellulose isotopes within weeks (Barbour et al., 2002; Gessler et al., 2009). The records were then investigated for potential lags between climate and isotope changes by finding the highest correlation between monthly isotope and climate records within one year prior to cellulose creation. Raw isotope values were used rather than normalised as there are clear changes in the mean and range of $\delta^{18}$O from year to year and is was hypothesised that if climate is the major driver of intra-annual isotopic cycles then these inter-annual changes should be reflected in the climate record.

In order to assess whether an holistic understanding of climate and tree physiology would explain more isotopic variability than single climate factors, Barbour et al.’s (2004) mechanistic model for cellulose $\delta^{18}$O was applied to DK. The relevant variables and parameters used within the model are included below in Table 5.1. Full details of the model and required inputs can be found in Barbour et al. (2004). Mechanistic modelling can be used as an iterative process to investigate the validity of the variables and parameters fed to the model as much as for comparison of modelled and observed time-series. Such an investigation is worthy of full consideration in its own right but too lengthy to include here. Instead, a single iteration of Barbour et al.’s model is applied, based on the best available parameters and variables from the literature and available climate archives (Table 5.1).
Table 5.1: Input variables and constants for the Barbour et al (2004) mechanistic model of cellulose δ¹⁸O.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculating leaf temperature, air (ea) and intercellular (ei) water vapour pressure and E (transpiration rate)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stomatal conductance</td>
<td>0.1 (mol m² s⁻¹)</td>
<td>Measured for juvenile <em>Agathis australis</em> (Haworth et al., 2011)</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>Monthly Average (3.3-4.5 m s⁻¹)</td>
<td>VCSN 1997-2010 (NIWA, 2011) average</td>
</tr>
<tr>
<td>Leaf width</td>
<td>0.012m</td>
<td>Characterised by Ecroyd (1982)</td>
</tr>
<tr>
<td>Air Temperature</td>
<td>Daily Mean Monthly Average (4.3-14.9 °C)</td>
<td>VCSN 1972-1983 (NIWA, 2011)</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>9am Monthly Average (66.0-87.5 %)</td>
<td>VCSN 1972-1983 (NIWA, 2011)</td>
</tr>
<tr>
<td>PAR</td>
<td>Average Accumulated Monthly (343-1134 µmol m² s⁻¹)</td>
<td>2008-2013 Dunedin measured PAR (Energy-Studies-Program, 2013) average</td>
</tr>
<tr>
<td><strong>Craig-Gordon Parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmospheric/Vapour δ¹⁸O</td>
<td>δ¹⁸O_source + -Ɛ* (-19.0--15.9‰)</td>
<td>-Ɛ*is the equilibrium fractionation factor (Barbour, 2007)</td>
</tr>
<tr>
<td>Source/Precipitation δ¹⁸O</td>
<td>Monthly Average (-8.23--6.01‰VSMOW)</td>
<td>IAEA Invercargill 1961-2008 (IAEA/WMO, 2013) average</td>
</tr>
<tr>
<td><strong>Peclet Effect</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effective Length</td>
<td>0.043</td>
<td>Mean value from all species studied by Wang et al (1998).</td>
</tr>
<tr>
<td><strong>Δcellulose</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pe - Proportion of carbohydrate oxygen exchanged with stem/xylem water during conversion to cellulose</td>
<td>0.4</td>
<td>Approximate average value from the literature (Roden et al., 2000; Barbour et al., 2004; Cernusak et al., 2005)</td>
</tr>
<tr>
<td>Ps – Proportion of unenriched source water in the developing cells during cellulose creation</td>
<td>1.0</td>
<td>(Barbour et al., 2002; Barbour et al., 2004; Cernusak et al., 2005)</td>
</tr>
</tbody>
</table>
5.3 Results

5.3.1 Range of values and amplitude of intra-annual change

The first stage of characterising intra-annual cycles is to establish the range of δ-values at the two sites and the amplitude of intra-annual changes. The high-resolution stable isotopic determinations on DK tree-rings demonstrate that δ¹³C ranges from -26.90‰ to -21.66‰, about a mean of -23.73‰ while δ¹⁸O ranged from 27.22‰ to 35.50‰ about a mean of 31.60‰. Intra-annual ranges are up to 4.6‰ for δ¹³C and 8.1‰ for δ¹⁸O during a single year, with mean amplitudes of 3.31 and 4.27‰ respectively (Table 5.2, Fig. 5.3).

LH kauri δ¹³C ranges from -25.21 to -20.77‰, about a mean of -22.88‰ while δ¹⁸O ranges from 26.80 to 34.97‰ about a mean of 30.13‰. The amplitude of intra-annual variability is generally lower than DK, with δ¹³C values varying by up to 3.13‰ and δ¹⁸O by as much as 7.42‰, with mean amplitudes of 1.48 and 3.96‰ (Table 5.2, Fig. 5.3).

5.3.2 Characterising the Annual Cycle

The investigation of annual cycles within DK shows clear isotopic patterns within DK and, to a lesser extent, LH. The pattern for δ¹³C is characterised by an early maximum close to the ring boundary with the prior growth season. For δ¹⁸O the maximum is relatively brief and even closer to the ring boundary, followed by a steady decline to a minimum late in the ring, before δ¹⁸O values rebound sharply just before the ring boundary. For δ¹³C the major difference is that the initial maximum is characterised by a broader peak, followed by a more rapid decline than δ¹⁸O to an earlier minimum and rebound. For LH, δ¹³C is characterised by an early maximum, followed by a less abrupt (than DK) decline to a late season minimum which appears to coincide with the ring boundary rather than falling before it (Fig. 5.3). It is difficult to discern any cyclical behaviour in LH δ¹⁸O.

Table 5.2: Maximum and mean intra-annual ranges observed within DK and LH rings.

<table>
<thead>
<tr>
<th>Series</th>
<th>Period</th>
<th>Samples (per yr)</th>
<th>Max Annual Range</th>
<th>Mean Annual Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>δ¹³C (%)</td>
<td>δ¹⁸O (%)</td>
</tr>
<tr>
<td>DK 2.1</td>
<td>1979-1982</td>
<td>78 (19.5)</td>
<td>3.2</td>
<td>4.7</td>
</tr>
<tr>
<td>DK 2.2</td>
<td>1979-1982</td>
<td>85 (21.25)</td>
<td>3.3</td>
<td>6.3</td>
</tr>
<tr>
<td>DK 3.1</td>
<td>1979-1982</td>
<td>89 (22.25)</td>
<td>4.3</td>
<td>5.7</td>
</tr>
<tr>
<td>DK 3.2</td>
<td>1979-1982</td>
<td>118 (29.5)</td>
<td>4.6</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Grand Mean:</strong></td>
<td><strong>Grand Mean:</strong></td>
</tr>
<tr>
<td>LH6</td>
<td>'79,'87,'03</td>
<td>30 (10)</td>
<td>3.13</td>
<td>5.38</td>
</tr>
<tr>
<td>LH7</td>
<td>'79,'87,'03</td>
<td>30 (10)</td>
<td>2.66</td>
<td>7.42</td>
</tr>
<tr>
<td>LH8</td>
<td>'03</td>
<td>10 (10)</td>
<td>1.51</td>
<td>3.93</td>
</tr>
<tr>
<td>LH9</td>
<td>'79,'87</td>
<td>20 (10)</td>
<td>0.83</td>
<td>1.55</td>
</tr>
<tr>
<td>LH11</td>
<td>'79,'87</td>
<td>20 (10)</td>
<td>2.18</td>
<td>3.58</td>
</tr>
<tr>
<td>LH18</td>
<td>'03</td>
<td>10 (10)</td>
<td>0.78</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Grand Mean:</strong></td>
<td><strong>Grand Mean:</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>3.3</strong></td>
<td><strong>4.3</strong></td>
</tr>
</tbody>
</table>
Fig. 5.3: $\delta^{13}$C and $\delta^{18}$O data for all cores, binned according to the Fowler et al (2005) growth model to provide an indication of sampling resolution throughout the year. The figure shows the amplitude of intra-annual variability within DK and LH records and the concentration of samples in the spring months when growth binning is applied, up to 7 per month in Oct/Nov of 1980 for DK3.2. For DK the dashed lines/circles are DK2.1 and 3.1 while the solid lines/diamonds are 2.2 and 3.2. For LH, the dashed line/circles represent LH6, the solid line/crosses represent LH11, large dashes/diamonds represent LH7, dotted line/crosses represent LH9 and dotted line/diamonds. The solid line/triangles and dotted line/open diamonds that appear in 2003 only represent LH8 and LH18 respectively.
The qualitative description of DK δ\(^{13}\)C and δ\(^{18}\)O above is substantiated by quantitative observation of a clear cycle with annual periodicity (Fig. 5.4). Morlet wavelet analysis of the normalised, linearly interpolated four year record of δ\(^{13}\)C and δ\(^{18}\)O from DK showed both δ\(^{13}\)C (Fig. 5.4a) and δ\(^{18}\)O (Fig. 5.4b) have a significant \((p < 0.05)\) spectral frequency of ~1 year/17 samples. Due to padding with zeroes to reduce edge effects, and the cone of influence, periodicity can only quantitatively be ascribed significance for the central portion of the record. The periodicity is stronger for the latter section of the δ\(^{18}\)O record, reflecting the larger amplitude of intra-annual changes in those years (see Fig. 5.5). For both records, particularly δ\(^{13}\)C, there is a higher frequency signal that is almost significant at the ~½ year period. This is discussed in section 5.3.3 and 5.4.3 in relation to the sinusoidal modelling of intra-annual signals. It should be noted that the ‘½ year’ periodicity is a misnomer, as the linearly interpolated composite is spatially rather than temporally divided; the ½ year here is more accurately characterised as half ring width (or ~8 sub-samples).

### 5.3.3 Fitting a model to the seasonal pattern

The modelling of annual patterns at DK for investigation into sampling schemes/biases shows that both δ\(^{13}\)C and δ\(^{18}\)O time series from DK are well fitted by a combination of a primary sinusoid with period of 1 and a secondary, higher frequency sinusoid. Secondary sinusoids, originally fitted by ‘blind spectral analysis’ had a period of 0.5±0.05 years, which corresponded to the higher frequency periodicity evident in the Morlet wavelet (Fig. 5.4). Consequently, the period of secondary sinusoids was set at 0.5 and models re-run (Table 5.3). The sinusoidal models explain the bulk (74-88%) of variability in the normalised DK δ\(^{13}\)C and δ\(^{18}\)O records (Fig. 5.5a); in both cases the fitting of the second sinusoid improves the \(r^2\) markedly (10-15%) without significantly raising the AIC, suggesting that the models are not over-fitted. Similar sinusoid models with 1 and 0.5 year periods also fit the pattern of intra-annual, similarly well for raw δ\(^{13}\)C time series (\(r^2 = 0.89\)) but for raw δ\(^{18}\)O these models are less able to describe the inter-annual changes in amplitude of the cycle (\(r^2 = 0.59, \text{ Fig. 5.5b, Table 5.3} \)).

### Table 5.3: Equations for the sinusoidal models fitted to the composite DK linearly interpolated time-series in Fig. 5.5

<table>
<thead>
<tr>
<th>Record</th>
<th>Equation</th>
<th>(r^2)</th>
<th>Chi Sq</th>
<th>AIC</th>
<th>(p = )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK δ(^{13})C Normalised</td>
<td>δ(^{13})C = 1.01*(\cos(2\pi(x-1979/1.0-1.81))) + 0.455*(\cos(2\pi(x-1979/0.5-0.844)))</td>
<td>0.88</td>
<td>5.55</td>
<td>14.19</td>
<td>&lt;&lt;0.01</td>
</tr>
<tr>
<td>DK δ(^{18})O Normalised</td>
<td>δ(^{18})O = 0.876*(\cos(2\pi(x-1979/1.0-1.07))) + 0.343*(\cos(2\pi(x-1979/0.5-1.08)))</td>
<td>0.74</td>
<td>10.69</td>
<td>19.32</td>
<td>&lt;&lt;0.01</td>
</tr>
<tr>
<td>DK δ(^{13})C Raw δ</td>
<td>δ(^{13})C = 0.978*(\cos(2\pi(x-1979/1.0-1.79))) + 0.435*(\cos(2\pi(x-1979/0.5-0.798)))</td>
<td>0.89</td>
<td>4.64</td>
<td>13.28</td>
<td>&lt;&lt;0.01</td>
</tr>
<tr>
<td>DK δ(^{18})O Raw δ</td>
<td>δ(^{18})O = 1.1*(\cos(2\pi(x-1979/1.0-1.02))) + 0.395*(\cos(2\pi(x-1979/0.5-1.05)))</td>
<td>0.59</td>
<td>32.60</td>
<td>41.24</td>
<td>&lt;&lt;0.01</td>
</tr>
</tbody>
</table>
5.3.4 Sampling effects – real and modelled

Early-season and whole-ring analyses on DK kauri, designed to assess the potential to capture a distinct seasonal EW signal, produced several consistent results (Table 5.4a), including: 1) strong and statistically significant ($p << 0.01$) correlations between early-season and whole-ring $\delta^{13}C$ and $\delta^{18}O$ time series; 2) statistically significant differences ($p << 0.01$) between early-season and whole ring mean $\delta^{13}C$ and $\delta^{18}O$ values; 3) more positive $\delta$-values in early-season wood compared to whole wood (Table 5.4a).

The observed isotopic values are well matched by the theoretical data generated from the sinusoidal models of seasonal cycle. The mean differences between modelled EW and WR are larger than those in the observed data and the maximum differences smaller, but given the very different sampling depths.

Fig. 5.4: The wavelet power spectra (left) and global wavelet power spectra (right) for a) normalised $\delta^{13}C$ and b) normalised $\delta^{18}O$ from DK. For the wavelet power spectra (left), the contour levels are chosen so that 75%, 50%, 25%, and 5% of the wavelet power is above each level, respectively. The cross-hatched region is the cone of influence, where zero padding has reduced the variance. Black contour is the 5% significance level, using a red-noise (autoregressive lag1) background spectrum. The global wavelet power spectra is the solid black line (right), overlain by the dashed line representing the significance for the global wavelet spectrum, assuming the same significance level and background spectrum as in the wavelet power spectra (Torrence and Compo, n.d.)
Fig. 5.5: Linearly interpolated composite records of $\delta^{13}C$ and $\delta^{18}O$ compared with their best-fit sinusoids (see Table 5.3). a) normalised $\delta^{13}C$ and $\delta^{18}O$ from DK, showing the regular seasonal cycle captured well by sinusoid models. b) raw $\delta^{13}C$ and $\delta^{18}O$ from DK, showing $\delta^{13}C$ is well fitted by the sinusoidal model but the inter-annual amplitude changes in $\delta^{18}O$ are not. Error bars represent the RMS error of the composite time series.
Annual cycles in stable isotopes from New Zealand (<400 observed, 16 modelled) this is not unexpected. More important, the significant positive offset of ESW and the strong and significant correlation between ESW and WR values are consistent between modelled and observed data (Table 5.4b).

The model-based user-error scenario shows that raw isotope values representing 40% and 60% ring-width samples are significantly ($p < 0.05$) different, with the 40% sample having higher $\delta^{13}C$ and $\delta^{18}O$ (Table 5.4c). However, as with ESW and WR samples (both real and modelled), while the $\delta$-values were significantly different, the records are significantly ($p < 0.05$) correlated.

### 5.3.5 Intra-annual series compositing

The growth model ‘binning’ of non interpolated, original sub-annual sample determinations (See section 5.2.3) suggests that from DK kauri 4-7 samples per month were retrieved during the early-season (Oct-Nov) using the DK$_{F}$ growth model, equating to sub-weekly data resolution (Fig. 5.3). In wider rings, weekly resolution was maintained into mid-summer but declined to approximately fortnightly-to-monthly by February for all cores/years. Across the four year record, the RMS error for a given month ranged from 0.2-2.2‰ for $\delta^{13}C$ and 0.3-3.0‰ for $\delta^{18}O$, with a mean of 1.0‰ for $\delta^{13}C$ and 1.1‰ for $\delta^{18}O$ (Fig. 5.6a). If the DK$_{W}$ growth model is applied, resolution increases to 5-11 samples per month in October/November, with a decline to fortnightly-to-monthly resolution by February. The RMS errors associated with this model are similar, ranging from 0.1-2.0‰ for $\delta^{13}C$ and 0.5-2.1‰ for $\delta^{18}O$, with a mean of 1.0‰ for $\delta^{13}C$ and 1.1‰ for $\delta^{18}O$ (Fig. 5.6b). The RMS errors for both growth-binning models are generally smaller than the amplitude of the composite series’ cycles.

In contrast, the lower resolution sampling of LH rings means that the maximum resolution is between

### Table 5.4: Observed (a) and modelled (b) differences between ESW and WR samples showing a strong and significant correlation between the two records despite a consistent enrichment in ESW for both $\delta^{13}C$ and $\delta^{18}O$. A simulated operator error in 50% sampling (c) reveals a similar correlation between 40 and 60% ring-width sub-samples.

<table>
<thead>
<tr>
<th>Record</th>
<th>Sample Pairs</th>
<th>Max difference (ESW-WR %)</th>
<th>Mean Difference</th>
<th>Difference significance ($p =$)</th>
<th>Correlation ($r$)</th>
<th>Correlation significance ($p =$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK $\delta^{13}C$</td>
<td>420</td>
<td>2.74</td>
<td>0.40</td>
<td>&lt;&lt;0.01</td>
<td>0.76</td>
<td>&lt;&lt;0.01</td>
</tr>
<tr>
<td>DK $\delta^{18}O$</td>
<td>418</td>
<td>7.04</td>
<td>0.44</td>
<td>&lt;&lt;0.01</td>
<td>0.73</td>
<td>&lt;&lt;0.01</td>
</tr>
</tbody>
</table>

b. Record

<table>
<thead>
<tr>
<th>Record</th>
<th>Max difference (ESW-WR %)</th>
<th>Mean Difference</th>
<th>Difference significance ($p =$)</th>
<th>Correlation ($r$)</th>
<th>Correlation significance ($p =$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKHR $\delta^{13}C$</td>
<td>16</td>
<td>0.80</td>
<td>0.59</td>
<td>&lt;&lt;0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>DKHR $\delta^{18}O$</td>
<td>16</td>
<td>1.20</td>
<td>0.64</td>
<td>&lt;&lt;0.01</td>
<td>0.86</td>
</tr>
</tbody>
</table>

c. Record

<table>
<thead>
<tr>
<th>Record</th>
<th>Range of Difference 40%-60% (%)</th>
<th>Mean Difference 40%-60% (%)</th>
<th>Difference significance ($p =$)</th>
<th>Correlation ($r$)</th>
<th>Correlation significance ($p =$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK $\delta^{13}C$</td>
<td>0.00-0.33</td>
<td>0.15</td>
<td>&lt;0.01</td>
<td>0.99</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>DK $\delta^{18}O$</td>
<td>0.01-1.07</td>
<td>0.48</td>
<td>&lt;0.01</td>
<td>0.99</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
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The binning suggests that there is monthly coverage from September to February, with one sample per month for Sep, Dec, Jan and Feb. March was skipped with the final sample falling in April. Across the three year record, the RMS error for a given month ranged from 0.02-2.55‰ about a mean of 0.46‰ for $\delta^{13}$C and for $\delta^{18}$O, from 0.02-2.66‰ about a mean of 0.68‰.

According to the DK$_F$ model, isotopic maxima at DK are achieved in spring for both $\delta^{13}$C (September-November) and $\delta^{18}$O (September or October) while isotopic minima fall between February and April (Fig. 5.6a). The DK$_W$ model shifts the $\delta^{13}$C maxima to November and the $\delta^{18}$O maxima to October for all years except 1979 (November). Minima for $\delta^{14}$C fall in either January or February before a rebound in February.
or March. For δ¹⁸O, the 1979-1981 minimal fall in January before a rebound in February and March. The 1982 minimum falls in January, and is maintained in February and March (Fig. 5.6b). LH does not exhibit a consistent δ¹⁸O pattern but, like DK, δ¹³C generally peaks in October although it does not decline as quickly, with relatively positive values sometime maintained into summer. LH’s isotopic minima also occur in Feb-April (Fig. 5.6c).

5.3.6 Isotope - Climate Correlations

Having established the pattern and periodicity of annual/seasonal cycles and created two potential monthly resolved composite records, their significance is investigated through comparison with local monthly climate data. There are numerous statistically significant contemporaneous correlations between DK monthly isotope records and climate parameters (Table 5.5). The bulk, however, are not strong (i.e. \( r < 0.5 \)). For the DK\(_F\) time-series, the only contemporaneous correlation where \( r > 0.5 \) is with relative humidity; it is also the only contemporaneous record to achieve a significance of \( p < 0.01 \) (with DK δ¹³C) (Table 5.5a). For DK\(_W\) time-series there are no significant contemporaneous correlations for δ¹⁸O but there are significant negative correlations between δ¹³C, temperature and relative humidity (Table 5.5b). The correlation between relative humidity and δ¹³C is also one of the highest, although not statistically significant, contemporaneous relationships for LH (Table 5.5c).

In contrast, nearly all lagged correlations provide highly statistically significant (\( p < 0.01 \)) results with a number of climate variables approaching \( r = 0.90 \) with δ¹³C. Correlations with δ¹⁸O were generally lower but a number still approached \( r = 0.70 \). Most of these correlations are based on lag-times of 7-10 months, aligning the isotope signal for September growth commencement with the prior summer’s climate.

5.3.7 Mechanistic Modelling of δ¹⁸O

Given the lack of strong contemporaneous climate correlations with isotope data, mechanistic modelling was employed to investigate whether a more holistic approach, incorporating multiple climatic variables and physiological parameters, could improve the explanation of isotopic variability. For the period covered by DK high-resolution analyses mechanistic modelling predicts a mean δ¹⁸O of 24.7‰ for the 1979-1982 growth years, with a minimum of 20.4‰ and maximum of 28.6‰. For all years the minima fall in June, while maxima occur in November or December. The mean annual range of values is 7.8‰, ranging from 7.3‰ in the 1981 growth year to 8.1‰ in the 1980 growth year. If the growth months (Sep-Jun) for DK\(_F\) are considered then the mean δ¹⁸O increases to 25.5‰ but the maximum, minimum and intra-annual range are unchanged. If DK\(_F\) growth months (Oct-Mar) are considered then mean modelled δ¹⁸O is 26.8‰ and while the maximum modelled δ¹⁸O remains unchanged, the minimum rises to 24.2‰ and the mean intra-annual range drops to 3.6‰, ranging from 3.1‰ in 1979 to 4.1‰ in 1980. Neither DK\(_F\) nor DK\(_W\) time-series correlate significantly with mechanistically modelled monthly δ¹⁸O unless a lag 2-3 month lag is introduced (Table 5.5d).
Table 5.5: Contemporaneous and lagged correlations between monthly climate and $\delta^{13}$C and $\delta^{18}$O from a) DK using the Fowler et al. (2005) monthly binning (DK$_{m}$), b) DK using the Wunder et al. (2013) binning (DK$_{w}$), c) from LH using Fowler binning. d) shows correlations between DK$_{m}$ and DK$_{w}$ $\delta^{18}$O and expected $\delta^{18}$O, modelled using Barbour et al. (2004).

![Table 5.5](image)

- **a.** DK$_{m}$ $\delta^{13}$C
  - $r =$
  - $df =$38
- **b.** DK$_{w}$ $\delta^{18}$O
  - $r =$
  - $df =$19
- **c.** LH $\delta^{13}$C
  - $r =$
  - $df =$19
- **d.** Modelled $\delta^{18}$O
  - $r =$
  - $p <$ ($df =$ )
5.4 Discussion

5.4.1 Amplitude and pattern of seasonal signal in kauri data

The comparison of juvenile and mature kauri from different environments allows the characterisation and comparison of sub-annual cycles from two very different stands, contributing to the first major research objective. DK and LH display similarities in the ranges isotopic values found at each site but significantly different mean values. $\delta^{13}C$ values overlap considerably but their means are significantly different (0.85‰, $p < 0.05$). At its simplest, the difference in $\delta^{13}C$ suggests a difference in the ratio of internal (intercellular) CO$_2$ partial pressure relative to atmospheric CO$_2$ partial pressure (Francey and Farquhar, 1982; Farquhar et al., 1989). Such $\delta^{13}C$ differences within a species can be driven by climate or physiological and microenvironmental differences. While morphological differences between juvenile and mature kauri leaves have been shown to cause $\delta^{13}C$ off-sets between age classes (Walcroft, 1994), these were in the opposite direction to the more positive mean $\delta^{13}C$ of mature trees here. A more likely morphological/microenvironmental explanation is the general trend for older trees to have more positive $\delta^{13}C$, due to the so called ‘juvenile effect’ (McCarroll and Loader, 2004; Leavitt, 2010). In this scenario, the canopy emergent, open crowned mature LH specimens are likely to have higher $\delta^{13}C$ due to their increased access to light (Francey and Farquhar, 1982), a well mixed atmosphere (Schleser and Jayasekera, 1985) and, potentially, changes in bark photosynthesis (Cernusak et al., 2001) and hydraulic conductivity (McCarroll and Loader, 2004). Equally, the climatic differences between the two sites could
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account for a lower ratio of intercellular $\text{CO}_2$ partial pressure to atmospheric $\text{CO}_2$ partial pressure; the LH trees are likely to have higher photosynthetic rates due to the greater availability of light (~200+ more sunshine hours each year (NIWA, 2012)), further enhanced by their canopy emergent status compared with DK’s dense ‘ricker’ thicket growth. Further, detailed investigation of a range of tree ages is required to assess the relative impacts of morphological and climatic differences on kauri $\delta^{13}\text{C}$, an important question for establishing the relative importance of climate versus age and microenvironmental effects in longer records from living trees, archaeological timbers or sub-fossil trees are sensitive to.

Like $\delta^{13}\text{C}$, the $\delta^{18}\text{O}$ ranges for DK and LH overlap considerably but with significantly different means (1.45‰, $p < 0.05$). The higher mean $\delta^{18}\text{O}$ at DK defies the general trend of precipitation $\delta^{18}\text{O}$ depletion with latitude (Dansgaard, 1964; Rozanski et al., 1993; Darling et al., 2005; Fig. 5.1). This suggests either a localised climatic enrichment of $\delta^{18}\text{O}$ through evaporative/evapotranspirative regimes or a circulation anomaly providing $\delta^{18}\text{O}$ enriched source water. Unfortunately, the spatially and temporally limited meteoric $\delta^{18}\text{O}$ data available in New Zealand prevent detailed conclusions regarding source water patterns (Blackstock et al., 2011; Blackstock et al., 2012). Based on the data available from Invercargill (IAEA/WMO, 2013), there is likely to be a long-term seasonal pattern to precipitation $\delta^{18}\text{O}$ at DK but monthly values are highly variable between years. However, the mean annual range of $\delta^{18}\text{O}$ at Invercargill is ~2.2‰ which is approximately half that of the mean amplitude of the DK $\delta^{18}\text{O}$, suggesting that seasonal source changes are not the sole driver for intra-annual $\delta^{18}\text{O}$ in cellulose. Seasonal changes in precipitation $\delta^{18}\text{O}$ are included as a variable in mechanistic modelling of DK $\delta^{18}\text{O}$, discussed below in section 5.4.4.

Despite a slightly larger amplitude in seasonal precipitation at Kaitaia, closer to LH, there appears to be no comparable cycle in the LH $\delta^{18}\text{O}$. This may be due to the sampling of discrete, ex-tropical cyclone years and/or the lower sampling resolution employed. A study of numerous consecutive years, similar to that conducted at DK, is required to establish whether similar seasonal signals in $\delta^{18}\text{O}$ occur in kauri within their natural range.

5.4.2 Sampling implications for seasonal and inter-annual studies

The prominent isotope cycles in DK highlight the importance of this research’s second objective, understanding the magnitude and pattern of intra-annual variability synthesised in lower resolution sampling schemes (e.g. early-wood, late-wood and/or whole-ring). The first step of assessing sub-annual resolution here was to compare the early-season growth wood with the traditional whole-ring measurement. The finding of strong correlations between ESW and WR for DK $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is not unexpected given that October-November growth frequently constitutes ~50% of ring-width for kauri (Fowler et al., 2005). The consistent positive off-set between ESW and WR $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ means for DK are explained by the cyclical seasonal pattern observed in both isotopes, from which the ESW sample consistently draws the most enriched isotopic portion of the year. These findings from DK data were reinforced by simulated sampling of the sinusoidally-modelled seasonal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cycles.

Similarly, slight changes in sampling position based on a 50% ESW target (i.e. sample proportions of the
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annual ring shifting between 40-60% of the total ring-width) resulted in small but statistically significant changes in mean δ-values. However, the two modelled time-series (40% and 60% ring-width samples) remain significantly correlated, which suggests subtle variations in manually sampling the annual ring for ESW analysis may not greatly affect data’s utility for seasonal climate reconstruction, as either way the bulk of the isotopic signal is still composed of relatively enriched ESW. This is promising for studies that propose sampling ESW of kauri to isolate early season climatic conditions (e.g. Lorrey et al., in prep). In such cases, where researchers wish to focus on a particular portion of the annual ring to target a particular climatic phenomenon studies would benefit from preliminary investigation at sub-monthly resolution to provide a base-line indication of the magnitude and timing of δ13C and δ18O changes throughout the annual growth period. Without base-line data about the seasonal cycle, researchers may increase the potential impact of subtle changes in sampling strategy on their datasets, and therefore climate reconstructions, by missing seasonal or climatic events by sampling the wrong portion of the ring or unnecessarily dampening those same signals by including them in a whole-ring sample.

5.4.3 Potential for event-scale reconstruction

While linear interpolation allowed sinusoidal modelling spatial variability within the ring, to assess the temporal resolution achievable the growth-model binning of high-resolution samples based on kauri dendrometer studies was used. For DK models indicated that resolution ranged from a maximum of ~1 sample every 3-4 days in October-November down to monthly by late summer/autumn. At LH sampling resolution was lower, never achieving weekly scale. These results suggest a much finer sampling method is probably required to detect any Summer-Autumn aberrant weather events, such as ex-tropical cyclones, which LH sampling originally targeted. While ETCs can result in distinct precipitation signatures in New Zealand (Blackstock et al., 2011; Blackstock et al., 2012), they generally occur for the Auckland region during February and March (Lorrey et al., 2013), at which point LH sampling resolution was approximately monthly due to the slow late-season growth. Consequently, spring growth dominance for kauri may mean they can be more practically accessed to reconstruct seasonal climate, or in the case of palaeotempestology, sub-polar storms (contributed to by a more negative Southern Annular Mode), which commonly occur during austral spring.

DK isotopic records with approximately weekly temporal resolution indicated the variability between consecutive samples can be relatively large, with changes of up to ~2‰ in δ18O in individual cores (DK2.2 and 3.2 in December 1980; Fig. 5.3) and smaller high frequency changes in the composite records (February 1981, Fig. 5.5a). The variation amongst the δ18O cycle for both DK and LH suggests that trees are recording short, sharp changes within their environment. In DK these abrupt weekly to sub-weekly δ18O changes are best described as high frequency departures from an underlying seasonal cycle similar to that observed for δ13C. While the LH record also documents some large inter-sample shifts, these have no underlying pattern and often coincide with large RMS errors (Fig. 5.5c), suggesting variability within the data is obscuring any coherent seasonal or event signals, perhaps due to the limited sampling resolution. In contrast, δ13C for both sites generally has smaller inter-sample changes, suggesting either a consistent
and strong physiological control or a more gradual response of $\delta^{13}C$ to seasonal climate variability and change. From this perspective, it seems that $\delta^{18}O$ is a more promising isotopic candidate for weather event reconstruction.

A qualitative observation of intra-annual sampling’s potential to aid in reconstruction of climatic ‘events’ of longer duration can also be made from these data, which cover one of New Zealand’s strongest documented El Niño events in the 1982-83 growth year. Data for 1982 show the largest intra-annual range for $\delta^{18}O$ out of all years analysed, incorporating the most enriched and depleted values of the entire record and some of the largest and most sustained departures from the modelled $\delta^{18}O$ cycle (Fig. 5.3). The absence of analysis of other significant ENSO events for comparison, prevents verification of this relationship but these data present the tantalising prospect that $\delta^{18}O$ in kauri tree rings may enable identification of past significant El Niños.

Large changes between consecutive samples at weekly resolution at DK showed event scale reconstruction potential for kauri but, in this context the relatively primitive sampling strategy within this study was a limiting factor, particularly at LH. The use of specialised equipment such as a retrofitted microtome (Helle and Schleser, 2004) or micromill would certainly help address this issue, as might whole-core processing to $\alpha$-cellulose as demonstrated by Li et al. (2011). For future dendroisotopic studies targeting high-resolution events, these results show that using young, fast-growing trees can provide abundant material that enables weekly or better resolution for some parts of the year with limited specialised resources. Seasonal cycles of $>3\%$o for DK $\delta^{13}C$ suggest that intra-annual cycles provide useful data despite the potential for juvenile effects (generally 1-3\%o over decades to centuries (Jansen, 1962; Leavitt and Long, 1985; Leavitt, 2010)) to compromise longer inter-annual records. The sub-annual cycles observed in wide juvenile rings could provide complementary information to ring-based and isotope-based reconstructions from mature trees.

**5.4.4 Monthly climate correlations**

While the prospects for event reconstruction were mixed, the time-series provide ample resolution for seasonal and/or monthly climate reconstruction. For, DK$_F$ $\delta^{18}O$ there are weak negative relationships with relative humidity and temperature. Both correlations can be explained if the primary fractionation of source water occurs during evapotranspirative fractionation within the leaf. Higher relative humidity results in a higher ratio of ambient-to-inter-cellular vapour pressures, which in turns decreases evapotranspirative enrichment of leaf water (Barbour et al., 2004; Barbour, 2007). Higher temperature lowers the fractionation associated with the proportional depression of water vapour pressure by the heavier $H_2^{18}O$ molecule (termed $\varepsilon^*$, see Barbour, 2007), also resulting in decreased evapotranspirative enrichment of leaf water (Barbour et al., 2004; Barbour, 2007). The DK$_W$ time-series has no significant correlations with monthly climate data.

Stronger negative correlations occur between $\delta^{13}C$ and relative humidity for both the DK$_F$ and DK$_W$ time-series. DK$_F$ has an additional significant negative correlation with soil moisture deficit while the DK$_W$
time-series is negatively correlated with temperature. The negative correlation with relative humidity can be explained by periods of low relative humidity reducing stomatal conductance, limiting the supply of inter-cellular CO₂, leading to decreased carboxylation discrimination against \(^{13}\)CO₂ (McCarroll and Loader, 2004). The negative correlations with temperature and soil moisture deficit make less theoretical sense. Both temperature and soil moisture deficit are expected to positively correlate with \(\delta^{13}\)C, the former through its control of photosynthetic rate and the latter through its regulation of stomatal conductance (McCarroll and Loader, 2004). It seems likely that these correlations are the result of common seasonal cycles rather a causative climatic forcing of \(\delta^{13}\)C.

While the negative correlations between \(\delta^{13}\)C and \(\delta^{18}\)O and relative humidity make theoretical sense, unfortunately they are not strong enough to be of great practical use in intra-annual climatic reconstruction. McCarroll and Pawellek (2001) suggest that isotope-climate correlations of 0.70 are an minimum requirement as the isotope record can then explain ~50% of climatic variability; the highest correlation observed here can only account for 35% of intra-annual relative humidity changes.

An alternative explanation for climate-isotope relationships is that an environmental lag is involved. The highest correlations between monthly binned isotopes and climate were generally universally at 7-10 months lag. This could be explained for \(\delta^{18}\)O by current season use of groundwater affected by prior evaporative processes. However, kauri are generally shallow rooted surface feeders (Ecroyd, 1982) and almost immediate growth responses have been observed to rainfall events in kauri near Auckland (Wunder et al., 2013). These physiological traits arguing against groundwater related lags, combined with the evidence that \(\delta^{18}\)O climatic signals are generally incorporated withing cellulose within weeks (Gessler et al., 2009), plus the lack of a similar environmental lag justification for \(\delta^{13}\)C, suggest that the lagged correlations observed are purely the correlation of off-set signals with similar cyclicity rather than a causative relationship.

Ultimately, the climatic correlations with DK and LH intra-annual isotope time-series yields a number of strong but unjustified lagged correlations and weak contemporaneous correlations, a number of which run contrary to well established isotope theory. The weak negative correlation with relative humidity is the only well established relationship between climate and multiple time-series and it explains little of the consistent, large seasonal cycles in \(\delta^{13}\)C and \(\delta^{18}\)O. This suggests that either there is an added physiological component to the seasonal isotopic cycle or that a more holistic approach to the interpretation of isotope-climate relationships is required. Both ideas are addressed in the following section.

5.4.5 Mechanistic modelling of \(\delta^{18}\)O and implications for the role of physiology in annual cycles

The integration of multiple climatic variables and physiological parameters into a mechanistic model of \(\delta^{18}\)O provides the opportunity to assess whether observed annual \(\delta^{18}\)O cycles are better explained by an holistic understanding of physiological-climate interactions relative to simple linear correlation against monthly climate variables. The large offset in modelled and observed mean \(\delta^{18}\)O can be accounted for by inaccuracies in multiple input parameters. First, the source water \(\delta^{18}\)O values are from Invercargill,
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~170km WSW of Dunedin. While broadly representative of regional precipitation $\delta^{18}$O, there may be some discrepancies between the DK site and source water data used. Second, a related uncertainty surrounds vapour $\delta^{18}$O, for which direct measurements are difficult to obtain (Barbour, 2007), resulting in most studies relying on estimates. Third, there is uncertainty surrounding two of the primary physiological parameters: $p_{ex}$, the proportion of carbohydrate oxygen exchanged with stem water during conversion to cellulose and $p_x$, the proportion of unenriched source water (as opposed to relatively enriched phloem or leaf water) in the developing cells during cellulose creation. In a number of tree species $p_{ex}$ has shown a relatively narrow range centred around 0.4, but values may range from ~0.3-0.5 (Roden et al., 2000; Cernusak et al., 2005; Barbour, 2007). In large trees, $p_x$ has been assumed to be close to 1 at the site of cellulose synthesis in the stem, which is far from the leaf (Barbour et al., 2002; Barbour et al., 2004) and as a result, phloem water has time to exchange with stem/xylem water (Barbour, 2007). While recent evidence suggests that this assumption is correct (Cernusak et al., 2005) relatively small changes in $p_x$ can have a significant effect on modelled cellulose $\delta^{18}$O. For instance, a $p_x$ reduction to 0.8, with all other factors equal, results in a $\sim+1‰$ shift for DK modelled $\delta^{18}$O. Other physiological variables may also contribute to the underestimation of cellulose $\delta^{18}$O, including the effective length of the evaporative pathway within the leaf, a factor that is difficult to quantify and requires further study (Barbour, 2007).

Ultimately the pattern and magnitude of intra-annual variability are an equally important component of climate reconstruction as the mean $\delta^{18}$O. The amplitude of variability indicated by the DK$_w$ growth months (3.6‰) is similar to the average of 4.3‰ observed. Unfortunately, despite the similarities between the DK$_w$ model and observed annual ranges, the two records to not correlate strongly or significantly correlated to a meteorological variable unless a lag is introduced. However, that lag creates a negative correlation when the modelled and observed values should co-vary positively. The DK$_t$ time-series shows similarly poor correlation with the model.

Given the lack of a strong contemporaneous link between climate and intra-annual isotope changes, even when multiple variables and parameters are included in a mechanistic model, the potential for non-climatic influences on $\delta^{13}$C and $\delta^{18}$O at the sub-annual scale must be considered. This study was not designed to investigate physiological influence on seasonal stable isotope signatures within tree-rings so discussion is limited to brief qualitative observations based on the data. This issue needs to be specifically addressed for kauri at a later date, potentially using non-natural abundance isotope labelling.

The major physiological cycle linked to seasonal isotope cycles is the use of stored photosynthates in promoting spring growth. Generally speaking deciduous trees store large quantities of photosynthe (mainly as starch) late in the growth season in order to provide enough energy for the following spring (Kramer and Kozlowski, 1979; Wilson, 1984). This cycle has prompted some authors to advocate for latewood only sampling for isotope dendroclimatology (McCarroll and Loader, 2004 and references therein). Evergreen trees also store photosynthe at the end of the growing season, often in old leaves rather than twigs/roots/stems but it is generally a smaller amount designed to promote rapid shoot growth
(Wilson, 1984) and/or root growth (Kramer and Kozlowski, 1979). Consequently, the incorporation of stored photosynthate into stem wood is likely to be less significant in evergreens than deciduous trees.

Some evergreen species from the genus *Pinus* have been shown to rely almost entirely on current season photosynthate, prompting their use for intra-annual isotope studies (Barbour et al., 2002). This prompted the investigation of kauri, also an evergreen conifer, based on the hypothesis that its seasonal isotope cycles may be climatically rather than physiologically controlled. However, the contribution of stored photosynthate to growth varies between species (Kuptz et al., 2011), let alone genera. Furthermore, kauri often shed through branch, rather than leaf, abscission, resulting in an average leaf age of ~2.5 years, with some leaves remaining for up to 15 years (Silvester and Orchard, 1999). Given the uncertainty surrounding kauri’s utilisation of stored photosynthates, the extent to which spring δ¹³C and δ¹⁸O can be attributed to contemporaneous environmental conditions cannot be assumed.

The influence of physiological cycles may be evident in the prima facie similarities between Helle and Schleser (2004) and others (Jahren and Sternberg, 2008) data from deciduous trees and intra-annual DK δ¹³C data. DK δ¹³C exhibits the ‘tri-phase’ pattern that Helle and Schleser (2004) attribute primarily to physiological processes, characterised by: 1) a peak in δ¹³C shortly after ESW growth commencement, followed by 2) a gradual decline to a late-wood δ¹³C minimum and finally, 3) a rapid return to near ESW values at the ring-boundary, transitioning to the next year’s ESW maximum. This regular, cyclic change in the DK and, to a lesser extent LH, kauri suggests that physiology could be a contributor to δ¹³C cycles.

While less research has addressed physiological cycles in relation to δ¹⁸O, the primary storage carbohydrates’ (fructose, glucose, sucrose and starch (Magel et al., 2000)) molecular structures all incorporate similar amounts of oxygen to carbon. Consequently, physiology seems a reasonable explanation for the strong underlying δ¹⁸O cycle, which is broadly similar to δ¹³C. However, while δ¹⁸O time-series from DK also show regular seasonal cycles, compared with δ¹³C, there are larger inter-annual changes in the magnitude of those cycles (Fig. 5.5b) as well as short-term departures from the seasonal pattern in DK (Fig. 5.5a). This variability is characterised by the weaker fit of sinusoidal models to δ¹⁸O time-series and the weaker periodicity evident in the wavelet analysis of the first half of the time-series. The most likely explanation seems to be that seasonal and event-scale external forcings (climate and meteorological variability, respectively) may be recorded in kauri δ¹⁸O which is overprinted on an underlying physiological pattern. Such forcings may be evident in δ¹⁸O but not δ¹³C for two reasons. First, those forcings include changes in source water δ¹⁸O, while the δ¹³C of atmospheric CO₂ is relatively constant. Second, approximately 40% of carbohydrate oxygen is exchanged with xylem/stem water O during cellulose formation (Roden et al., 2000; Barbour, 2007; Cuntz et al., 2007), so even during a growth period reliant on cellulose reserves, current season oxygen will be incorporated (Sternberg, 2009). The greater responsiveness of δ¹⁸O to environmental forcings would seem to suggest that it has the greater potential for high frequency climate reconstruction from kauri. Further intra-annual research, designed specifically to observe physiological processes in kauri, with reference to the synthesis of δ¹³C and δ¹⁸O, within their natural range is warranted before these qualitative observations can be substantiated.
5.5 Conclusion

In relation to specific research objectives this research makes four key findings. First, kauri from the south of New Zealand exhibit clear annual cycles for both δ\(^{13}\)C and δ\(^{18}\)O. In comparison, a stand of mature northern kauri show less regular cycles and different isotopic means but overlapping ranges. Qualitatively there are less regular cycles in the northern trees but direct comparison is hampered by different sampling regimes. Second, the regularity of the seasonal cycle in southern kauri isotope values means that sub-annual sampling schemes based on a 50% early-season-wood split are well correlated with whole-ring analyses. Small errors in sampling position appear to have little effect on the utility of stable isotope data for seasonal climate reconstruction. Third, using fast growing juvenile trees, sub-weekly resolution can be obtained from kauri during their spring growth period even with basic sampling methods, indicating that sufficient resolution can be achieved for event-scale climate reconstruction using kauri isotopes. Capturing events such as ex-tropical cyclones that occur in summer/autumn, however, will require improved sampling resolution. Fourth, seasonal δ\(^{13}\)C changes do not correlate well with contemporary climate, suggesting the use of stored carbohydrates in spring growth. δ\(^{18}\)O is also poorly correlated with contemporary climate and mechanistic modelling of cellulose δ\(^{18}\)O, suggesting that non-climatic, physiological cycles of stored photosynthate use may play a dominant role in intra-annual kauri isotope cycles for carbon and oxygen. However, the larger inter-annual changes in the mean δ\(^{18}\)O and amplitude of annual patterns, along with large changes between consecutive samples, suggest that δ\(^{18}\)O may be more responsive to high-frequency climatic changes than δ\(^{13}\)C. These traits suggest high-frequency climatic modulation of the underlying physiological signal in juvenile trees, which may add value for palaeoclimate reconstruction. Further investigation targeted at physiology is required to establish the relative contributions of climate and physiological cycles, before the seasonal to event-scale potential of intra-annual kauri stable isotopes can be realised.
6. REGIONAL HYDROCLIMATE RECORDED IN TREE-RING OXYGEN ISOTOPES FROM TWO NEW ZEALAND CONIFERS

In response to the findings presented in Chapter 5, two key research opportunities became immediately apparent. First, to pursue the issue of variability (intra-annual, intra-tree, inter-tree) through a further detailed, intra-annual resolution investigation targeted at separating climatic and physiological responses. The second was to use the existing time-series to investigate whether climate reconstruction could be achieved in spite of the variability within the record. The former, while extremely valuable, was seen as ‘another PhD’ worth of work that would be impossible to thoroughly pursue given time constraints. In contrast, the latter made use of existing data and represented a chance to address, even if only in a preliminary manner, the original research goal of inter-annual climate reconstruction.

Given the varied collection of time-series including carbon and oxygen isotope data from early-season and whole-ring wood from cedar and kauri, it was necessary to narrow the inter-annual climate investigation by selecting either a single species or single isotope. The strong correlations between DK and MtC observed in Chapter 4 suggested that there was potential for a multi-species climate record, so the decision was made to pursue that line of enquiry. Oxygen was regarded as the more promising isotope record for two reasons. First, Chapter 4 demonstrated that inter-annual δ¹⁸O time-series have consistently higher EPS scores and stronger inter-site/species correlations than δ¹³C, suggesting greater potential for a strong, regional climate signal. Second, δ¹⁸O showed greater inter-annual variability than δ¹³C in high-resolution records (Chapter 5), suggesting a more pronounced inter-annual response to climate. Consequently, the potential for inter-annual δ¹⁸O records to reconstruct climatic changes was investigated, in the hope that this research could at least partially fulfil its original goal of palaeoclimate reconstruction by demonstrating foundation relationships between tree-ring δ¹⁸O and climate.

6.1 Introduction

6.1.1 Project rationale

Reconstructing past changes in climate is a crucial step in understanding, modelling and adapting to the modern period of rapid climate change (Bernstein et al., 2007; Jansen et al., 2007). Increasingly, changes to the amount and distribution of precipitation (i.e. hydroclimate) are recognised as one of the greatest challenges posed by climate change (Treydte et al., 2006). Chemical changes in tree-rings offer the unique ability to create calendar-dated reconstructions of climate, particularly hydroclimate (McCarroll and Loader, 2004), across sub-annual to millennial-scale temporal resolutions during the period of anthropogenic impacts (i.e. Anthropocene), the late-Pleistocene and Holocene.

Preliminary dendroisotopic studies, spanning seasonal to inter-annual time-scales (Poussart, 2004; Lorrey
et al., submitted; Chapter 4; Chapter 5) show that at least two New Zealand tree species, New Zealand kauri (*Agathis australis*) and New Zealand cedar (or Pahautea, *Libocedrus bidwillii*), have potential as stable isotope dendroclimatic proxies. Chapter 4 showed that oxygen isotope records from cedar and kauri preserve a stronger common signal (measured by Expressed Population Signal (EPS; Wigley et al., 1984; Briffa and Jones, 1990)) than carbon. In addition, the oxygen isotope records from stands of cedar and kauri were strongly correlated, suggesting potential for reconstruction of a common regional climate signal. Consequently, this chapter focuses on developing those oxygen isotope records further, in order to establish whether the two species preserve a common, regional hydroclimate signal.

### 6.1.2 Research focus

This chapter focuses on inter-annual oxygen isotope time-series from two South Island sites in order to identify what relationship(s), if any, exists between tree-ring $\delta^{18}$O and climate variables. Based on the findings reported in scientific literature it is hypothesised that $\delta^{18}$O values are determined by a combination of atmospheric conditions external to the tree that determine precipitation $\delta^{18}$O, and local evaporative processes that alter the $\delta^{18}$O of soil water and water within the tree. Potential source effects determining meteoric water $\delta^{18}$O are investigated through correlation analysis of two circulatory indices related to the prevailing air-flow over New Zealand: the Southern Oscillation Index (SOI; Troup, 1965; Trenberth, 1976b) and MZ3 (Trenberth, 1976a) [Fig. 6.1]. The SOI is the measure of the southwest Pacific atmospheric component of El Niño Southern Oscillation (ENSO) action, which affects prevailing wind direction, temperature and rainfall in New Zealand (Mullan, 1995; Sturman and Tapper, 2006). The MZ3 is a direct measure of the relative strength of south westerly versus north easterly flow over the South Island of New Zealand (Trenberth, 1976a; Salinger and Mullan, 1999). The seasonal influence of local precipitation that others (Nakatsuka et al., 2004; Treydte et al., 2006) have observed in $\delta^{18}$O records is explored through correlation analysis using monthly rainfall totals. Local evaporative conditions affecting the tree are investigated through comparison of cellulose $\delta^{18}$O records with local relative humidity, soil moisture deficit and temperature records.

### 6.2 Study sites and Methodology

#### 6.2.1 Site description and dendrochronological methods

Tree-ring samples for the four (~30 year) inter-annual time-series presented here were taken from two sites near Dunedin, in the South Island of New Zealand [Fig. 6.1]. The sites’ geographical and climatic settings, along with the collection, preparation, processing and analysis of samples are outlined in Chapter 4, with more detailed methodological overview provided in Appendix 8.5 and extra site profiles contained in Appendices 8.6 and 8.7.
6.2.2 Statistical Techniques

Time-series analysed here are the same inter-annual $\delta^{18}O$ series presented in Chapter 4. They were stripped of analytical outliers following the method outlined in Chapter 4. Inter-annual stable-isotope time series were stripped of analytical outliers using a box and whisker probability density estimation method. To facilitate a focus on inter-annual changes rather than low frequency signals, all data were de-trended using linear regression and ‘normalised’ to a common scale of inter-annual variability (as in Chapter 5).

The resulting isotope time-series considered here are a 27 year (1983-2009) whole ring record from DK (WR) based on 18 cores from 7 trees, a matching (same cores) 28 year (1983-2010) early-season wood (ESW) $\delta^{18}O$ series and a 28-year (1983-2010) record of WR $\delta^{18}O$ from MtC (8 trees, 21 cores). While a sub-set of 3 MtC trees (6 cores) were also analysed for ESW $\delta^{18}O$ over the same time period, the sample depth was determined insufficient for reliable palaeoclimate reconstruction based on the low EPS score of 0.37 (Chapter 4). The MtC WR and DK ESW $\delta^{18}O$ time series have EPS scores of 0.81 and 0.85 respectively and while DK WR $\delta^{18}O$ has a lower EPS (0.71) it is also included here due to its strong correlation with both DK ESW ($r = 0.60$, $p < 0.01$) and MtC WR $\delta^{18}O$ ($r = 0.64$, $p < 0.01$) (Chapter 4). While an EPS score of 0.85 is the benchmark for chronology quality (Briffa and Jones, 1990; McCarroll and Loader, 2004), records that do not meet this arbitrary figure have been used for palaeoclimate reconstruction (Porter et al., 2013).

Climate response functions were initially developed using a (Pearson’s product moment) linear correlation matrix comparing $\delta^{18}O$ values with monthly climate data spanning the growth season corresponding to ring formation (t-0, Austral Spring-Autumn) back to the previous (t-1) Austral Spring. ‘T-1’ was included to account for the potential of isotope signatures relying on photosynthates stored from the previous growth season and other environmental lags such as groundwater processes. Where consecutive months showed correlations of the same sign, the commonly applied approach of pooling months (Robertson et al., 1997; McCarroll and Pawellek, 2001; Robertson et al., 2001; Porter et al., 2013) to investigate idealised ‘seasonal’ relationships was adopted. Monthly weather data were retrieved from the Virtual Climate Station Network (VCSN; NIWA, 2011), as many of the weather stations around Dunedin were (de)commissioned during the period covered by the isotope time-series. The VCSN is an interpolated climate surface based on a thin plate smoothing spline, with a resolution of 5x5km (Tait et al., 2006). The gridded daily dataset is aggregated into monthly values which are used here. Initially two stations (14055 and 19867) were used but all isotope time-series showed stronger correlations to agent 19867, so analysis proceeded with 19867 (Network number P092036, 45.825°S, 170.575°E).

The isotope records from DK and MtC are too short to facilitate separate calibration and verification assessment of climatic relationships, so bootstrapped correlations were applied to monthly and pooled relationships to obtain a more rigorous measure of correlation strength than the initial linear climate-isotope correlations, as suggested by McCarroll and Pawellek (2001). The bootstrapped correlations (with 1000 repetitions) were acquired using the DENDROCLIM 2002 software package (Biondi and Waikul, 2004). Significance is assigned at the $p < 0.05$ level. The strongest bootstrapped correlations were
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Fig. 6.1: Map of New Zealand broken into Kidson’s (2000) climate regions with ENSO and MZ3 circulation features represented. The magnified Dunedin shaded Digital Elevation Model study area and climograph compiled from NIWA’s virtual climate station network show the geographical and local climatic context for DK and MtC sites.
used to select which climate variables to include in subsequent multiple linear regression. The multiple regression, conducted using the PAST software package (version 2.17; Hammer et al., 2001), indicates whether, in the absence of a single dominant variable, multiple climate variables can be compiled to better explain inter-annual $\delta^{18}O$ changes. Multiple regression results are reported using the adjusted r-squared statistic, which accounts for the number of variables included in the model, to guard against over-fitting (McClave and Sincich, 2003).

6.3 Results

6.3.1 Isotope-climate correlations

6.3.1.1 Mean Relative Humidity

Average monthly relative humidity is significantly correlated with all $\delta^{18}O$ time series. For DK and MtC WR records, the strongest single month correlations are for May (t-1) ($r = -0.50$ for MtC [Fig. 6.2], $p < 0.05$) ($r = -0.71$ for DK [Fig. 6.3], $p < 0.05$). The (t-1) correlation remains significant ($r = 0.58$, $p < 0.01$) for DK WR $\delta^{18}O$ if the months of March-June (t-1) are pooled. There is also a significant correlation ($r = 0.39$, $p < 0.05$) between MtC WR $\delta^{18}O$ and relative humidity for the pooled months of October-January (t-0). For DK ESW, t-1 correlations are significant ($p < 0.05$) but weaker than for WR time-series, the strongest being pooled May-June ($r = -0.46$) [Fig. 6.4]. Current growth season correlations are, however, stronger: October ($r = -0.56$, $p < 0.01$) and December ($r = -0.32$, $p < 0.05$) are significantly correlated with $\delta^{18}O$ in their own right and contribute to a significant correlation for the pooled months of September-December ($r = -0.47$, $p < 0.05$).

6.3.1.2 Mean Monthly Temperature

$\delta^{18}O$ from DK and MtC were only weakly correlated with temperature, regardless of month/season. For MtC WR [Fig. 6.2] there are weak but significant ($p < 0.05$, bootstrapped) correlations between $\delta^{18}O$ and October and July (t-1, positive) and April temperature (t-0, negative). Correlations are not improved by grouping multiple months. DK WR $\delta^{18}O$, however, has a significant ($r = 0.44$, $p < 0.05$) positive correlation with pooled May-July (t-1) temperature, as well as with May and January (t-1) temperatures individually [Fig. 6.3]. DK ESW $\delta^{18}O$ is significantly ($p < 0.05$) positively correlated with October, January, June and July (t-1) temperatures but its strongest correlation is with pooled June-July (t-1) temperature ($r = 0.51$) [Fig. 6.4].

6.3.1.3 Monthly Accumulated Rainfall

As with temperature, rainfall at MtC shows both positive (January t-1, January-February t-1) and negative (June t-1, November t-0, February t-0, September-November t-0) significant ($p < 0.05$) correlations with $\delta^{18}O$ [Fig. 6.2]. The strongest relationship is for the pooled September-November rainfall ($r = -0.49$). DK
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WR δ^{18}O has only one significant monthly correlation with rainfall (November t-0, $r = -0.34$, $p < 0.05$) but when rainfall from April (t-1) to November (t-0) are pooled, the correlation is -0.53 (Fig. 6.3). DK ESW δ^{18}O follows a similar pattern, with weak but significant negative correlations for the single months of April (t-1) and December (t-0), in contrast to stronger correlations for the pooled months of April-June (t-1, $r = -0.59$), September-December (t-0, $r = -0.52$) and April (t-1) to December (t-0), $r = 0.70$ (Fig. 6.4).

6.3.1.4 Mean Soil Moisture Deficit

Soil moisture deficit (SMD) correlations with δ^{18}O are consistently negative from May (t-1) onwards for all time-series. It is important to note that this variable is measured as a deficit so a negative correlation reflects increasing δ^{18}O with increased deficit (i.e. drier soil = more positive δ^{18}O). For all time-series the strongest single month correlation between δ^{18}O and SMD is for July (t-1), ranging from $r = -0.47$ for MtC WR to $r = -0.58$ for DK ESW. MtC δ^{18}O is also significantly negatively correlated with SMD for the months of November, December, February and March (t-0). June (t-1) is the only other significant single month correlate for DK WR while June (t-1), November and December (t-0) are significant for DK ESW. Pooling multiple months produces significant negative correlations with δ^{18}O for all time-series. Both MtC WR (Fig. 6.2) and DK ESW (Fig. 6.4) have two groups of months that can be pooled separately to produce significant correlations. For DK ESW those two periods can also be joined to create a June (t-1) to January (t-0) correlation of -0.60. For DK WR the only significant pooled SMD correlation with δ^{18}O is compiled from the individually significant months of June and July (t-1) (Fig. 6.3).

6.3.1.5 MZ3 Trenberth Index

MtC and DK WR δ^{18}O both have significant negative correlations with the MZ3 index in August (t-1) and weaker but significant positive correlations in April (t-1). DK ESW has one positive significant correlation with MZ3 in current season December. Unlike previous climate variables, which generally have a consistent direction to their correlations (i.e. maintaining a negative or positive sign for consecutive months) the correlations between MZ3 and δ^{18}O, while occasionally strong, are highly variable in direction.

6.3.1.6 Southern Oscillation Index

The only significant correlations between δ^{18}O and the SOI are weak positive relationships for MtC WR in May (t-0) and October (t-1). Generally correlations between monthly SOI and δ^{18}O are very weak ($r < 0.20$) and variable in direction for all time-series.
Fig. 6.2: MtCWR δ¹⁸O bootstrapped correlations with monthly climate for current growth season to the beginning for the prior year’s (September (t-1)) growth season. Correlations marked * are significant (p < 0.05) according to the bootstrapped correlation with 1000 repetitions. Months grouped with a black line and r-value indicate the strength the correlation between δ¹⁸O and the composite signal of those months. All composite correlations are significant at the p < 0.05 level based on bootstrapped correlation with 1000 repetitions. n = 27. Black and red dashed lines indicate the p < 0.05 and p < 0.01 levels of significance for linear correlation. While they cannot be directly translated to a bootstrapped significance, they nonetheless provide a good approximation of correlation significance.
Fig. 6.3: DK ESW $\delta^{18}$O bootstrapped correlations with monthly climate for current growth season to the beginning for the prior year’s (September (t-1)) growth season. Correlations marked * are significant ($p < 0.05$) according to the bootstrapped correlation with 1000 repetitions. Months grouped with a black line and $r$–value indicate the strength the correlation between $\delta^{18}$O and the composite signal of those months. All composite correlations are significant at the $p < 0.05$ level based on bootstrapped correlation with 1000 repetitions. $n = 28$. Black and red dashed lines indicate the $p < 0.05$ and $p < 0.01$ levels of significance for linear correlation. While they cannot be directly translated to a bootstrapped significance, they nonetheless provide a good approximation of correlation significance.
Fig. 6.4: DK WR $\delta^{18}$O bootstrapped correlations with monthly climate for current growth season to the beginning for the prior year’s (September (t-1)) growth season. Correlations marked * are significant ($p < 0.05$) according to the bootstrapped correlation with 1000 repetitions. Months grouped with a black line and $r$-value indicate the strength the correlation between $\delta^{18}$O and the composite signal of those months. All composite correlations are significant at the $p < 0.05$ level based on bootstrapped correlation with 1000 repetitions. $n = 28$. Black and red dashed lines indicate the $p < 0.05$ and $p < 0.01$ levels of significance for linear correlation. While they cannot be directly translated to a bootstrapped significance, they nonetheless provide a good approximation of correlation significance.
6.3.2 Summary of Climate Correlations and Multiple Regression Analysis

Relative humidity, soil moisture deficit and accumulated monthly rainfall are considered most useful for further investigation/discussion as they all show consistently negative moderate to strong ($r \geq \pm0.4$) and significant ($p < 0.05$) correlations across multiple months with $\delta^{18}O$ time-series from both DK and MtC. In addition, correlations for those variables exhibit a similar pattern across time-series, with the generally negative correlations from May (t-1) to February (t-0) accentuated by two ‘peaks’ in $r$– values, centred around late Autumn/early Winter and late Spring/early Summer. This general negative correlation and the distinct peaks are both accounted for below, with a series of multiple regression models incorporating the strongest monthly and/or pooled relationships for each time-series. Another set of models covers the generally negative period of correlations for all time-series (~April (t-1) to December (t-0)). Results are summarised in Table 6.1.

Optimised multiple regressions, using the strongest single and pooled month correlations for each variable are all highly ($p < 0.01$) significant: the combination of rainfall (September-November, (t-0)), relative humidity (May (t-1)) and SMD (July (t-1)) for MtC WR $\delta^{18}O$ explains 43% of inter-annual $\delta^{18}O$ changes, compared to the maximum of 25% explained by any of those variables separately. The most successful multiple regression for the DK WR time-series incorporates the same relative humidity and SMD months but a longer set of pooled months of accumulated rainfall (April (t-1) to November (t-0)). That model explains 58% of $\delta^{18}O$ variability over the 1983-2010 time period, a ~9% improvement on the best single $\delta^{18}O$ correlate, May (t-1) relative humidity. Multiple regression shows smaller improvements for DK ESW, which generally has stronger pooled correlations for each climate variable than MtC and DK WR. The combination of rainfall (April (t-1) to December (t-0)), relative humidity (October (t-0)) and soil moisture deficit (June-August (t-1)) explains only slightly more $\delta^{18}O$ variability (51%) than the relationship with rainfall alone (49%) (Table 6.1).

In contrast, DK ESW is the strongest record if the generally negative correlations from the April (t-1) to December (t-0) are pooled for all three variables to create a seasonal composite. The DK ESW multiple regression model for that time period is highly significant ($p = 0.0004$) and explains 47% of variability within the $\delta^{18}O$ time-series. In contrast, the relationships between DK WR $\delta^{18}O$ and MtC $\delta^{18}O$ and relative humidity, rainfall and SMD across the same time period are not significant ($p > 0.05$, Table 6.1), suggesting their use is restricted to the more specific temporal periods of their strongest individual correlations.
6.4 Discussion

6.4.1 Major Drivers of Kauri and Cedar δ¹⁸O

Despite the differences between the three δ¹⁸O time series presented here (ESW and WR, two different species, separate sites), they are strongly correlated [Fig. 6.5a] and there are numerous similarities in the responses of the δ¹⁸O time-series to observed climate. This is qualitatively apparent from the similarities in the direction, strength and timing of monthly climate correlations between δ¹⁸O and hydroclimatic indicators: relative humidity, SMD and rainfall (Fig. 6.2-6.4). The similarities are quantitatively substantiated by the time-series’ uniformly significant relationships with multiple regression models incorporating those same hydroclimate variables (Table 6.1), suggesting a strong regional climate forcing.

Table 6.1: Multiple regression models for MtC WR, DK WR and DK ESW δ¹⁸O incorporating relative humidity, soil moisture deficit and rainfall amount. The first series of models is based on a combination of the strongest individual or pooled correlations between the δ¹⁸O time-series and each climate variable (Fig. 6.2, Fig. 6.3, Fig. 6.4). The second series applies a uniform April-December pooled signal for each climate variable.

<table>
<thead>
<tr>
<th>δ¹⁸O Time-series</th>
<th>Rainfall Months</th>
<th>Relative Humidity Months</th>
<th>SMD Months</th>
<th>Multiple r</th>
<th>Multiple R²</th>
<th>Adjusted R²</th>
<th>N</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>MtC WR</td>
<td>Sep - Nov</td>
<td>May (t-1)</td>
<td>July (t-1)</td>
<td>0.70</td>
<td>0.49</td>
<td>0.43</td>
<td>28</td>
<td>7.75</td>
<td>0.0009</td>
</tr>
<tr>
<td>DK WR</td>
<td>Apr (t-1) –</td>
<td>May (t-1)</td>
<td>July (t-1)</td>
<td>0.79</td>
<td>0.63</td>
<td>0.58</td>
<td>27</td>
<td>12.96</td>
<td>0.00004</td>
</tr>
<tr>
<td>DK ESW</td>
<td>Dec (t-0)</td>
<td>Oct (t-0)</td>
<td>Jun – Aug</td>
<td>0.75</td>
<td>0.57</td>
<td>0.51</td>
<td>28</td>
<td>10.4</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

A consistent challenge in establishing stable isotope dendroclimatological proxies is finding isotope records that have a sufficiently strong relationship with a single climate variable to facilitate robust palaeoclimate reconstruction (McCarroll and Pawellek, 2001). This is particularly the case when a single isotope is used, as in this study, rather than a multi-proxy approach (McCarroll and Pawellek, 2001; McCarroll and Loader, 2004). This challenge led McCarroll and Pawellek (2001) to suggest that isotope-climate correlations should achieve $r = ±0.70$ (explaining ~50% of observed variability) for robust climate reconstruction. Based on that criterion, both DK WR and DK ESW exhibit climate responses viable for stand-alone palaeoclimatic reconstruction. The bootstrapped correlation between May (t-1) relative humidity and DK WR δ¹⁸O alone explains 49% ($r = -0.71$) of inter-annual isotopic variability [Fig. 6.5b].
Similarly, pooled rainfall amount for April (t-1) to December (t-0) explains 49% of the variability in the DK ESW δ¹⁸O time-series (Fig. 6.5c). In contrast, MtC, despite the stronger common variance (higher EPS) of its WR δ¹⁸O time series compared to DK WR, appears to record a less pronounced climatic signal, falling short of $r = \pm 0.70$ for any single climate variable.

**Fig. 6.5:** Comparison of δ¹⁸O time-series with each-other (a) and the single climate variables that reached the $r = 0.70$ criterion for climate reconstruction for their respective time series; b) DK WR δ¹⁸O and May (t-1) relative humidity; c) DK ESW δ¹⁸O and April (t-1) – December (t-0) rainfall amount. Error bars are the Root-Mean-Square error of the composite δ¹⁸O time-series.
Despite MtC WR’s limitations as a stand-alone record of single climate variables, however, it provides valuable reinforcement of the otherwise stand-alone May (t-1) relative humidity-δ\(^{18}\)O correlation observed for DK WR. Relative humidity is commonly regarded as a primary candidate for tree-ring cellulose δ\(^{18}\)O reconstruction (McCarroll and Loader, 2004) as it is the major climatic regulator of internal (i.e. leaf-water) fractionation processes; low relative humidity leads to increased evaporative enrichment of leaf water and subsequently, cellulose (Roden et al., 2000; Barbour et al., 2004; Sternberg, 2009), explaining the negative correlations observed here. The common May (t-1) timing of the primary relative humidity correlation for both MtC and DK WR suggests that there is a prior autumn leaf-water signal incorporated within current season α-cellulose. Chapter 5 suggests that it is likely that stored photosynthates contribute to current season growth in kauri. A scenario where May (t-1) relative humidity determined the δ\(^{18}\)O of photosynthates that were then stored and remobilised for current-season growth seems the most likely explanation of the relationship observed here. The exception to this pattern is DK ESW δ\(^{18}\)O, which has a significant correlation with May (t-1) relative humidity, but has stronger correlations in the current growth season (September-December). The differences in timing of the strongest correlations between relative humidity and ESW and WR may reflect changes in the reliance on stored photosynthe through the growth season. The storage of carbohydrates is a well observed phenomenon (Kramer and Kozlowski, 1979; Wilson, 1984; Barbour et al., 2002; Kuptz et al., 2011), and is one of the key reasons that dendroclimatic studies include climate data from a year (t-1) or more before growth. The spring-focussed remobilisation of photosynthate means that a lagged correlation between climate and inter-annual isotope data is proposed here, whereas such lags over an entire growth season were rejected as a reasonable explanation for seasonal changes in high resolution data (Chapter 5).

Unlike relative humidity, soil moisture deficit is not explicitly linked to internal fractionation processes. Its relationship to tree-ring δ\(^{18}\)O is likely to be based on a combination of evaporative fractionation of soil water prior to uptake and, potentially, influence on leaf-water fractionation due to the physiological impact of water stress. Soil moisture deficit provides an indication of the local hydrologic balance and therefore, the level of evaporative enrichment that water might experience after rainfall, interception and percolation of source water into shallow aquifers and infiltration into soil root zones. The correlations shown in Figs. 6.2-6.4 suggest that greater soil moisture deficit in winter, particularly in July (t-1), leads to more positive δ\(^{18}\)O in tree-ring cellulose. The positive co-variance makes sense, as the greater evaporation/limited water availability implicit in high SMD means the remaining water is relatively enriched in the heavier H\(_2\)\(^{18}\)O molecule (McCarroll and Loader, 2004). The timing of the correlation is most likely explained by a lag between the evaporative enrichment of the water and its use by the tree; kauri and cedar are unlikely to be actively growing during mid-winter but water subject to evaporation in July could well be used by trees during their growth season (commencing 2-3 months later), as observed by Robertson et al. (2001) in English oak. The continued significant correlations between δ\(^{18}\)O and SMD into Spring and early Summer (Figs. 6.2-6.4) may indicate continued reliance on evaporatively enriched water during Summer/Autumn late-wood formation. Alternatively, at this time SMD may also begin to exert influence on current season leaf-water fractionation; greater SMD is likely to prompt a physiological response from trees, closing their stomata and decreasing stomatal conductance in response to moisture
stress. Lower stomatal conductance increases leaf temperature and the ratio of ambient to intercellular water vapour, both of which lead to increased fractionation of leaf water (Roden et al., 2000; Barbour, 2007). The addition of growth season physiological regulation to evaporative enrichment of soil water in previous months would help explain the two peaks evident in SMD correlations.

Of the three primary climate correlates for δ\(^{18}\)O, rainfall amount is the most independent of leaf-water processes, providing the ‘source water’ upon which cellulose δ\(^{18}\)O is ultimately based. DK ESW and WR δ\(^{18}\)O both show significant correlations with rainfall over extended periods (8-9 months) stretching from prior Autumn to current Spring/Summer, while MtC WR is restricted to current Spring growth. All those correlations are negative, suggesting that lower than normal rainfall prior to, and during, the growth season results in more positive cellulose δ\(^{18}\)O. There are multiple potential explanations for this relationship: 1) an isotopic ‘amount effect’ resulting in higher δ\(^{18}\)O during years with less frequent, smaller rainfall events; 2) increased SMD and/or lower humidity coincident with low rainfall in dry years; or 3) circulation patterns that combine low rainfall with precipitation from an \(^{18}\)O enriched source; or 4), potentially related to 3, a seasonal pattern to precipitation δ\(^{18}\)O such that greater rainfall across a certain period consistently results in higher/lower δ\(^{18}\)O. While there is significant precedent for the ‘amount effect’ (Dansgaard, 1964; Rozanski et al., 1993; Lachniet and Patterson, 2009; Scholl et al., 2009) explaining changes in tree-ring δ\(^{18}\)O (Evans and Schrag, 2004; Brienen et al., 2012; Brienen et al., accepted) it is generally considered a tropical phenomenon. The alternative explanations for negative correlations between δ\(^{18}\)O and rainfall amount also have flaws. First, while rainfall amount is an important component of SMD and relative humidity, and some autocorrelation is to be expected, rainfall correlations observed here are not uniformly coincident with SMD or relative humidity, indicating that rainfall amount is important in its own right. This is substantiated by its improvement of multiple regression models using the adjusted-\(r^2\) statistic, which would decrease due to ‘over-fitting’ of the model if rainfall did not explain additional δ\(^{18}\)O variability. Second, a source-water effect related to inter-annual circulation changes seems unlikely given the lack of any strong or persistent correlations between cellulose δ\(^{18}\)O and the two circulation indices included in correlation analysis. A consistent seasonal bias towards high/low δ\(^{18}\)O may still explain the strong negative correlation with rainfall amount across a number of months. Unfortunately, the limited temporal and spatial resolution of precipitation δ\(^{18}\)O records in New Zealand (Taylor, 1990; IAEA/WMO, 2013) makes robust reconstruction of source water trends problematic.

In the absence of a strong correlation to a circulation pattern that might explain the multiple, similarly significant climate correlations for each δ\(^{18}\)O time-series, the utility of the time-series for climate reconstruction is limited; the relative influence of each variable on δ\(^{18}\)O is not possible to extrapolate beyond the period of observed climatic record. However, in this case, relative humidity, rainfall and soil moisture are inter-related climate variables that all describe hydroclimate at monthly to seasonal scales. While the strength of correlations between δ\(^{18}\)O and these variables changes from month-to-month and between time-series, ultimately all three time-series suggest that dry conditions between approximately May (t-1) and December (t-0) result in higher δ\(^{18}\)O. DK ESW δ\(^{18}\)O is particularly strong in this regard,
with a consistent negative correlation to all variables across the entire period. The result is consistent with a scenario in which low rainfall amount leads to more positive precipitation δ¹⁸O, a signal which is then enhanced by evaporative enrichment of soil water prior to its uptake by the tree and, finally, by increased evaporative fractionation of leaf-water, driven by a combination low relative humidity and low stomatal conductance due to moisture stress. Similar relationships between tree-ring δ¹⁸O and hydroclimate have been demonstrated in numerous locations (Robertson et al., 2001; Nakatsuka et al., 2004; Treydte et al., 2006; Rinne et al., 2013), providing ample precedent to support the findings of this study that δ¹⁸O in long-lived New Zealand conifers may be used as an effective proxy for late-Autumn (t-1) through early-Summer (t-0) hydroclimate for the East Coast of the South Island. Further studies of kauri from their current natural range and cedar across New Zealand, as well as detailed monitoring of the oxygen isotope composition of meteoric waters and meteoric-derived soil and plant waters, are crucial to determining whether the record of hydroclimate presented here can be extended across pre-historic intervals.

6.4.2 Limitations of the observed relationships

While the data presented here suggest potential for hydroclimatic reconstruction using kauri and/or cedar in New Zealand, there are a number of limitations that need further experimental exploration before these relationships can be applied to long time-series:

1) Plantation trees: for kauri, similar preliminary studies need to be conducted on trees growing in natural stands within the species’ natural range. While the trees studied here had minimal silvicultural intervention, their growth in a plantation setting was free of a number of the competing factors (shade, nutrient and water availability) that may play an enhanced role in a natural stand. Similarly, the limiting climatic factors observed for the DK plantation may differ from those in the species’ warmer, wetter natural range.

2) Juvenile trees: for kauri, it is equally important that similar investigations occur on mature trees. Only by coring to the juvenile rings of mature trees and analysing full time-series will any juvenile effects associated with δ¹⁸O (and δ¹³C) be evident. While there is limited evidence for systematic δ¹⁸O juvenile effects, there is some suggestion that stronger common signals are retrieved in δ¹⁸O records from mature trees (Treydte et al., 2006; Loader personal communication).

3) Series length: For both species, it is important to assess the stability of δ¹⁸O-climate relationships over longer time-periods. Records covering a minimum of 60-100 years, facilitating independent calibration and verification of climate correlations are required before the preliminary results presented here can be used for pre-historic reconstruction purposes.

6.5 Conclusion

This research documents new insights into the potential application of conifer tree-ring δ¹⁸O to questions
regarding palaeoclimate conditions in the mid-latitude Southern Hemisphere. First, δ¹⁸O records from nearby stands of New Zealand kauri and cedar are significantly correlated with each-other and with the same climate variables (relative humidity, soil moisture deficit and rainfall amount), suggesting potential for the use of multiple species to improve spatial coverage of stable isotope dendroclimatic reconstructions. Second, while the timing and strength of correlations between observed δ¹⁸O and the above climate variables changes between species and between early-season wood and whole-ring analyses, all correlations are ultimately tied to regional hydroclimate between the previous (t-1) Autumn through the current growth (t-0) Summer. Conifer tree-ring δ¹⁸O is shown to be a promising tool for regional hydroclimatic reconstruction. In New Zealand, where there is a dearth of high-resolution records of prehistoric rainfall and many catchments are currently considered to be fully or over-allocated for irrigation, further exploration of this tool has potential to provide palaeoenvironmental information critical to the long-term sustainability of the agriculturally-based economy.
7. RESEARCH SYNTHESIS

This thesis aimed to establish a framework from which future studies in stable isotope dendroclimatology in New Zealand could be developed. Perhaps the single-most significant contribution of this research is its documentation, and data-based demonstration, of the challenges inherent to dendrochemical climate science. The findings presented in this thesis relate to three key research themes, as outlined in Chapter 1:

1) Methodological refinement;

2) Documenting natural variability and its effect on chronology quality; and

3) Establishing foundation relationships between oxygen isotopes and climate.

The research outcomes achieved under each of these thematic goals are outlined below (7.1), followed by discussion of the still unanswered questions relevant to the research topic (7.2), and finally, an overview of the future potential for stable isotope dendroclimatology in New Zealand (7.3).

7.1 Major Findings

7.1.1 Methodological Refinement

This research ambitiously started with aspirations of swiftly establishing the basis for, and then creating a multi-centennial palaeoclimate record. However, the realities of establishing a research program from scratch soon became apparent; significant processing and analytical groundwork was required before even preliminary modern isotope time-series could be developed. The process began with outfitting a wet chemistry lab to conduct α-cellulose extractions based on the SBrendel method. Ultimately, this seemingly simple task led to the first major isotopic investigation, contained in Chapter 3. Kauri wood samples were often brown/yellow after SBrendel processing, suggesting incomplete removal of whole-wood constituents, most likely resins. Personal communication with Andrew Lorrey revealed that this was a common problem for kauri and further communications with Trevor Porter (working with white spruce (Picea glauca)) and Tom Whittaker (working with Pinus ponderosa), suggested that although the problem was more pronounced in kauri, it was not unique to the species.

Rather than adopt the common approach of reprocessing samples that retained colour, the decision was made to rigorously investigate the efficacy of the SBrendel procedure on a series of resinous species commonly used for dendrochronological investigation. Through a systematic isotopic trial of SBrendel variants on resinous conifers that investigation (Brookman and Whittaker, 2012; Chapter 4) revealed that variations in time, temperature and reagent amount during SBrendel processing could prove the difference between under-processed and fully extracted samples. Kauri proved particularly resistant to processing and retained more resin and lignin than other species, which noticeably lowered $\delta^{18}O$ values. Conversely, some samples may have been over-processed and affected by acetylation, lowering $\delta^{13}C$; this particular
point requires further investigation. In a broad context these results showed the importance of preliminary investigations and quality control of α-cellulose processing to all dendroisotopic investigations, particularly where species new to stable isotope dendroclimatology are the focus.

After streamlining the wet-chemistry extraction method, attention turned to achieving maximum analytical efficiency. Given that this research sought to provide the foundation for both carbon and oxygen dendrochemical investigation in New Zealand, the potential for retrieving both determinations from a single analysis provided a number of significant benefits: 1) a >50% reduction in analytical time, 2) greatly reduced analytical consumable costs, and 3) a halving of the required sample size, meaning narrow rings could be analysed for both isotopes rather than choosing between one analysis or the other. The last aspect could prove crucial for narrow-ringed sub-fossil kauri, from which limited material is available. Experimentation with dual-element low-temperature pyrolysis (Chapter 5 and Appendices 8.7 and 8.8) showed that the UC system could replicate the precision of separate high-temperature pyrolysis for δ¹⁸O and combustion for δ¹³C. The adoption of such methodological advances greatly reduces the temporal and financial pressures of stable isotope dendroclimatology.

7.1.2 Documenting and Interpreting Natural Variability

The fundamental basis of this thesis was to establish the isotopic ‘qualities’ of New Zealand kauri and cedar for the generation of long-term climate records. Their potential was first addressed by assessing the level of common variability within and between trees. Results show that isotopes in both cedar and kauri vary as much, if not more, within single trees as between trees, contrary to most published studies. Few studies have documented the level of intra-tree variability showed here and even inter-tree variability was at the upper end of the scale reported in the literature. The significant variability meant that kauri and cedar isotope records required greater sample depth than many other published studies to achieve an EPS score >0.85, the widely adapted benchmark of chronology quality. Consequently, primary sampling for future studies is recommended to include 10-15 trees to provide ample cross-dated material (~7-10 trees) for isotopic analysis to account for the intra and inter-tree variability observed in both kauri and cedar. While preliminary analysis of multiple (2-3) cores per tree is advisable to characterise variability, the bulk of analyses could be conducted on pooled radial samples to reduce the number of analyses required. These recommendations come with multiple caveats:

1) For kauri, the data presented here were taken from juvenile plantation trees. As such the sample depth required here may differ from mature trees in natural stands; juvenile trees are often subject to a ‘juvenile effect’ which imparts a significant δ¹³C trend, and may influence δ¹⁸O such that correlations with climate are reduced.

2) For cedar, no quantitative investigation of the purity of the cellulose produced was undertaken. Incomplete and inconsistent processing may contribute to intra and inter-tree variability and further study is required prior to the generation of long time-series to determine whether the low EPS results observed here may be an artefact of the processing methodology.
3) For both species, the particular variant of the SBrendel method may influence the purity of cellulose being analysed. Low temperature variants may not remove all lignin and/or resin while products from both low temperature and high temperature methods need to be carefully scrutinised for acetylation of cellulose, the most likely cause of a ‘pasty’ consistency which affects δ¹³C. Even in cases where the pasty consistency is not evident, the formation of cellulose acetate may result in depleted δ¹³C values.

Generally δ¹⁸O records achieved higher EPS scores than δ¹³C, most likely reflecting stronger regional climate forcing compared to the micro-climatic and physiological factors that contribute to δ¹³C records. Despite the relatively low EPS scores, however, a number of the time-series from DK and MtC were significantly correlated, suggesting that common regional climatic signals were present. Before pursuing the promising climatic relationships, however, intra-tree variability was further investigated to assess whether intra-annual natural variability and/or sub-annual sampling strategies may be contributing to poor intra and inter-tree reproducibility. The comparison of sequential samples from wide DK growth rings were compared with similar high resolution data from kauri within their natural range (Lower Huia) provided a number of key findings in terms of sampling strategies:

1) δ¹³C and δ¹⁸O have consistent annual cycles at the DK site that are well described by sinusoid models.

2) Kauri early-season wood generally has more positive δ¹³C and δ¹⁸O than late-wood, explaining the consistent δ¹³C and δ¹⁸O offset between early-season and corresponding whole-ring samples for DK.

3) The consistency of the intra-annual cycles observed in kauri and the strong correlations between ESW and WR samples suggest that any climatic phenomena influencing δ¹³C and δ¹⁸O at high frequencies have a relatively minor effect compared with the amplitude of the seasonal cycle. Sampling approximately 50% of a ring for ESW consistently retrieves the most enriched portion of the annual cycle and small operator errors in sampling position have little effect in the context of a composite isotope time-series.

4) Application of kauri growth models based on dendrometer-band measurements suggests that sub-weekly resolution was obtained from fast-growing kauri ‘rickers’. However, detailed physiological study, perhaps using non-natural abundance isotopes, is required to determine cell lifetimes in kauri and substantiate whether the integration of climate signals can occur over such short time-periods.

Comparison of DK high-resolution data with observed climate data shows that annual isotopic patterns are not well explained by climate:

1) The most significant contemporaneous climate correlations with growth-modelled kauri δ¹³C and
δ¹⁸O time series are with relative humidity. However, the correlations are weak, explaining little of the consistent annual isotopic cycles documented.

2) Numerous climate variables correlate well with intra-annual isotope time-series when 7-10 month lags are applied but there is insufficient environmental or physiological basis to justify the lags involved.

3) For δ¹⁸O, mechanistic modelling of the expected climate-driven isotope cycle for DK produced similarly poor contemporaneous correlations with observed data.

4) The annual cycle for δ¹³C is similar to that observed in numerous, mainly deciduous, trees from various locations, generally ascribed to annual physiological cycles. The same pattern has been postulated for δ¹⁸O, as its basis is the spring use of stored photosynthates/carbohydrates, which contain both carbon and oxygen fixed during the previous summer.

5) While both δ¹³C and δ¹⁸O follow regular patterns at DK, δ¹⁸O shows considerably more variability in the amplitude of cycles between years and larger departures from the modelled cycle within any given year. These results suggest that δ¹⁸O is more responsive to high frequency climatic changes.

7.1.3 Foundation Relationships Between Oxygen Isotopes and Climate

The higher EPS scores for δ¹⁸O time-series, and greater inter-annual variability observed during high-resolution investigation, prompted oxygen’s selection for pursuing inter-annual climate correlations. The strong and significant correlations between DK and MtC δ¹⁸O time-series, despite significant microclimatic differences, suggest that the two species may be recording a similar regional signal.

Both DK and MtC whole-ring δ¹⁸O correlate significantly with local relative humidity, soil moisture deficit and accumulated monthly rainfall. All three variables are linked to local hydroclimate, but contribute to oxygen isotope fractionation at different stages prior to creation of tree-ring cellulose. First, correlations with accumulated rainfall prior to and during the growth season suggest that rainfall amount affects the δ¹⁸O of water available to the tree, although the mechanism behind this relationship is, at present, unclear. Similarly, correlations with soil moisture deficit prior to the growth season may reflect pre-uptake fractionation through evaporative fractionation of soil water, which is then utilised by the tree as groundwater months later. A further, current Spring correlation with soil moisture deficit may also indicate a physiological response to moisture stress, resulting in increased fractionation of leaf water. Relative humidity is likely responsible for the final stage of fractionation, as it is the major climatic controller of leaf-water δ¹⁸O. While the relative strength of each correlation varies between time-series, the similarities are marked and suggest potential for regional hydroclimate reconstruction extending from the Autumn/Winter prior to growth, through to the current growth season Summer.
7.2 Research Evolution and Shortcomings

In reaching the above conclusions this research explored a number of unanticipated avenues. The series of changes in research direction that occurred during the course of this research were:

1) Initial progress in processing and analysing α-cellulose was much slower than expected, partially due to highly variable results in α-cellulose extraction from kauri.

2) Due in part to the time constraints introduced by 1), the DK site was elevated from ‘an easily accessible site for preliminary investigation in a marginal climate’, to the primary research site.

3) The idea of creating a latitudinal transect using plantation kauri from Dunedin, Wanganui, New Plymouth and natural kauri from near Auckland was proposed in order to document kauri’s response across different environments and, potentially, document the influence of latitudinal changes in oxygen isotopes in precipitation. Fieldwork was conducted to facilitate this study but poor chronology quality from Wanganui and New Plymouth plantations forced the idea to be abandoned.

4) The goal of maintaining the research’s relevance beyond kauri’s limited natural range evolved to incorporating cedar, a more widespread species. The Mt Cargill site was cored along with a West Coast stand at Camp Creek (Appendix 8.6), to provide a longitudinal comparison but due to chronology quality issues and time constraints, Camp Creek was not investigated.

5) Through a combination of 1-4, the original goal of a multi-centennial climate reconstruction using kauri tree-ring isotopes gradually evolved to focus more on the fundamental questions regarding the quality of the tree-ring isotope record. The result was a number of well replicated short time-series records suitable to contrasting species, and observing seasonal, intra and inter-tree variability.

The evolution of the research noted above has yielded some important findings (outlined in 7.1) for future stable isotope dendroclimatology. However, as well as creating opportunities, changes to the project have resulted in some shortcomings:

1) First and foremost, the time-series described in point 5 above do not provide a record of pre-instrumental climate change due to their short (28-29 year) duration. This period is shorter than ideal for establishing significant climate-isotope correlations, as it does not allow separate calibration-verification periods. While bootstrapped correlations were used to counter this, ultimately longer time-series are required to establish links between climate and kauri and cedar isotopes. A corollary of the short time-series is that the original goal of creating a palaeoclimate reconstruction was not achieved. A number of potentially interesting research avenues into decadal and longer scale climatic climate cycles (e.g. IPO and longer term trends in ENSO and SAM) were consequently unable to be investigated.
2) The research lacks latitudinal or longitudinal transects. The latter is arguably more important in the context of the South Island’s axial division by the Southern Alps. Concurrent records from east and west of the divide could provide insight into the contrasting effects and timing of ENSO teleconnections for those regions, as well as changes in westerly circulation and associated circulatory regimes such as the IPO and SAM. More widespread sites would also facilitate the assessment of spatial stability of isotope-climate responses.

3) While targeting kauri growing so far south of their natural range arguably increased their climatic sensitivity and facilitated comparison with an established cedar stand, it limited the utility of kauri isotope results for future palaeoclimate reconstruction using Holocene or ancient kauri. Similar investigations still need to be conducted in kauri’s natural range before long kauri isotope chronologies can be constructed. Collaborators are undertaking this work with promising preliminary results. The use of the DK kauri also introduced two complicating factors to the results presented: tree-age and stand dynamics. Ultimately, the possibility for isotopic juvenile effects, discussed at various points throughout the thesis, means that similar preliminary studies of mature kauri are required before the relationships demonstrated here can be broadly applied. Similarly, trees from natural stands may show different long-term isotopic trends, particularly related to the transition from juvenile to adult trees, from the plantation trees analysed here.

7.3 Future Directions for Stable Isotope Dendroclimatology in New Zealand

It is important to accept that the above shortcomings can also be viewed as opportunities for future researchers, as can the questions raised by a number of the results presented. Some of the key future research areas are outlined below:

7.3.1 Methodological refinement

The sampling and processing methods used for this research were not at the cutting edge of stable isotope dendroclimatology; the preference for simple, well established methods was required due to the UC laboratory being set up from scratch and limited expertise being locally available. More advanced sampling techniques such as UV–laser microscopic dissection (Schollaen et al., 2014) or the use of microtomes (Helle and Schleser, 2004) could provide higher resolution intra-annual records. Alternate processing methods such as the Jayme Wise (Green, 1963; Loader et al., 1997) or Modified Brendel (Gaudinski et al., 2005) might also reduce the isotopic variability shown in this research, as could a move to analysis of particular moieties of cellulose glucose oxygen, by isolating phenylglucosazone (Ellsworth et al., 2013).

7.3.2 The relative influences of physiology and climate

A crucial problem arising from this research is the lack of information on cedar and kauri physiology
with respect to the intra- and inter-annual isotopic cycles. The same could likely be said for the numerous other New Zealand native tree species likely to be used for stable isotope dendrochronology. Improved knowledge of the photosynthate usage and storage processes in those species would increase confidence in climate reconstruction based on previous growth season climatic conditions, or interpretation of intra-annual data. This could be achieved through non-natural abundance pulse labelling using highly enriched $^{13}\text{CO}_2$ for $\delta^{13}\text{C}$ (as demonstrated by Kagawa et al., 2005; Kagawa et al., 2006b; 2006a) or evaporatively enriched water for $\delta^{18}\text{O}$. Such experiments could track the apportionment of photosynthates preceding cellulose formation. Additional direct measurement and calculation of leaf gas-exchange parameters and internal leaf pathways would facilitate improved mechanistic modelling of kauri and other species. An alternative approach currently pursued by Lorrey et al. (in prep) is assessing the best-fit physiological parameters to observed isotope data using monte-carlo simulations.

7.3.3 Stability of climate-isotope relationships through time

The climatic responses documented here should be expanded to longer records, providing the opportunity for separate calibration and verification periods. Less detailed analysis (i.e. focusing on WR or ESW, not both) and pooling multiple radii prior to analysis would minimise sample numbers for long records. However, future researchers should consider analysing multiple cores from each tree separately for at least a short time-period to gain an indication of the level of intra and inter-tree variability in their record.

7.3.4 Expansion of species/coverage

There is immense scope for geographical expansion of the work presented here, using multiple species. In addition to cedar, silver pine and pink pine provide prospects for long climate reconstructions within the North Island and along the South Island’s West Coast. Cedar and pink pine can be found in pockets to the east of the Main Divide in the South Island, providing potential for longitudinal and latitudinal transects using those species. Dendrochemical reconstruction can be further expanded spatially in the far-north using kauri.

7.3.5 Holocene tree-ring and ancient kauri records

Perhaps most exciting from a palaeoclimate perspective is the potential for further research to provide annually resolved climate records extending into the Holocene and Late-Pleistocene. A number of New Zealand tree-ring chronologies cover the last ~500-1100 years (Cook et al., 2002; Palmer and Xiong, 2004; Boswijk et al., 2006; Cook et al., 2006; Palmer et al., 2006), spanning two periods of recent abrupt climatic change, the Little Ice Age (LIA) and Medieval Climatic Optimum (MCO). These periods represent key ‘targets’ for stable isotope dendroclimatology in New Zealand, particularly using the extensive modern kauri network.

Both the MCO and LIA are more reliably documented in the Northern Hemisphere (Mann et al., 2009; PAGES-2k-Consortium, 2013). This may be due to a decoupling of the hemispheres such that the
Southern Hemisphere did not experience the LIA and MCO to the same degree, or due to the relative sparseness of the Southern Hemisphere palaeoclimate record (Goodwin et al., 2013; PAGES-2k-Consortium, 2013). The MCO is well established as the period from approximately 900-1300 CE in proxy records from the North Atlantic and neighbouring regions (Mann, 2002b), potentially linked to a persistent positive North Atlantic Oscillation mode (Trouet et al., 2009) and/or dominant La Niña conditions (Mann et al., 2009). However, recent research the New Zealand region support this idea, suggests that there were switches between dominant La Niña (Lorrey et al., 2011) and El Niño regimes (Goodwin et al., 2013), with little evidence for a prolonged warming in New Zealand proxy records (Cook et al., 2006; Schaefer et al., 2009; Winkler, 2013).

Following soon after the MCO, the LIA climate period is generally defined as occurring between ~1570-1900 CE in Europe and other areas neighbouring the North Atlantic (Mann, 2002a; Matthews and Briffa, 2005). While the PAGES 2k Consortium (2013) suggest there was no globally synchronous LIA, generally cold conditions were widespread between ~1580-1880 CE, potentially linked to the dominance of the El Niño phase of ENSO (Mann et al., 2009). Synoptic-type reconstructions for New Zealand align with this idea, suggesting that generally cooler conditions for the period were driven by the predominance of southerly and south-westerly flow generated by El Niño and negative SAM (Lorrey et al., 2013). Numerous New Zealand palaeoclimate proxies show general cooling across the LIA (Winkler, 2000; McKinzeey et al., 2004; Winkler, 2004; Cook et al., 2006; Schaefer et al., 2009; Winkler, 2013). However, there is significant disagreement in the timing of maximum glacial advance and the timings of peak glaciation are neither synchronous nor rhythmically asynchronous with Northern Hemisphere records (Schaefer et al., 2009). The combination of high (annual) to low (centennial) frequency signals from tree-ring isotope records could play an important role in understanding such (a)synchronicities in inter-hemispheric climate.

Looking beyond the MCO and LIA, discontinuous portions of the Late-Pleistocene from Oxygen Isotope Stage 3 (OIS3) onwards (~23-60 ka BP) are covered by the ‘Ancient Kauri’ (AK) record (Palmer et al., 2006; Hogg et al., 2007; Turney et al., 2007; Turney et al., 2010). There is a substantial gap between the ‘Holocene Kauri’ (HK) and OIS 3 AK, with limited material dated to the Younger Dryas and Antarctic Cold Reversal periods. Similarly, coverage of the Last Glacial Climate Period is limited to two records from Finlayson Farm (covering ~23.5-25 ka BP) (Turney et al., 2010) and Omaha Flats (~28.5 ka BP) (Palmer et al., 2006). Nonetheless the tantalising prospect of future AK discoveries that improve coverage of these crucial palaeoclimate periods remains. Whether the lack of sub-fossil kauri from cool, dry periods such as the LGCP and ACR is simply a coincidence or a function of environmental changes that may mean those periods are never part of the AK record is still unresolved. It may be that the preservation of kauri in bog environments is specific to periods both warmer and wetter than normal (Lorrey et al., 2008; Lorrey et al., 2009).

7.3.6 Targeted hydroclimate reconstructions

There is a growing recognition that changes in the hydrological cycle will be equally, if not more
important, than changes in temperature in terms of humanity’s ability to adapt to current and future climate change (Treydte et al., 2006). In New Zealand this focus on water resources was reflected in the recent creation of the Land and Water Forum and their acknowledgement that improved understanding of fresh-water resources is crucial (Land-and-Water-Forum, 2010), particularly given the current level of abstraction from sensitive East Coast catchments (Land-and-Water-Forum, 2012). Carbon and oxygen stable isotopes are linked to various hydroclimatic variables and have been used as effective proxies for water availability and drought (see review in section 2.4.2). Integration of dendrochemical research has the potential to generate a multi-proxy record within tree-ring based stream-flow (Gray et al., 2011; Meko et al., 2012; Treeflow, n.d.) and/or drought atlas type (Cook and Krusic, 2004; Cook et al., 2010) databases created for New Zealand, based on the successful models applied in North America and Asia.

All of the above areas for study would contribute to an improvement in the understanding of New Zealand’s hydroclimate, vital for the agriculturally dependent local economy. Many of the research paths described above also have global implications in terms of the potential for high-resolution palaeoclimate records from the Southern Hemisphere to contribute to understanding globally significant circulation patterns and inter-hemispheric teleconnections. The research presented here provides baseline information from which committed scientists can develop projects that target specific components of the highly relevant and promising future of stable isotope dendroclimatology in New Zealand.
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8. APPENDICES

8.1 Other Species With Stable Isotope Dendroclimatology Potential

Pink (Yellow) Pine (*Halocarpus biformis* (Hook.) Quinn, formerly *Dacrydium biforme* and *Podocarpus biformis*):

While not sampled for this research, Pink Pine is reviewed as a potential candidate for future work. Pink pine is a small, slow growing tree found as far north as the Coromandel Range in the North Island (~36° 50’S) to Stewart Island (~47° S) in the extreme South of New Zealand (Salmon, 1996; Fowler et al., 2008b; Wardle, 2011). Within the North Island its distribution is localised and generally restricted to subalpine forest above 900m (Wardle, 2011). Further south it grows from sea level to approximately 1400m altitude. Pink pine generally favours high rainfall areas with rich soils, and adopts two primary forms: a dense rounded shrub in swamp and marsh areas and a slender tree in alpine forests where it can reach 10m high with trunk diameter generally up to 60cm (Salmon, 1996) but up to 1m in extreme cases (Wardle, 2011). Pink pine can grow for in excess of 600 years (Fenwick, 2003) and the rings are slender, averaging just 0.44mm (Fenwick, 2003). The wood is extremely resinous (Fowler et al., 2008b), making it a prime candidate for further investigation of the Brendel α-cellulose extraction method. A potential drawback of pink pine for stable isotope dendrochronology is its tendency to produce wavy ring boundaries (Fenwick, 2003), making sampling for isotopic analysis challenging.

While the focus of this thesis was to not develop Pink Pine chronologies, the potential for multi-species chronologies exists at the Mt Cargill and Camp Creek sites, where pink pine and cedar co-exist. Pink pine may have an important role to play in the future of New Zealand stable isotope dendroclimatology, either in generating stand alone records from the far south of New Zealand or in providing supporting/contrasting records to cedar in their overlapping ranges. Dendrchronology has already shown pink pine to be a climatically sensitive species. Early research showed that pink pine, similar to cedar, was sensitive to warm-season temperature (Xiong et al., 1998) and provided evidence that the warming experienced in New Zealand since 1950 is the most significant for ~500 years (D’Arrigo et al., 1995; D’Arrigo et al., 1998). Both pink pine and cedar have also been used to reconstruct changes in sea-level pressure variability in the Tasman Sea (D’Arrigo et al., 2000). While the genus is endemic to New Zealand it is closely related to *Lagarostrobus* which improves its credentials as an Australasian regional climate reconstruction tool.

Silver Pine/Westland Pine (*Manoao colensoi* (Hook.) Molloy, formerly *Lagarostrobus colensoi* and *Dacrydium colensoi*):

While this study has not engaged in study of silver pine, even in the preliminary field assessment sense as with pink pine, its dendrochronological pedigree makes it worthy of note here. After cedar and pink pine, which are more widely distributed, it is probably the tree with most promise for stable isotope
dendroclimatology. Like pink pine, silver pine can grow as a shrub or a tall, slender canopy species depending on conditions. Also like pink pine, individuals can grow for ~800 years. Its most common form is a 6-12m tall tree with a tapering trunk of 30-60cm DBH, devoid of branches until the crown which is conical in young trees (Wardle, 2011) but becomes more open, irregular and ‘egg-shaped’ with age (Eckenwalder, 2009). Its distribution is patchy, occurring, generally between 350-900m above sea-level, from north (~Kaitaia) to central North Island and then reappearing in Nelson and Westland as far south as Te Anau, from sea-level to ~500m altitude (Wardle, 2011). Silver pine is most successful on poorly drained, boggy terraces in Westland and western Nelson.

Silver pine’s close relationship to huon pine means that it has great potential for trans-Tasman regional climatic reconstruction, as demonstrated by high profile dendrochronological studies (Cook et al., 2002; Cook et al., 2006). The distinction between the two genera is still debated (Farjon, 2010). Like huon pine, silver pine has shown a strong relationship between ring-width and high summer temperature, resulting in multi centennial annual temperature reconstructions (Cook et al., 2002; Cook et al., 2006). Its tendency to grow in boggy conditions and resinous wood mean that long (~1300 year) chronologies can be created using living and sub-fossil specimens (Cook et al., 2006), making it another ideal candidate for reconstructing Late-Holocene environmental changes in New Zealand including the Little Ice Age and Medieval Climate Anomaly periods.
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8.2 Kauri’s Spiritual and Economic History

New Zealand’s forests play a key role in Māori knowledge; they are seen as te waonui-a-Tāne (the great forest of Tāne), the god who separated the earth and sky and brought the world into being (Royal, 2012). Tāne’s domain included the forest and in this context he is referred to as Tāne-mahuta (Royal, 2012), also the name of the largest living kauri in Waipoua state forest between Dargaville and Kaitaia in Northland. Kauri, being large canopy emergents, are seen as embodiments of Tāne, standing erect and holding the sky and earth apart (Boswijk, 2005). This reverence transferred to an anthropomorphically associated large trees, particularly kauri in Northland, with chiefly status, due to the mana (prestige, spiritual value/quality, authority) of the large trees. Great chiefs were often compared with kauri and perhaps this human association contributed to the reluctance to fell large kauri; such trees were seldom felled unless for special purposes such as the building of a large war canoe, done with caution and respectful ceremony befitting an elder (Orwin, 2004).

Kauri wasn’t as utilitarian as many of the smaller species associated with it and it was revered from a spiritual perspective rather than as a provider like tōtara (*Podocarpus totara*), tanekaha (*Phyllocladus thrichomanoides*), manuka (*Leptospermum scoparium*) and miro (*Podocarpus ferrugineus*) which had multiple other medicinal or practical uses and/or provided berries which attracted birds, a vital food source (Orwin, 2004). Kauri gum was more regularly used than the wood; it was a good fire starter, and its bright burning meant it could be used in torches to attract eels and fish or repel insects troubling crops (Best, 1931; Servant, 1973; Orwin, 2004). The gum also had uses in painting canoes (Best, 1925), medicinal remedies (Adams, 1945) and the blue-black soot created by its burning was used in tattooing (Taylor, 1855; Bell, 1890; Colenso, 1892). Kauri’s spiritual importance also prompted its use in the creation of significant carved items such as he kōrere, (the funnels used to feed rangatira (Māori leaders) during the application of moko (facial tattoos)), and waka huia (feather boxes used to store small taonga (significant items)) (Stewart, 2008). Numerous less auspicious kauri tools have also been recovered, including beaters, mauls and weapons (Wallace, 1989).

With the arrival of Europeans, some of the kauri’s spiritual significance was put aside for the practicalities of tribal power struggles. The kauri became an integral part of the trade relationships between Māori and early European traders and settlers. Those relationships were a source of mana and practical power for many far north chiefs (Stewart, 2008).

The earliest exports of kauri for spars may have been in the late 1700’s, by visiting English ships, although most of these spars from the Hauraki region were likely kahikatea (*Dacrycarpus dacrydioides*). Early French and English visits, which identified kauri as an excellent potential timber source, had been unsuccessful, sometimes fatally, in retrieving them. It is possible that in the early 1800’s kauri spars were taken on as extra cargo by sealing and whaling ships resupplying in the Bay of Islands but like the Hauraki spars before them, most are likely to have been kahikatea (Orwin, 2004). Ships visiting New Zealand during this period were infrequent, likely than ten each year up until approximately 1830 (Chappell and Lorrey, 2013).
Appendices

By 1815, however, there is little doubt that kauri spars were harvested as part of the trade introduced by missionary Samuel Marsden during his establishment of the first mission at Rangihoua (Orwin, 2004). Marsden’s success sparked a renewed interest in kauri as a naval resource but it was short lived as spar location and retrieval were fraught with difficulties, including a growing backdrop of Māori unrest as the inter-tribal ‘musket wars’ escalated (Stewart, 2008). Despite an early, probably spiritually driven, reluctance to engage in the felling of kauri, local Māori embraced the kauri trade in return for muskets and gun-powder, which provided a significant military advantage and the opportunity to expand tribal territories and mana and pursue utu (revenge) against rival neighbours (Stewart, 2008). Increased Māori participation in logging, combined with European land purchases and associated settlement and industry in the 1820’s saw the timber trade begin to flourish, first in the Hokianga and then the Kaipara (Orwin, 2004).

After the establishment of saw mills and with the rapidly increasing British presence in New Zealand after the signing of the Treaty of Waitangi in 1840, the kauri timber industry grew rapidly, expanding to sawn timber for construction as well as boat-building. In 1865 the first steam driven saw mill was built and the peak of the kauri logging in the late 1800’s and early 1900’s was imminent. During this period the demand for timber began to outstrip its availability as the more accessible kauri had been depleted. Production in 1903 was 340 000 cubic metres of sawn timber from 36 mills and a government report from the same time suggested that at that rate, kauri would be exhausted within 8 years (Sale, 1978).

Another kauri industry, however, arose to augment the timber; the kauri gum preserved in vast swamp, scrub and cleared forest lands had many useful applications including linoleum and paint manufacture and as a lacquer of exceptional quality. Gum digging began in the 1830’s but remained a relatively small industry, dominated by Māori, until the 1860’s when soaring gum prices prompted a large expansion (Orwin, 2004; Stewart, 2008). Production peaked in the 1890’s to 1930’s with approximately 6000 tons exported annually, recovered by almost 10000 gum diggers, over half of whom worked full time on the fields (Stewart, 2008). The readily available labour drew large numbers of immigrant workers, particularly from the Dalmatian coast (Orwin, 2004).

By the 1940’s both kauri industries were in major decline as ancient reserves of timber and gum were almost depleted. The kauri conservation movement, ironically championed in the first instance by loggers who refused to log the Waiau kauri grove, gathered momentum with ecologically focussed Pākehā (New Zealanders of European descent) campaigning against logging in the 1940’s and ‘50s. At the same time Māori became increasingly worried about the spiritual loss that the potential extinction of kauri could cause. The public outcry that resulted in the creation of the Waipoua Forest Sanctuary in 1952 was the first nationwide conservation campaign in New Zealand and heralded the end of the commercial kauri timber industry.

In the 80-100 years of the kauri timber industry’s dominance, estimates suggest that old growth kauri forest was reduced from approximately 400 000 ha to under 8000 ha, of which only half retained its original timber (Sale, 1978). Many of these mature trees bear the scars of gum harvesting. While
kauri gum can still be found, it is generally of lower quality, with the bulk having been harvested in a rush which was the north’s equivalent of Otago’s gold rush around the same time; approximately $25 million worth of gum, by Sales’ 1978 estimate, was harvested between 1850 and 1930. While the economic contribution of exports of kauri timber and gum were significant in New Zealand’s early European history, the contribution of the timber industry is perhaps more fundamentally preserved in the nation’s architectural heritage; kauri supplied much of the timber that built a growing nation (Boswijk, 2005; Stewart, 2008). In the context of dendrochronological studies of kauri, this widespread use in construction has proved invaluable; the ‘link’ between sub-fossil specimens and living trees is filled by chronologies developed from salvaged architectural timbers (Boswijk, 2005; Boswijk et al., 2006). From its original spiritual significance to Māori, to its brief economic climax and, now, its position as a natural heritage icon and source of scientific fascination, kauri has maintained a prominent role in New Zealand’s human history. It has become a “potent symbol of people and place.” (Boswijk, 2010)
Appendices

References


8.3 Potential Adverse Impacts of Tree Coring

(Prepared by Dr Jonathan Palmer – Gondwana Tree Ring Laboratory)

Trees, like most biological organisms, use natural defense mechanisms to maintain their vitality (Shigo, 1984; Loehle, 1988). This is especially true of vigorous dominant and co-dominant individuals (Meyer and Hayward, 1936; Lorenz, 1944; Hepting et al., 1949). Holes from more than half of all trees cored in core damage studies healed within 2-3 years. Trees that did not heal well were typically of short-lived species or suppressed individuals (Meyer and Hayward, 1936; Lorenz, 1944; Hepting et al., 1949; Toole and Gammage, 1959). Generally the older a tree lives, the stronger its defense to disease and injury (Loehle, 1988). Since the focus of most dendroclimatic studies are species that live many centuries, biological theory suggests that these trees have a defense system that allows them to sustain centuries of physical damage. Therefore, evidence indicates that boring canopy dominant trees will not significantly change mortality rates. The small wounds created by coring are likely to heal rapidly and be insignificant injuries.

Coring creates wounds that may cause some internal decay. There is no evidence, however, of tree mortality after increment coring (Meyer and Hayward, 1936; Lorenz, 1944; Hepting et al., 1949; Toole and Gammage, 1959; Hart and Wargo, 1965; Cleaveland, 1998; Eckstein and Dujesiefken, 1999; van Mantgem and Stephenson, 2004). In fact, little effect on mortality was observed when stem wedge sections were removed using a chainsaw (Heyerdahl and McKay, 2001). To mitigate these potential impacts, one solution has been to dip the increment borer in alcohol following the extraction of each core to sterilize the borer. This prevents the potential transfer of fungus between trees. Sometimes people suggest that the cored wounds should be plugged with pruning paste or with a fungicide but plugging does little to reduce discoloration or decay (Meyer and Hayward, 1936; Lorenz, 1944; Hepting et al., 1949). Additionally, modern arborists do not seal the wounds because they have learned that leaving wounds open allows them to: 1) dry out and 2) naturally clean the wound like blood flow cleans our wounds, which discourages infection.

Finally, although tree-ring research is a relatively “new” area of science, there have still been a significant number of trees sampled from many different countries but no reports of mortality have occurred. An indication of the magnitude of tree-ring sampling can be obtained from the International Tree-Ring Data Bank (ITRDB) where the data from over 3,300 tree-ring chronologies from over 100 different species sampled from more than 50 different countries spread around the world are held. With such diverse and extensive collections having been made over the last couple of decades or more, any significant impacts from coring would have been identified/reported. As such then, the overwhelming evidence is that coring simply does not affect trees.
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8.4 Biosecurity Issues and Management

Prepared by Tom Brookman (Department of Geological Sciences, University of Canterbury)

Of paramount concern to all parties is the well-being of the trees being studied. As researchers it is in our interest that the trees remain healthy for future research and for public enjoyment; there is no quicker way to damage one’s scientific reputation or access to resources than developing a reputation for careless sampling.

Consequently, we undertake strict measures to prevent any biosecurity hazards that may be posed by our activity. The most likely hazard to kauri plantations arises from the transmission of fungal infection between trees. The best-practice measures routinely followed by our research team are outlined below:

1) The team is equipped with a phytosanitary kit to limit the spread of any fungal disease between kauri stands.

2) Before entering each site all footwear is thoroughly cleaned of soil and disinfected using TriGene (the recommended fungicide). All movement about sampling areas is restricted to as small an area as possible. If vehicle access to the site is used then vehicle tyres are similarly disinfected.

3) Coring equipment is thoroughly cleaned with ethanol between sampling sites and between trees within a site, to prevent the transmission of any tissue-borne diseases between stands.

4) Any evidence of diseased kauri is reported to the private landholder and/or the Kauri Dieback Response Team (0800 69 52874).

Further consideration is given to the fact that kauri have shallow feeding roots and build up ‘litter mounds’ around the trunk. Access to the kauri to be cored will be by foot only and researchers take measures to minimise disturbance to the forest floor.

The broader biosecurity issues of tissue and disease transport have little bearing in this project. The material will be dried and stored at the University of Canterbury before being analysed and will have virtually no opportunity to contaminate the natural environment. The wood cores, being solid wood from healthy trees, pose little or no risk of transporting any parasites.

The standard procedures outlined above meet those suggested by the Kauri Dieback Response team based in Auckland. Our research group made contact with experts in disease transmission during a seminar series at the University of Auckland Tree Ring Laboratory. We have subsequently adopted even more rigorous cleaning procedures based on research by Prof Roberta Farrell (U. Waikato) and Dr Nick Waipara (Auckland Regional Council). These include:

1) Before each increment borer is used, it will be treated in a 96% ethanol solution (full immersion of the
steel boring shaft in a long plastic vessel containing the ethanol solution).

2) Borers will be alternated between trees, allowing maximum time (generally 5-15 minutes) for sterilisation to occur. Discussion with Professor Roberta Farrell (University of Waikato fungi expert) suggests the ethanol treatment will destroy fungus, and ethanol residue will not harm the kauri trees.

3) Use of disposable latex gloves may also be employed to minimize physical contact between trees. If warranted (i.e. in areas of thick vegetation), a disposable Tyvek suit could also be employed for use at sample sites to mitigate transfer of fungus that might adhere to clothing during the short tramp into and out of the sample location.
8.5 Methods Overview

8.5.1 Generating Ring-Width Chronologies

8.5.1.1 A brief overview of tree-coring

Cores from living trees are traditionally taken from a tree using an increment borer; a narrow, hollow tube with a threaded cutting end that is wound into the tree, enabling a cylinder of wood inside the borer to be retrieved (Fig. 3.1). Generally, at least two cores per tree are taken as growth anomalies can result in ‘partial rings’, i.e. rings that are ‘missing’ from parts of the tree’s circumference. A common example is a conifer growing on a steep slope may sometimes develop ‘reaction’ wood on the downhill/stressed side but not on the uphill side (Stokes and Smiley, 1968). Similarly, in areas close to the loss or development of a branch, rings can be ‘wedged out’ making them locally ‘missing’ (Norton et al., 1987). In other situations, during periods of limited photosynthesis, trees may concentrate their growth in the canopy, meaning that a ring does not form lower on the trunk where sampling generally occurs (Norton and Ogden, 1987). Conversely, trees can also produce ‘false’, or ‘double’, rings within a single growth season. Often they are not clearly delineated because the ‘false’ latewood blends with earlywood on either side and careful microscopic investigation can provide other clues such as the presence of earlywood cells throughout the ‘false ring’.

Obtaining multiple cores per tree facilitates the identification of missing and false rings, and therefore cross-dating. For stable isotope studies of tree-rings this practice has the further benefit of facilitating quantification of intra-tree isotopic variability and in particularly narrow-ringed species, multiple cores may be the only means of providing sufficient material for annual isotope analyses (e.g. Porter et al., 2009; Porter et al., 2013).

Evidence, both published and anecdotal, suggests that increment boring has little, if any, adverse effect on trees (Norton, 1998 and Appendix 3). The wound (just over 5mm in diameter in this study) is small enough that, depending on the species, it may be blocked by resin within hours or sometimes days of the coring taking place (Fig. 3.6). At a number of our field sites there was concern surrounding disease transport; since the identification of Phytophthora taxon Agathis (PTA) in native kauri stands any scientific activity involving kauri has been subject to rigorous biosecurity protocols (see Waipara et al., 2013). A field plan for minimising contamination risk was followed, including the sterilisation of field equipment, particularly borers and footwear. Full details are found in Appendix 4. Since this field-work was conducted, Dr Andrew Lorrey of NIWA has created an ingenious phytosanitary coring field-kit, and some details of its use are found in Lorrey et al. (submitted). Despite the decreased risk of disease transport when sampling/assessing other species, it was deemed best practice to continue to follow the biosecurity protocols relating to footwear and borers.
8.5.1.2 Increment boring and core preparation for this study

At all sites 2-3 cores per tree, >90° apart where possible, were collected at breast height (~1.4m) using 40cm-long, 5.15mm diameter increment borers (Fig. 3.1). For the duration of the fieldwork, the cores were stored in plastic straws. They were then air dried over two or more days whilst tied loosely into grooved wooden mounts with string to prevent warping. Dried cores were then fixed into the mounts;

Fig. 8.1: The coring process in pictures, showing a increment borer being wound into a tree at DK, an extracted DK core being examined after extraction and a close-up of a borer alongside an old core wound.
kauri samples in this study (section 3.2.1) were generally short cores with wide rings and it was sufficient to tape them in place with low-stick painter’s tape, which made later destructive isotope sampling much easier. The mature cedar sampled (section 3.2.2) generally produced longer cores with much narrower rings. For these cores tape did not sufficiently immobilise the cores in preparation for cross-dating; these were secured using water soluble PVA glue (drying overnight). The use of glue was not ideal as it has its own isotopic signature (Beghin et al., 2011). The contamination potential was minimised by avoiding/removing lumps of glue when sampling cores for isotope analysis. Any residual glue was removed by the subsequent chemical extraction process (See 3.3.2) (Nakatsuka et al., 2004; Dodd et al., 2008). Every effort was made to mount the cores with the transverse aspect facing upward in order to improve ring definition when the cores were sanded with 120, 240, 400 and 600 grit sandpaper. The common North-American approach to core surfacing (Stokes and Smiley, 1968), using a razor blade, has proved problematic with New Zealand’s often narrow-ringed natives (Norton and Ogden, 1987).

8.5.1.3 Cross-dating and measurement

The measurement and cross-dating within this study was conducted by Dr Pavla Fenwick, a local dendrochronologist based in Christchurch with extensive experience analysing New Zealand’s native trees. A brief description of the dendrochronology process is provided here.

Both ‘missing’ and ‘false’ rings can generally be identified through cross-dating, the process of matching common growth patterns or marker (very narrow or wide) rings within and then between trees (Fig. 3.2). Even nearby trees of the same species can grow at very different overall rates due to a number of factors including age, canopy position, water availability etc. Comparison of the average ring-width does little to inform age determination or climatic reconstructions but, provided the tree’s growth is responding to climate, the width of a ring relative to those around it should be similar between trees. Consequently, trees growing at vastly different rates can still be cross-dated by creating an internally relative standard ‘growth index’.

For this study, visual cross-dating was
undertaken in the first instance, generally with the naked eye for kauri samples and under binocular microscope for cedar. Then, ring width measurements were recorded using a Velmex measuring stage with a precision of 0.001mm attached to a binocular microscope [Fig. 3.3]. COFECHA software (Holmes, 1983) was then used to confirm or refine the visual cross-dating. COFECHA converted the raw ring-widths into growth-indices, averaged them into a site ‘master chronology’, and calculated correlations between the individual cores and that master.

The Southern Hemisphere growing season spans two calendar years, beginning in Austral spring of one and ending in Austral summer/autumn of the next. For dating purposes, we followed Schulman’s (1956) convention for the Southern Hemisphere, which assigns each tree-ring to the year in which radial growth started. For example, the ring that began growing in spring of 2000 and finished in autumn of 2001, is labelled 2000 in the chronology.

8.5.2 Preparing wood samples for isotopic analysis

8.5.2.1 Core sub-sampling

Only cores that reached the critical 99% ring-width correlation across the relevant time-period (~1980-2011) during cross-dating were selected for isotope analysis to ensure the most accurate isotope chronologies possible. Cores were sliced by hand with a straight-bladed scalpel. For most DK cores, with relatively wide rings, rings were divided with the naked eye. However, for rings with less distinct boundaries and for narrow-ringed cedar from MtC, slicing was conducted under an illuminated 5x magnifying glass. All DK rings that contributed to the long (~28 year) record presented in chapters 4 and 5 were divided into three pieces: a ‘whole-ring’ sample, an ‘early-season’ sample taken from the first ~50% of the ring and a ‘late-season’ sample from the latter 50%. The ‘late-season’ samples were archived to ensure that early-season:late season and/or late season:whole ring comparisons could be conducted in the future. The division into early and late-season was based on kauri’s tendency to form most of its annual ring in a growth spurt from September to December, including 38-50% in October and November (Palmer and Ogden, 1983; Fowler et al., 2005; Wunder et al., 2013). Unfortunately similarly detailed growth-data for cedar does not exist so kauri growth data was used as an approximation and some wide cedar rings were sampled in the same way. Early-season samples were preferred for comparison with whole-ring in this study as they form during spring when the effects of ENSO are generally strongest in New Zealand.

For high resolution, intra-annual analyses of DK (see Chapter 5) rings were sequentially sliced perpendicular to the growth axis, creating thin disks of ~1mg. High resolution analyses targeted the period 1979-1982 for 3 major reasons:

1) Sampling practicality – This period yielded wide rings in a number of DK cores. For those cores sampled the average ring width was 4.9mm, with a range of ~3.3-6.5mm. This allowed up to 32 samples to be taken from a single ring, despite the rudimentary sampling technique
2) ‘Main’ Record length – 25 years was seen as a minimum length for the whole-ring and early-wood site chronologies so high resolution samples were necessarily taken outside that period.

3) El Niño – 1982-83 was one of the strongest El Niño events in New Zealand’s recent history, so 1979-1982 was seen as an opportunity to assess high-resolution sampling’s potential to capture such events (Chapter 5).

After initial sampling, high resolution disks and early-season and whole-ring samples were diced using a razor blade in order to increase surface area for the subsequent chemical processing.

### 8.5.2.2 Chemical extraction of α-cellulose from tree-ring samples

Samples were chemically processed to α-cellulose in a dedicated wet chemistry laboratory at the University of Canterbury using the ‘High Temperature 3x SBrendel’ method outlined by Brookman and Whittaker (2012; Chapter 3) but with sample sizes up to 4.5mg (as opposed to 1.5mg). The method consists of an acetic/nitric acid-digestion at 120°C in which the resin, lignin and holocelluloses are released from the wood samples. These are then removed from the vial by a series of wash and centrifugation steps utilising ethanol, distilled-deionised water and acetone. As its name suggests, the method is based on Brendel et al.’s (2000) original process, which was then modified for small samples by Evans and Schrag (2004). The High Temperature 3x SBrendel with 4.5mg samples was initially adopted for kauri samples based on an up-scaled reagent-to-sample ratio from Evans and Schrag (2004). The method encountered processing problems, leading to further investigation by Brookman and Whittaker (2012; Chapter 3), the result of which was the adoption of the 3x SBrendel as a standard method for samples of any mass under 4.5mg. A step-by-step processing description can be found in Appendix 6 (Supplementary information to Brookman and Whittaker, 2012).

Once processed the samples were dried in a low (50°C) oven and then re-suspended in distilled-deionised water. Suspended samples were chilled to ~4°C in a refrigerator before fragmentation and mixing with an ultrasonic probe (Omni Inc, Sonic Ruptor 400) for ~30 seconds. Ultrasonic fragmentation is much more efficient in cold water (see Laumer et al., 2009). Samples were then returned to the 50°C oven until dry (~3-4 days) at which point they were essentially ready for analysis.

### 8.5.2.3 Massing and preparation for analysis

Dried α-cellulose samples were massed into the smallest practical silver capsules, generally 5x3.5mm or 4x3.2mm, to minimise any δ¹⁸O ‘blank’ associated with the capsule (Wang et al., 2008). Capsules from the same manufacturer (OEA laboratories) were used throughout and where possible capsules from the same batch were used throughout major analytical periods. DK samples were generally 250 ± 25 µg and the MtC samples 125 ± 10 µg; the smaller sample size reflected the much smaller amounts of α-cellulose recovered from the narrow-ringed cedar. 125 µg samples still gave more than sufficient signal for reliable data provided Helium (He) dilution was not used within the run (see Appendix 9, Fig. 8.15, Fig. 8.16).
Capsules were folded and transferred to a vacuum dessicator for a minimum of 2 days. After dessication, samples were transferred into the 100 space Costech zero-blank autosampler and purged with He for 10 minutes to flush the autosampler of atmosphere. Following purging the isolation valve to the reactor of the Costech 4010 Elemental Analyser (EA) was opened and samples and were left in the He stream for a minimum of 3 hours prior to run commencement, allowing backgrounds to stabilise and facilitating the removal of any atmospheric H$_2$O adsorbed to the silver during transport from dessicator to autosampler. Before each run the internal precision of the system was tested with at least two CO zeroes and a CO linearity check (See Chapter 4 for analytical details).

8.5.3 Dual Element Low Temperature Pyrolysis of Cellulose

The analytical methodology employed is covered in detail in Chapter 4 and a general review of the technique’s origins and development is provided in Appendix 9.
References


8.6 Detailed Site Chronologies For MtC, CC, WaK, BP and FC

The research presented in Chapters 4-6 originates from two primary field sites sampled between 2009 and 2012. A number of additional sites were sampled and developed as ring-width chronologies but not developed as stable isotope chronologies as they were considered lower priority or displayed inferior chronology quality. The site network covers much New Zealand’s latitudinal range and the large climatic divide between east and west of the Southern Alps in the South Island (Table 3.1; Fig. 3.3).

The two sites from which stable isotope chronologies were developed are a stand of kauri at Wairongoa Springs near Dunedin (DK, for Dunedin Kauri) and a cedar stand at Mt Cargill (MtC). These two sites are profiled in detail here, along with other sites for which stable isotope chronologies were not developed.

The lack of recent stable isotope dendroclimatic research on New Zealand native tree species meant there was little dendrochemical information on which to base site selection. Consequently, initial site selection focussed on finding an accessible kauri stand at the margins of the species’ tolerance for temperature and/or moisture. Temperature and moisture availability are the basis for most dendroclimatic reconstructions in the literature (covered in Chapter 2) and selecting trees in marginal environments is an established technique to target strong climatic signals in ring-width and dendrochemical records (Stokes and Smiley, 1968; Schweingruber, 1988; McCarroll and Loader, 2004).

Maximising climatic signal by assessing trees in marginal climates is common practice in traditional dendrochronology. For instance, if moisture availability is known to be the limiting growth factor, as in much of the Southwest of the United States, then trees from sites more likely to be subject to moisture stress will provide a better annual record of rainfall. Trees on flat sites with a deep soil profile and access to groundwater will most likely produce ‘complacent’ rings regardless of annual rainfall variability (Stokes and Smiley, 1968). A similar approach has been suggested for stable isotope dendroclimatology (McCarroll and Loader, 2004); $\delta^{13}$C is often controlled by stomatal conductance in regions of moisture stress, so a seasonal record of moisture availability is best sought in a species in areas where growth conditions are marginal due to low precipitation. However, this can provide misleading results if the object of a study is to provide calibration for sub-fossil chronologies (Stokes and Smiley, 1968; Schweingruber, 1988) when the modern site selected is in fact very different from the more ‘complacent’ sites where sub-fossil wood originates. In such cases, the application of the calibration data may provide misleading conclusions (McCarroll and Loader, 2004). Ultimately, site selection may be determined by the availability of trees but in areas where suitable species/specimens are available, careful thought should be given to the vegetative structures, altitude, climatic regime and soil characteristics in order to determine the optimum sample site (Schweingruber, 1988).

Once the DK site profiled below (3.2.1) was established, finding a nearby site with a different species (cedar) was seen as the priority. The proximity of DK and MtC allow Chapters 4 and 6 to make comparisons between the two species and assess the relative influence of species physiology, regional climate and site microclimates.
Fig. 8.3: Field sites across New Zealand with magnified insert of the New Plymouth area: 1) Brooklands Park (BP); 2) Fred Cowling Reserve (FCK); 3) Wanganui (WaK); 4) Camp Creek (CC); 5) Mt Cargill (MtC) and 6) Wairongoa Springs (DK)
8.6.1.1 Mount Cargill (MtC) Site Profile

Mount Cargill, on the east coast of South Island overlooking Dunedin, is home to remnant patches of mature native forest including stands of cedar and scattered pink pines. The area was previously investigated by LaMarche et al. (1979) who attained a chronology in excess of 500 years. The site (-45.808 S, 170.5664 E) (Fig. 3.7) is less than 20 km from DK but lies closer to the coast (<10km) and at higher elevation (~500-550m). Sullivan’s Dam (~3.5km W, 300m asl), receives ~1220mm of annual rainfall, and Swampy Summit (~6km W, 700m asl) has a mean annual temperature of ~7.3°C (Fig. 3.8). Rainfall is spread uniformly throughout the year but temperature is distinctly seasonal. The ability to make a regional comparison between two species, one in a young plantation outside its natural range and the other a mature, natural stand, was the reason that MtC was chosen as the second primary study site. It is also approaching the southern limit of cedar, suggesting that it may be close to the species’ climatic tolerances and therefore responsive to climate.

The sampled stand of cedar is slightly north-east of where LaMarche et al. (1979) are thought to have worked. The walking track through the area, likely established since LaMarche et al’s visit, provided easy access to a large stand of mature trees and minimised the need for trampling native vegetation. The trees were growing on a gentle (~10°) north-north-west slope at ~500-550m above sea level. 24 trees, ranging from 37 to 77cm DBH were sampled, totalling 67 cores. It was impossible to mark each tree due to canopy interference with GPS; all were located within 125m of those marked in Fig. 3.7.
Appendices

Fig. 8.4: Mt Cargill climograph compiled from nearby weather stations (Swampy Summit and Sullivan’s Dam)

Fig. 8.5: Mt Cargill site map with insets of the Otago Peninsula and New Zealand.
Fig. 8.6: Mt Cargill site compilation, showing the canopy emergent cedar viewed from above, followed by images capturing the dense undergrowth surrounding the mature trees.
Table 8.2: Summary of the MtC ring-width record. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

<table>
<thead>
<tr>
<th>Tree</th>
<th>Core</th>
<th>DBH (cm)</th>
<th>Record length</th>
<th>Correlation with master (1975-2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MtC01</td>
<td>1</td>
<td>45.0</td>
<td>1678-1905</td>
<td>-</td>
</tr>
<tr>
<td></td>
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<td></td>
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Range/Mean: | 1619-2010 | 0.68 | 50.4 | 237.8 |
8.6.1.2 Camp Creek (CC)

At Camp Creek (Fig. 8.7), near Inchbonnie on the west coast of the South Island, both pink pine and cedar grow in the montane forest. Mean annual rainfall at Inchbonnie, 10km from the site, is ~4770mm/yr, spread evenly throughout the year and rainfall in the headwaters of the catchment reaches 6000mm/yr. Mean annual temperature at the Otira Substation (~14km inland at 343m elevation) is 10.0°C (NIWA, 2011). Temperatures vary seasonally with lowest monthly average in July (4.5°C) and the highest average in February (14.7°C). The Camp Creek site is likely to have a similar temperature range being at higher altitude but in closer proximity to the coast. The site was chosen as its West Coast location is one of the most sensitive regions to SAM and ENSO driven precipitation and temperature changes in New Zealand (Renwick and Thompson, 2006; Ummenhofer and England, 2007).

There is a 700 year unpublished cedar chronology for this location (J. Palmer, personal communication) and the oldest pink pines previously cored at this site began growing ~600 years ago (Fenwick, 2003). The site’s credentials for producing long tree-ring records were well established. Of additional interest at this site was the observation by Fenwick (2003) that the response of ring growth to climate differed for pink pine and cedar. The reason for this is unclear and it is uncertain whether this effect would also apply to the stable isotopic composition of growth ring cellulose.

The vegetation at the site is montane forest with a canopy of rata (*Metrosideros umbellate*), rimu (*Dacrydium cupressinum*) and cedar and a thick understory of shrub and vine Fig. 8.8. The main sample site, behind the Camp Creek hut in the centre of the basin, is on a gentle slope (~10°). Although the slope generally has an approximately northerly aspect it is frequently dissected by ridges and gullies, meaning sampled trees were growing on a variety of aspects and slopes. Cedar become more frequent at ~700m above sea level and can be found right up to the tree-line at ~1100m. Samples were taken between 7-800m above sea level. Apart from the sample site close to the hut the surrounding topography below the bush-line is steep and heavily dissected. Above the bush-line the tussock tops are relatively gently contoured.

16 trees were sampled, for a total of 48 cores (Table 8.3). Originally fewer samples were planned but the prevalence of heart-rot prompted us to take extra samples to ensure sufficient replication. Ultimately heart-rot was not the limiting factor for this record’s utility for modern isotope dendroclimatology, in fact it provided the longest chronology of this study (860 years). Many of the trees exhibit extremely narrow rings for much of the 20th and all of the 21st centuries. Whether this is due to their great age or some site specific or climatic phenomenon is beyond the scope of this investigation, which requires rings of sufficient width to sample over the last ~30 years to create records easily compared with modern weather data. Further coring at Camp Creek to establish sufficient cross-dateable material between 1900-present could unlock the potential of a long site record.
Fig. 8.7: Camp Creek site map with inset digital elevation models of the surrounding mountains (near Inchbonnie) and New Zealand.
Table 8.3: Camp Creek ring-width record summary. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

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Range/Mean: 51.5 1150-2010 0.60

325.3
8.6.2 Wanganui (WaK)

These trees were planted between 1917-1928 in Kowhai Park, Wanganui, along the bank of the Wanganui River. Local growth conditions are also favourable for kauri; Spriggens Park EWS weather station records show a mean annual temperature of ~13.8°C and mean annual rainfall of ~900mm (NIWA, 2011). The trees are well spaced in a park-like setting (Fig. 8.8) and have most likely benefitted from park water and fertiliser regimes, as well as access to a shallow water table due to their proximity (~50-150m) to the Wanganui River.

The Wanganui kauri were initially sampled as they provided an opportunity to fill out a latitudinal transect. However, they did not provide a robust chronology. Their park-like setting negating any competition for light, probable access to a shallow water table and periodic fertilisation ultimately meant that their growth patterns have been too disrupted to create an accurate chronology. Consequently, no stable isotopic analysis was undertaken on these samples. Of the 20 cores taken at WaK, only 12 visually cross-dated (Table 8.4). Of those 12, only 9 achieved the 99% significance level of correlation with the master record.

Table 8.4: Wanganui Kauri ring-width record summary. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

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<td>54.2</td>
<td>1931-2008</td>
<td>0.29B</td>
</tr>
<tr>
<td>WaK07</td>
<td>.1</td>
<td>64.2</td>
<td>1932-2008</td>
<td>0.31A</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1932-2008</td>
<td>0.51</td>
</tr>
<tr>
<td>WaK09</td>
<td>.1</td>
<td>59.8</td>
<td>1942-2008</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1947-2008</td>
<td>0.50</td>
</tr>
<tr>
<td>WaK10</td>
<td>.1</td>
<td>67.0</td>
<td>1943-2008</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1944-2008</td>
<td>0.35</td>
</tr>
<tr>
<td>Mean:</td>
<td></td>
<td>57.9</td>
<td>68.9</td>
<td>0.42</td>
</tr>
</tbody>
</table>

8.6.3 Brooklands Park and Fred Cowling Reserve (BP and FC)

Both Brooklands Park (part of Pukekura Park) and the Fred Cowling Reserve (part of Barrett Domain) were planted with kauri between 1935 and 1940 (New-Plymouth-District-Council, n.d.-a; b) as part of the horticultural work of local horticulturalist Fred Cowling. In 1948 he donated the two and half hectares, originally planted with ~2000 trees, to the city of New Plymouth (Hoskin, 2008).

At Brooklands Park the mean annual temperature is ~14°C, with a mean annual rainfall of ~1650mm (NIWA, 2011). These are very similar conditions to those of kauri’s natural range further north. The Brooklands Park kauri are situated on a free draining, moderately steep slope of south-westerly aspect
with a stream at the western boundary. They form part of the canopy amongst a mixed native forest with rimu (*Dacrydium cupressinum*) being the other dominant canopy species. For much of its history the stand could be considered pseudo-natural in that minimal management was undertaken and the dense planting strategy somewhat mimicked the natural ‘ricker’ thicket growth habit. In 2002, however, the grove was selectively thinned to encourage growth of the ‘stronger’ specimens (Gould, 2002; Dick, 2009).

Climatic conditions are considered identical at the nearby the Fred Cowling Reserve, as is the forest ecology. Trees FC01-05 were growing on a gentle-to-moderate west facing slope amongst a mixed native plantation forest (Fig. 8.8). FC06-10 were growing at the base of the slope, in close proximity to Mangautuku stream. The entire stand was thinned in 2004 (Dick, 2009). Since then trees in both plantations have contracted Armillaria or ‘honey fungus’ and have been treated with phosphorous. Armillaria symptoms are similar to those created by Phytophthora taxon *Agathis* (PTA) or ‘kauri rot’ and while there was great concern that the New Plymouth kauri may have contracted PTA (Smith, 2009) (Pattinson, personal communication) samples from Brooklands Park indicated only Armillaria infection (Dick, 2009).

Of the 20 cores taken at each site only 13 at BP and 16 at FC visually cross-dated. Of those, only 10 and 11 respectively achieved a 99% significance level in their correlation with the master record (Table 8.5, Table 8.6). The combination of favourable growing conditions and silvicultural management is probably the cause of these disrupted records. The decision was made not pursue isotopic analysis of these stands due to the limited cross-dated sample pool.

**Table 8.5:** Brooklands Park Kauri ring-width record summary. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

<table>
<thead>
<tr>
<th>Tree</th>
<th>Core</th>
<th>DBH (cm)</th>
<th>Record length</th>
<th>Correlation with master (1980-2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP01</td>
<td>.1</td>
<td>43.9</td>
<td>1944-2008</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1948-2008</td>
<td>0.33 A</td>
</tr>
<tr>
<td>BP02</td>
<td>.1</td>
<td>36.8</td>
<td>1933-2008*</td>
<td>0.30 A</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1942-2008</td>
<td>0.60</td>
</tr>
<tr>
<td>BP03</td>
<td>.1</td>
<td>45.2</td>
<td>1951-2008</td>
<td>0.29B</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1944-2008</td>
<td>0.40A</td>
</tr>
<tr>
<td>BP04</td>
<td>.1</td>
<td>34.3</td>
<td>1953-2008</td>
<td>0.59</td>
</tr>
<tr>
<td>BP06</td>
<td>.1</td>
<td>44.0</td>
<td>1946-2008</td>
<td>0.42A</td>
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<td>1945-2008</td>
<td>0.28A</td>
</tr>
<tr>
<td>BP07</td>
<td>.1</td>
<td>34.7</td>
<td>1946-2008</td>
<td>0.36B</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1950-2008</td>
<td>0.42A</td>
</tr>
<tr>
<td>BP09</td>
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<td>35.0</td>
<td>1946-2008</td>
<td>0.29B</td>
</tr>
<tr>
<td>BP10</td>
<td>.2</td>
<td>40.2</td>
<td>1949-2008</td>
<td>0.24B</td>
</tr>
</tbody>
</table>

Mean: 39.6  1933*-2008  0.38  62.4
Table 8.6: Fred Cowling Reserve Kauri ring-width record summary. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

<table>
<thead>
<tr>
<th>Tree</th>
<th>Core</th>
<th>DBH (cm)</th>
<th>Record length</th>
<th>Correlation with master (1980-2009)</th>
</tr>
</thead>
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<tr>
<td>FC01</td>
<td>.1</td>
<td>58.4</td>
<td>1966-2008</td>
<td>0.38A</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1967-2008</td>
<td>0.40A</td>
</tr>
<tr>
<td>FC02</td>
<td>.2</td>
<td>43.6</td>
<td>1963-2008</td>
<td>0.65</td>
</tr>
<tr>
<td>FC04</td>
<td>.1</td>
<td>58.4</td>
<td>1953-2008</td>
<td>0.50</td>
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<tr>
<td>FC05</td>
<td>.1</td>
<td>33.4</td>
<td>1958-2008</td>
<td>0.69</td>
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<td>.2</td>
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<td>0.51</td>
</tr>
<tr>
<td>FC06</td>
<td>.1</td>
<td>39.6</td>
<td>1966-2008</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1962-2008</td>
<td>0.48</td>
</tr>
<tr>
<td>FC07</td>
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<td>49.2</td>
<td>1952-2008</td>
<td>0.34B</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1962-2008</td>
<td>0.49</td>
</tr>
<tr>
<td>FC08</td>
<td>.1</td>
<td>41.1</td>
<td>1958-2008</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1955-2008</td>
<td>0.29B</td>
</tr>
<tr>
<td>FC09</td>
<td>.1</td>
<td>45.4</td>
<td>1954-2008</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1959-2008</td>
<td>0.65</td>
</tr>
<tr>
<td>FC10</td>
<td>.1</td>
<td>43.5</td>
<td>1964-2008</td>
<td>0.40B</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1964-2008</td>
<td>0.74</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>45.8</td>
<td>1952-2008</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48.4</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 8.8: Collage of Wanganui, Camp Creek and Fred Cowling site photos
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8.7 Wairongoa Springs (DK) Full Site Profile


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Abstract

Background: We document the growth history of the second southern-most known stand of New Zealand kauri (Agathis australis), growing healthily near Dunedin, approximately 8° of latitude south of the modern natural range of the species. New Zealand’s endemic kauri is the southernmost species of the tropical genus Agathis. Established in the 1950s by avid botanist Alec Thompson, the plantation now approximates a natural ‘ricker’ stand of juvenile kauri.

Methods: Sample plot measurements document height and diameter growth of the stand, providing data for modelling self-thinning dynamics. Dendrochronological investigation using ring-widths from cores obtained by increment boring has created a 52-year record that shows a strong common pattern of long-term and inter-annual changes in growth. Carbon isotope analysis of annual rings from 1983-2009 reveal corresponding multi-decadal chemical trends. Segmented linear regression is used to compare the ring-width record with existing kauri growth and self-thinning models.

Results: The record documents rapid growth, comparable to other plantations of kauri without silvicultural tending and generally faster than that of natural stands. The trees’ growth can be broken into two apparent phases: the first, a 26-year period of relatively constant rapid growth with ring-widths averaging 3.5mm. The second phase shows a steady decline in annual growth thought to be indicative of self-thinning due to increasing competition. This ring-width decline is matched by a gradual decline in carbon isotope ratios.

Conclusions: Ring-width measurements and carbon isotope determinations compared with forestry-based modelling of self-thinning in kauri suggest that this stand is undergoing self-thinning much sooner than other kauri stands. We believe this highlights other possible influences beyond simple biomass accumulation triggering the onset of self-thinning. The plantation’s growth rate is comparable to others from the North Island, demonstrating that kauri can be grown, albeit in sheltered sites, throughout the length of New-Zealand.

Keywords: Agathis australis, kauri, plantation, growth-rate, self thinning, dendrochronology, ring-width, carbon isotopes
Appendices

8.7.1 Background

8.7.1.1 Kauri ecology and Growth

New Zealand kauri (*Agathis australis*) is a canopy-emergent tree that can reach heights of 30-60m when mature (Ecroyd, 1982). It generally has a straight, cylindrical trunk clear of branches for 12-25m (Bergin and Steward, 2004). The largest living kauri, Tāne Mahuta (based on estimated wood volume), is ~4.5m in diameter and over 50m high (Bergin and Steward, 2004; Stewart, 2008). Before extensive logging and gum-harvesting operations in the 19th and 20th centuries kauri were often larger, with the largest officially measured, Kairaru, being over twice the size (timber volume in m$^3$) of Tāne Mahuta, with a diameter of ~6.4m (Wardle, 2011). Typical longevity is thought to be approximately 600 years (Ahmed and Ogden, 1987) and while recent estimates suggest that maximum ages are probably generally in the order of 1500-1700 years (Steward and Beveridge, 2010) some individuals may exceed 2000 years of age (Palmer et al., 2006). This longevity makes kauri a useful resource for tree-ring studies into past climates (i.e. dendroclimatology); New Zealand has an exceptional dendrochronological record, compiled from living and sub-fossil kauri (Boswijk et al., 2006; Palmer et al., 2006; Turney et al., 2010).

One of the limitations of kauri for dendroclimatic study is that it currently only naturally occurs in the north of New Zealand, from approximately Te Puke/Kawhia (~38°S) to Cape Reinga (~34°S). Despite this, plantation kauri grow successfully in numerous areas outside their natural range (Pardy et al., 1992). There are individual specimens or small groups growing as far south as Invercargill and even Stewart Island and kauri are routinely planted as ornamental trees around the country (Niinemets et al., 2005). Their plantation success throughout New Zealand is less surprising after looking at the fossil record. Early records of kauri arise from very different environmental contexts to the modern day and while interesting, have little bearing on modern distribution: Lee et al. (2007) report leaf macrofossils in Southland during the late Oligocene-early Miocene, and Evans (1937) identified kauri resin in fossilised material in Tertiary lignite deposits from the Roxburgh and Mataura areas in the South Island. Araucarian ancestors of kauri first appeared in the Cretaceous period (Lee et al., 2007). More relevant to kauri’s current distribution, however are the findings of Mildenhall in (1985), who noted extensive palynological evidence of kauri around 300,000 BP (before present) at Lower Hutt in Wellington (~41°S), a period during which southern hemisphere climate was significantly cooler than currently (Petit et al., 1999; Jouzel et al., 2007). Pleistocene evidence of kauri’s more extensive distribution (Ecroyd, 1982) has led numerous authors to speculate on the causes of the species failure to recolonise land further south in recent times (e.g. Mitchell, 1991; Ogden et al., 1992; Ogden et al., 1993). A number of reasons, including climatic limitation, lack of suitable soils and terrain and simply slow expansion due to episodic stand regeneration have been suggested (Ogden et al., 1992; Steward and Beveridge, 2010). Recent permanent regeneration from planted stands south of the current natural limit suggest that kauri may only just be in a process of extending its range, recently curtailed by the episodic glaciations of the Quaternary (Steward et al., 2003).

The study of plantation species outside their natural limits is important to the long-term prospects of native forestry in New Zealand. The wood-quality reputations of many New Zealand natives were based
on the use of heartwood from mature specimens logged from old-growth native forests. To replicate these qualities, many species may require long plantation turn-around times (McConchie, 1999). Even those species, like kauri (Steward and McKinley, 2005), from which high quality sapwood can be utilised are estimated to take 2-3 times as long as common plantation species like *Pinus radiata* to reach harvestable proportions. Consequently, continued monitoring of plantations as they near their suggested harvest age (~80 years for kauri (Chikumbo and Steward, 2007)) is vital as more data on plantation density and thinning is required for effective long-term plantation management. The ability to extend the geographical boundaries is another area that requires further research; some species are likely to grow well in areas beyond their current natural limits, based on climatic and soil profiling of their preferred habitat (Burns, 1999). This point is illustrated for kauri by Bergin and Steward (2004) in their review of various *Agathis* species grown for plantation forestry outside their natural ranges, including Australian *Agathis robusta*, now grown more successfully outside its natural range (e.g. South Africa) due to the lack of insect predation. In the New Zealand context, Wairongoa Springs is evidence that kauri can be grown well south of its current distribution and early surveys suggest that the same may be true of other species including puriri (*Vitex lucens*) and kohekohe (*Dysoxylum spectabile*) (Pardy et al., 1992), identified by multiple authors as having hardwood plantation potential (McConchie, 1999; Steward, 1999).

This study aims to update and augment the earlier published profile (Pardy et al., 1992) of this botanically unique site. Burns (2009) recently called for a renewal of New Zealand-based research into native forest management, citing a dearth of new research particularly in the fields of plantation establishment and management. We hope to help redress that knowledge gap by employing a combination of methods to characterise growth in the Wairongoa Springs kauri. A sample plot for growth measurements and modelling is augmented with dendrochronological ring-width measurement approach to assess growth rates and patterns in individual trees. These data are compared with a short dendrochemical (carbon stable isotope) chronology from the site, facilitated by the site’s inclusion in a broader research program aimed at establishing New Zealand native trees’ potential as dendrochemical indicators of climate change. We see that dendrochemical record’s application here as a novel approach to characterising New Zealand native plantation growth processes.

Commonly, inter-annual growth changes in tree-rings are used to reconstruct climatic changes influencing tree-growth but such dendroclimatic studies tend to avoid juvenile trees due to strength of the strong age-dependent influences on growth (Fritts, 1976). Dendrochronology, the counting and measurement of annual growth rings is also commonly used in forestry as a means of analysing changes in growth throughout the life of plantation trees on annual to long-term scales. This is particularly useful in situations where a lack of regular monitoring means that detailed growth records cannot be retrieved from external diameter-based measurements (e.g. Baskerville, 1972).

Carbon stable isotopes in tree-rings are effective recorders of the balance between a tree’s stomatal conductance and photosynthetic rate (Farquhar et al., 1982; Francey and Farquhar, 1982). Consequently they can be used to assess physiological changes in trees’ photosynthetic systems relating to water use
efficiency (Farquhar et al., 1982; Farquhar and Richards, 1984; Stephens et al., 1999) and changes in light availability/photosynthetic performance (Farquhar et al., 1982; Francey and Farquhar, 1982; Farquhar et al., 1989; Walcroft et al., 2002). Stable isotopes in young trees from a number of environments are generally observed to exhibit a ‘juvenile effect’, with δ¹³C (the relative abundance of ¹³C to ¹²C) increasing with tree age (see McCarroll and Loader, 2004 and references therein for a review of the juvenile effect and a detailed review of carbon isotope theory; Leavitt, 2010). This same trend has been observed in early rings of mature kauri (Jansen, 1962; Grinsted and Wilson, 1979). However, the mechanisms behind the ‘juvenile effect’ are poorly understood and have been variously ascribed to numerous sources including increased light availability as trees grow (Francey and Farquhar, 1982) and a reduction in the photosynthetic use of canopy-respired CO₂ as trees grow (Schleser and Jayasekera, 1985); however, as yet, there is no consensus in the literature on a cause that fits the diverse range of environments in which the juvenile effect has been identified (Leavitt, 2010). Here we use carbon isotopes to assess whether that pattern is evident in plantation kauri.

8.7.1.2 Wairongoa Springs History

‘Wairongoa Springs’, on the north-eastern margin of the Taieri Plain near Dunedin, was owned in the late 19th and early 20th centuries by the Thomson family, proprietors of Thomson & Co. cordial manufacturers. Wairongoa Springs provided much of the naturally carbonated spring water for their beverages, from the springs that still flow today. Indeed, many of the business’s original buildings still stand on the property, within 100m of the kauri. A.C.B. Thomson, son of the proprietor, Alexander Thomson, lived on the property upon his return from the First World War as a somewhat reclusive and eccentric local character. He was an avid botanist and horticulturalist and established a marvellous arboretum on the property, including 110-112 juvenile kauri trees planted between 1955 and 1957 (Unknown, 1964). Thomson was in contact with Duncan and Davies Ltd, seed merchants from New Plymouth, where it is suspected the kauri stock may have originated, given New Plymouth’s already flourishing kauri plantations established by another avid botanist, Fred Cowling. Cowling had established the Brooklands Park and Fred Cowling Reserve kauri plantations in New Plymouth (~1935) (Herbert et al., 1996). It is highly likely that the New Plymouth stock, and therefore the Wairongoa Springs stock, originated from Waipou Forest (Steward, 2011, Barton personal communication). At the time, the Waipoua nursery was the only commercial source of kauri seed, originally collected from 17 trees between 1951-54 (Morrison, 1955) and then rapidly expanded until, in 1972, 94 trees were being harvested (Morrison and Lloyd, 1972). At the time of our initial sampling, approximately 60-70 of Thompson’s trees still thrived, constituting probably the largest kauri stand in the South Island. Shortly before our second visit, a number of trees were severely damaged in a strong north-westerly wind event (Fig. 8.11).

8.7.2 Site Profile and Sampling and Analytical Methods

The site, referred to henceforth as Dunedin Kauri (DK) is situated amongst gently rolling hills on
the north-eastern margin of the Taieri Plain, at an elevation of ~46m above sea level (asl) (45.833° S, 170.3614° E) (Fig. 8.10). Although less than 30km from the coast, the Taieri Plain has a microclimate created by shelter from hills to the east and the Silver Peaks Range to the north and north-east (Unknown, 2001). Nearby Invermay receives ~730mm of annual rainfall and has a mean annual temperature of ~10.3°C (NIWA, 2011). Rainfall is relatively uniform throughout the year but the seasonally variable temperature (NIWA, 2011) (Fig. 9.4) with warm summers and cold winters creates large seasonal evaporation gradients. Steward (2011 pp. 43) characterises the soils as “Typic Fluvial Recent Soils (RFT) (Warepa soils derived from Schist loess over schist, greywacke and igneous rocks) of low natural fertility” using Hewitt’s (1998) New Zealand classification system. The trees are growing on the relatively flat valley floor of an approximately north-south running valley. The surrounding forest is a mixture of planted indigenous species, generally pre-dating the kauri. The site is cooler and drier than most of kauri’s natural, mainly Northland, range which generally has mean annual temperatures ≥13°C and rainfall ≥1200mm (NIWA, 2012b).

Fig. 8.9: Site map of Wairongoa Springs (DK) on the north-eastern margin of the Taieri Plain, just west of Dunedin (inset) in New Zealand’s South Island.
In 1986, Pardy et al. (1992) used growth plots in planted native stands to obtain data on the height and diameter at breast height (DBH) growth of kauri in planted stands. In later assessments of the performance of planted kauri, a permanent sample plot (PSP) (Ellis and Hayes, 1991) was established overlying the original growth plot. The size of the PSP used was determined by the size of the stand and number of stems/ha. At Wairongoa it was difficult to install a standard size sample plot (0.04 ha) (Ellis and Hayes, 1997). However, where the kauri typically had adjoining plantings comprised of species of equal stature and similar growth rate, this enabled the use of all stems within the stand, including those that would otherwise be defined as edge-trees (Cancino, 2005). Diameter at breast height was measured for trees within the plot and a subsample of trees were also measured for height using a digital hypsometer Vertex with transponder.

The DBH data collected were used to calculate the quadratic mean diameter for the stand (using the below equation), as the quadratic mean diameter is considered a more accurate representation than the arithmetic mean when estimating stand volume (Curtis and Marshall, 2000).

\[
\text{Quadratic mean DBH} = \sqrt{\frac{\sum_{i=1}^{n} dbh_i^2}{n}}
\]

Height and diameter curves were plotted and a non-linear regression curve was fitted to the data. The regression equation was used to estimate total tree height of those stems measured for diameter but not height. Steward (2011) collected similar data from 25 stands of natural second growth and plantation kauri across the country. Data from all stands, where full site occupancy was assumed, were combined and a linear regression equation was fitted to assess the relationship between mean stand diameter and stand density. The relationship was strong \( r^2 = 0.88 \) for both planted and natural stands of kauri in a combined data set. This relationship indicates the point at which mean stand diameter and basal area increment slows, and where self-thinning is likely to occur unless thinning was undertaken.

Quadratic Mean Diameter = 660.69 x SD-0.456;

Steward’s (2011) model is applied here in preference to Ogden and Stewart’s (1995) model, as it...
incorporates recent and extensive measurements of plantation trees.

Mean top height and mean top diameter were calculated as the average height and quadratic mean diameter respectively of the 100 largest-diameter stems/ha based on the height-diameter relationship established by Steward (2011). Basal area was calculated as the sum/hectare of cross-sectional stem area at breast height (1.4 m).

Increment cores were taken without regard to the PSP due to different sampling criteria (see below). Cores were taken from bark to pith, at breast height, with a 5mm increment borer at a slight upward angle. In addition to general coring ‘good practice’ (Norton, 1998), strict biosecurity controls were observed in order to guard against the transmission of the spread of diseases, particularly the Phytophthora taxon *Agathis* (PTA) pathogen (Waipara et al., 2013), responsible for the kauri dieback in the North Island. Thirteen trees were sampled, with 3 cores taken from all trees other than DK01, totalling 38 cores over two fieldtrips in 2009 and 2011. Cores were taken >90° apart where practical in order to achieve maximum circumferential coverage of each tree. The mean diameter DBH and growth rates for trees sampled for dendrochronological purposes are not an accurate reflection of the entire stand as larger trees were preferred for ring-width study. The other main criteria were that the tree had a clear bole at breast height and a single main stem rather than a double leader.

Cores were air dried while loosely mounted in core mounts with multiple strips of low-stick painter’s tape to allow sanding to provide a ‘readable’ surface. Normally cores would be glued in place before sanding but the subsequent use of these cores for destructive stable isotope sampling meant non-permanent mounting was preferable. Sanded cores were visually cross-dated, using a binocular microscope when necessary. Ring-width measurements were taken using a Velmex measuring stage with a precision of 0.001mm. These ring-width data were then converted to a growth index (a process called standardisation) which compares the width of an individual ring to those rings around it, making it an internally relative standard; standardisation allows the comparison of fast and slow growing individuals on the same scale and removes trends related to age or stand dynamics. Growth-index data were then used to confirm the visual cross-dating using COFECHA software (Holmes, 1983).

Carbon isotope determinations were made on annual rings from 1983-2009 (sliced from 18 cores from 7 trees, using a straight bladed scalpel) as a pilot investigation to determine the potential for further studies. The rings were processed to α-cellulose using the Brendel method (Brendel et al., 2000) modified for small samples (Evans and Schrag, 2004; Brookman and Whittaker, 2012). α-cellulose samples of ~250µg were analysed using continuous flow low-temperature pyrolysis in the Stable Isotope Facility at the University of Canterbury, Department of Geological Sciences. The mean external precision (i.e. reproducibility) of the system (Costech 4010 ECS coupled with Delta V Plus Isotope Ratio Mass Spectrometer via a ConFlo II) was better than 0.10‰ for carbon, based on over 1500 measurements of reference standard α-celluloses (Sigma-Aldrich and IAEA CH-3). All data were corrected to the V-PDB international scale for δ^{13}C using a 1-point normalisation (i.e. an additive correction) based on the SAC (δ^{13}C: -25.44) and IAEA CH-3 (δ^{13}C: -24.724‰) reference materials analysed in each sequence.
Appendices

The quality of the DK ring-width and isotope chronologies were tested using the expressed population signal (EPS) (Briffa and Jones, 1990) which essentially measures the level of common ring-width/isotope variation between trees. For the carbon isotope chronology EPS was conducted after correction for post-industrial changes in atmospheric CO$_2$ (McCarroll and Loader, 2004), which result in a gradual decline in $\delta^{13}$C. Traditionally an EPS score of 0.85 on a scale of 0 to 1 has been used as the benchmark for chronology quality; it suggests that the record is providing 85% ‘signal’ and 15% ‘noise’. Kauri tend

Fig. 8.11: DK site sampling images, showing the coring process amongst the tightly planted stand, with open understory but dense canopy.
to show strong common ring-width signal, often achieving an EPS of 0.85 from 10 trees (Fowler and Boswijk, 2003) whereas other species may require up to 25 (Briffa and Jones, 1990). EPS was calculated using the ‘detrendeR’ (Campelo et al., 2012) package in ‘R’ (R-Core-Team, 2012) in overlapping 10 year windows as well as the entire length of the ring-width chronology, while the carbon isotope record was analysed only as a single time period due to its shorter duration. The site ring-width master record was analysed for growth-trend changes using the segmented regression freeware SegReg (Oosterbaan et al., 1990; Oosterbaan, n.d).

Table 8.7: Summary of the DK ring-width record. A: correlation under 99% significance level but highest as dated; B: correlation higher at other than dated position.

<table>
<thead>
<tr>
<th>Tree</th>
<th>Core</th>
<th>DBH (cm)</th>
<th>Record length</th>
<th>Correlation with master (1980-2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK02</td>
<td>.1</td>
<td>32.7</td>
<td>1961-2008</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1970-2008</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1961-2009</td>
<td>0.54</td>
</tr>
<tr>
<td>DK03</td>
<td>.1</td>
<td>39.7</td>
<td>1964-2008</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1970-2008</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1963-2009</td>
<td>0.77</td>
</tr>
<tr>
<td>DK04</td>
<td>.1</td>
<td>32.5</td>
<td>1974-2008</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1964-2008</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1963-2009</td>
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</tr>
<tr>
<td>DK05</td>
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<td>32.5</td>
<td>1967-2008</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1957-2008</td>
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</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
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<td>DK06</td>
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<td>33.7</td>
<td>1967-2009</td>
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</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1971-2009</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1960-2009</td>
<td>0.65</td>
</tr>
<tr>
<td>DK07</td>
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<tr>
<td></td>
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<td></td>
<td>1968-2009</td>
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<tr>
<td></td>
<td>.3</td>
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<td></td>
<td>.2</td>
<td></td>
<td>1964-2009</td>
<td>0.31B</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1964-2009</td>
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</tr>
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<td>DK09</td>
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<td>1965-2009</td>
<td>0.28B</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1969-2009</td>
<td>0.33A</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1959-2009</td>
<td>0.54</td>
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<tr>
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<td>1962-2009</td>
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<td></td>
<td>1967-2009</td>
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<td></td>
<td>1967-2009</td>
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</tr>
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<td>1962-2009</td>
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</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1963-2009</td>
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</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1964-2009</td>
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</tr>
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<td>1969-2009</td>
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</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1972-2009</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1963-2009</td>
<td>0.69</td>
</tr>
<tr>
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<td>1962-2009</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td></td>
<td>1962-2009</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td></td>
<td>1967-2009</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Range/Mean: 34.0 1957-2009 45.1 0.57
8.7.3 Results and Discussion

8.7.3.1 Sample plot growth results

Based on the average quadratic mean diameter at breast height of 30.6cm in the 55 year old trees (at time of measurement), the average annual growth for the DK stand is ~5.6mm/year. Individual tree diameters ranged from 16.9-38.2 cm. Measured tree heights ranged from 10.2 to 21.1m, with a mean of 17.8m. Based on height-diameter relationships this established a mean top height for the stand of 23.8m. In comparison, the trees surveyed by Pardy et al. (1992) in 1986 ranged from 11.3-24.8cm DBH, with a quadratic mean diameter of 19.1cm, suggesting an average annual growth of ~6.2mm/year. Trees measured by Pardy et al. (1992) ranged from 10.7 to 15.2m tall, with a mean top height of 14.9m.

The 5.6mm/year diameter growth established from the growth plot shows that the DK trees are growing more rapidly than most young native stands. Pardy et al. (1992) suggest that in the early ‘pole’ stages of growth it is not uncommon for 5mm annual diameter increases in native stands, which is in good agreement with Burns and Smale’s 4.3mm/year figure from ~1-200 year old trees, generally still in ‘ricker’ form, on the Coromandel Peninsula. Steward and Kimberley (2002) recorded somewhat slower growth (1.3-3.4mm/year) in another natural stand of trees 120-218 years old. Considering climate alone, the DK trees’ higher average growth-rate compared to native stands in an area that receives regular frost, 8° S of their natural range is remarkable. However, the site selection and silvicultural attention (even when restricted to hand releasing seedlings from competing vegetation as in this case) afforded plantation trees introduce a number of variables beyond climate. It is not unusual for plantations of many species, even beyond their natural range, to exceed natural growth rates (Pardy et al., 1992). A large part of the DK trees’ success is likely due to site selection: growth trials have shown that kauri grow best amongst gaps within taller surrounding vegetation (Barton, personal communication). It may be that the surrounding, established plantation of native species at Wairongoa Springs created a favourable microclimate for kauri growth. Surrounding forest cover may help explain why Bergin and Steward (2004) suggest that there is no evidence of frost damage to DK trees, despite the fact that the area would regularly receive frosts lower than -4 to -6°C, which Barton (1982; 1985) found caused lasting damage or death of kauri seedlings. Barton’s personal observation is that frost damage may be a primary cause of multiple leaders in kauri, which are very rare on naturally established trees in forest or scrub-land. There are multiple trees at DK with double-leaders which could suggest non-fatal frost damage to seedlings, contrary to Bergin and Steward’s (2004) suggestion.

Perhaps a fairer growth comparison is between DK trees and that of other surveyed plantations, all of which are in the North Island. Plantation kauri generally grow faster than native stands and in some cases trees have averaged 10mm (diameter) growth for up to 40 years (Steward and Beveridge, 2010). While DK trees don’t quite achieve this rapidity, the estimated mean growth rate of the stand, based on external DBH measurement of a quadrat selected without size bias, (5.6mm/year) is only 0.7mm slower than the mean of 25 stands surveyed by Steward (2011, Table 8.8). It is also comparable to the 6.9mm/yr average documented by Pardy et al.’s 1986 (1992) survey) when considering that prior to ~1983, ring-width data...
(see below) suggests that DK trees grew ~12% faster than their long-term mean, meaning that mean growth at the time of Pardy et al’s (1992) sampling was likely closer to 6.3mm/year.

Table 8.8: A comparison of the performance and productivity of the Taeiri planted kauri at the last assessment with A) all other plantations and natural stands (North Island) surveyed by Steward (2011) and B) the same plantation as measured in 1986 by Pardy et al. (1992). ‘Quad DBH’ refers to the Quadratic Mean Diameter at Breast Height. Quad MAI refers to ‘Quadratic Mean Annual Increment (ie. growth)’ and Mean Top DBH to the modelled DBH expected when kauri reach the theoretical ‘top height’ (ie. felling age/proportion in a forestry sense) at age 50.

<table>
<thead>
<tr>
<th>A. Stand</th>
<th>Age (Years)</th>
<th>Mean Top Height (m)</th>
<th>Quad DBH</th>
<th>Quad MAI</th>
<th>Stems/ha</th>
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<td>DK</td>
<td>55</td>
<td>23.8</td>
<td>30.6</td>
<td>0.56</td>
<td>875</td>
</tr>
<tr>
<td>All Stands</td>
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<td>20.0</td>
<td>33.1</td>
<td>0.63</td>
<td>804</td>
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</table>

<table>
<thead>
<tr>
<th>B. Tree</th>
<th>1986 DBH (cm) (Pardy et al. 1992)</th>
<th>2010 DBH (cm)</th>
<th>1986 Height (m) (Pardy et al. 1992)</th>
<th>2010 Height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>292</td>
<td>21.8</td>
<td>36.5</td>
<td>13.7</td>
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</tr>
<tr>
<td>295</td>
<td>11.3</td>
<td>16.9</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>296</td>
<td>24.4</td>
<td>37</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>15</td>
<td>18.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>19.7</td>
<td>32.6</td>
<td>11.6</td>
<td>19.9</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
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<td>23.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>305</td>
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<td>32.8</td>
<td>14.3</td>
<td>20.5</td>
</tr>
<tr>
<td>306</td>
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<td>17.4</td>
<td></td>
<td></td>
</tr>
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<td>31.9</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
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<td>25.6</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>309</td>
<td>16.5</td>
<td>25.4</td>
<td></td>
<td>21.1</td>
</tr>
<tr>
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<td>36.6</td>
<td>14</td>
<td></td>
</tr>
<tr>
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<td>26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>312</td>
<td>16.8</td>
<td>28.1</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>24.8</td>
<td>38.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>21.5</td>
<td>36.2</td>
<td>12.8</td>
<td></td>
</tr>
<tr>
<td>315</td>
<td>17.6</td>
<td>29.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>17.5</td>
<td>28.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>317</td>
<td>20.9</td>
<td>34.3</td>
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</tr>
<tr>
<td>318</td>
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<td>30.7</td>
<td>12.5</td>
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<tr>
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<td>21.2</td>
<td>36.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>321</td>
<td>20.2</td>
<td>32.9</td>
<td></td>
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</tr>
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<td>19.4</td>
<td>32.3</td>
<td></td>
<td></td>
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<tr>
<td>324</td>
<td>20.9</td>
<td>35.4</td>
<td></td>
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<td>325</td>
<td>23.8</td>
<td>36.6</td>
<td></td>
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<td>326</td>
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<td>31.5</td>
<td></td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>328</td>
<td>15.7</td>
<td>24.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Arithmetic Mean: 18.8 30.0 12.9 17.8

Quad Mean DBH: 19.1 30.6

Mean Top Height: 14.9 23.8
Not only have the DK trees maintained remarkable radial growth given their situation, their height growth has exceeded the average seen in 25 planted stands within and outside the current natural range of the species (Table 8.8). Models of height growth of kauri in planted stands have been produced in an ongoing study of the potential productivity of kauri (Bergin and Steward, 2004; Steward and McKinley, 2005; Chikumbo and Steward, 2007; Steward and Beveridge, 2010). Height growth is frequently used in forestry to determine a ‘site index’, which refers to the timber potential for a site, usually at a fixed age somewhere near the expected rotation length for the species. For kauri in planted stands site index was defined by Steward (2011) as Mean Top Height at age 50. The site Index for DK was 22.7 m, against a national average of 20.4 m (Steward 2011). A comparison of predicted height growth from five individual planted stands (Fig. 8.12, using data from Steward 2011) located from Whangarei to the Bay of Plenty with the DK stand shows that, despite their southern location, height growth for the DK trees is similar to plantations within or near kauri’s modern natural range.

8.7.3.2 Ring-width and isotope chronology quality

The dendrochronological investigation of the Wairongoa Springs kauri proved challenging due to a lack of distinct marker rings in the relatively brief (52-year) chronology. Five (of 37) cores failed to meet the 99% significance correlation level usually used to determine successful cross-dating. This could reflect a number of factors:

1) Youth: young kauri grow quickly before slowing after passing their ‘ricker’ phase. This accelerated growth may obscure climatic signals and often coincides with high attrition rates as young trees compete for limited resources; attrition within the stand often introduces micro-scale, non-climate variability to the ring-width record, lowering the coherent signal within the stand (Wunder et al., 2013).

2) Microclimate: the Wairongoa Springs kauri grow on a flat site in a sheltered environment, at the northern end of the Taieri Plain, that is subject to less severe weather than much of the surrounding region. It may be that the trees are subject to few growth-limiting/stressful conditions, creating a ‘complacent’ chronology.
While some studies ‘improve’ their chronologies using stripping techniques for poorly correlated cores (eg Fowler and Boswijk, 2003), here we include all data. EPS results for the site suggest that the common signal between trees is strong despite those cores that presented problems in cross-dating. The early section of the chronology, before all trees/cores are represented, is the only stage where EPS values are below 0.85. From 1967 onwards 10-year windows of ring-width data, overlapped by 5 years, show EPS >0.85 (Table 8.9). These results suggest that the trees’ growth responds cohesively to their environment.

### Table 8.9: EPS scores for 10-year segments of the DK chronology. The ‘common interval’ EPS is provided at the base of the table; it represents the overall EPS for the time period covered by all individual series (cores).

<table>
<thead>
<tr>
<th>Start Year</th>
<th>End Year</th>
<th>Trees</th>
<th>Cores</th>
<th>EPS</th>
</tr>
</thead>
<tbody>
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<td>1971</td>
<td>8</td>
<td>11</td>
<td>0.158</td>
</tr>
<tr>
<td>1967</td>
<td>1976</td>
<td>13</td>
<td>29</td>
<td>0.867</td>
</tr>
<tr>
<td>1972</td>
<td>1981</td>
<td>13</td>
<td>36</td>
<td>0.953</td>
</tr>
<tr>
<td>1977</td>
<td>1986</td>
<td>13</td>
<td>37</td>
<td>0.940</td>
</tr>
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<td>0.932</td>
</tr>
<tr>
<td>1987</td>
<td>1996</td>
<td>13</td>
<td>37</td>
<td>0.970</td>
</tr>
<tr>
<td>1992</td>
<td>2001</td>
<td>13</td>
<td>37</td>
<td>0.940</td>
</tr>
<tr>
<td>1997</td>
<td>2006</td>
<td>13</td>
<td>37</td>
<td>0.924</td>
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<tr>
<td>1974</td>
<td>2008</td>
<td>13</td>
<td>37</td>
<td>0.959</td>
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The EPS result for carbon isotope site chronology is much lower than ring-width (0.68). While a major factor here is likely the disparity in sample-depth between the ring-width record (32 cores) and isotope record (18 cores), the EPS is nonetheless low compared to results from other studies in which 4-6 trees have often been sufficient to produce EPS scores > 0.85 (e.g. Robertson et al., 1997a; Robertson et al., 1997b; McCarroll and Pawellek, 2001; Porter et al., 2009). We consider the most likely reason for this is a combination of the sensitivity of young trees to micro-scale endogenous influences and the difficulties of processing kauri wood to α-cellulose (Brookman and Whittaker, 2012). While the EPS score makes relying on inter-annual δ¹³C changes problematic, we believe long term trends in the data are worthy of consideration.

### 8.7.3.3 Interpreting ring-width growth patterns

Having established the ring-width chronology’s quality, we proceeded to assess the kauris’ growth trends. Over the length of this record the average ring-width is 3.10mm, which translates to a DBH increase of ~6.2mm/year. Across the record there is a decreasing trend in ring-width (Fig. 8.13a). When analysed using segmented linear regression, however, the plantation’s growth can be split into two phases centred around the ‘break-point’ of 1983 (± 5.6 years, 95% confidence interval). The early phase from 1957 to 1983 maintains a constant (slope < 0.01, r² = 0.01) mean ring-width (3.5mm/year). From 1983 onward
there is a steady and significant (0.06mm/yr, $r^2 = 0.71$, p < 0.05) decrease in ring-width (Fig. 8.13b). This segmented linear regression model provides an ‘explained coefficient’ of 0.61, showing the improved fit of the model compared to a ‘whole record’ linear regression ($r^2 = 0.47$).

**Fig. 8.13:** A) The mean, raw ring-width chronology, showing a gradual decrease in annual growth over the 52-year record. B) The same chronology broken into two portions using segmented regression, showing 26 years of relatively constant growth followed by a growth-rate decline after 1983 (Black, dashed box indicates 95% CI of 1983 break-point). C) The separately determined carbon isotope record, showing the gradual decline in $\delta^{13}$C from 1983-2009.
The early growth spurt, followed by a decline in growth-rate fits patterns observed in other native tree plantations with minimal silvicultural management (Pardy et al., 1992). The growth-rate models developed for kauri by Steward (2011) provide an explanation for the growth rate decline documented in the ring-width record. Generally, the most likely cause of growth rate decline is resource competition/limitation; the DK trees were densely planted by forestry standards (~1250 stems/ha) in a small plot surrounded by established plantings (Steward, 2011). While this is many times denser than estimated natural densities of 50-200 stems/ha for mature forest (Ahmed and Ogden, 1987), it is comparable to the densities observed by Barton (1982) in the ‘sub-dominant’ and ‘shrub’ strata of natural stands. Plantation density itself does not necessarily limit growth but experiments showed that nutrient availability has a profound effect on growth (Barton and Madgwick, 1987). Nutrient and root space competition as well as limited light access in a rapidly converging canopy often result in growth-rate decline, with weaker individuals dying when their leaves no longer receive enough light to maintain positive carbon balance. The magnitude of this ‘self thinning’ effect is much debated in general forestry literature but the general principle is well established (Sackville-Hamilton et al., 1995); we believe this is the most likely scenario at Wairongoa Springs. For kauri, the general hypothesis of self-thinning is supported by the observations of self-thinning made by Steward (2011) from plantation trees and Burns and Smale (1990) in second growth natural stands.

At the last measurement (March 2010) the Taieri stand had a quadratic mean diameter of 30.6 cm, at a stand density of 875 stems/ha (Table 2). At 875 stems/ha the model for self-thinning predicts a diameter of 30.1 cm as the point where radial growth-rate will decline and natural mortality becomes likely to occur if thinning is not undertaken. As the Taieri stand only recently (~2009) exceeded the predicted diameter at last measurement (2010), it may be some time before actual mortality occurs. In other densely stocked kauri stands that are close to or have exceeded the self-thinning line, self-shading within the stand results and the lower crown collapses. Initially height growth may replace diameter growth as individual kauri compete for growing space and dominance. Artificial thinning of kauri in planted stands at New Plymouth resulted in a delay of one-two years before crown replacement and a rapid return to diameter growth. Similarly, results from thinned natural stands indicate that trees in a dense natural stand endured a long period of suppressed growth (Madgwick et al., 1982) before rapid diameter growth post-thinning (Barton and Madgwick, 1987).

The DK ring-width record suggests that the onset of self-thinning may have preceded the density-modelled timing (2009) by 26±5.6 years based on the 1983 break-point evident in the segmented regression, although the 2009 and 1983 dates are only approximately comparable as the former is based on an ‘over-bark’ measure of DBH while the latter excludes bark. The early onset of self-thinning may serve to explain why the DK trees exceed the plantation height average, as they have prioritised height growth over diameter growth in an extended competition for light. The earlier onset of light-based competition at DK compared to observations from other kauri stands could be explained by the other, more mature mixed native plantings surrounding the DK site shading the kauri and creating an enhanced level of light competition. The shorter growing season and reduced sunshine hours at the DK
site compared to kauri’s natural range may also contribute. The DK site generally receives <1700 hours of sunshine annually, compared to the bulk of kauri’s natural range which receives >1900 hours (NIWA, 2012a).

8.7.3.4 Interpreting the carbon isotope record

Further support for the early onset of self-thinning and resource limitation is provided by the carbon isotope record compiled from DK trees. Across the 1983-2009 period there is a significant ($p < 0.05$) decreasing trend in $\delta^{13}C$ (Fig. 8.13c) despite correction for the post industrial atmospheric CO$_2$ depletion trend. The direction of the trend is opposite to the positive trend generally considered characteristic of the ‘juvenile effect’ so we suggest that this trend is not directly age related. In fact it may be considered to exist ‘in spite’ of age, as the ‘juvenile effect’ documented for kauri lasted 200 (Jansen, 1962) or more (Grinsted and Wilson, 1979) years. Walcroft (1994) was the first to note a reversal of the normal juvenile pattern when he observed higher $\delta^{13}C$ in juvenile kauri leaves compared to mature leaves. He suggested that the most likely cause was the morphological differences between juvenile and mature foliage; juvenile leaves have a thinner cuticle and consequently are likely to lose more water through peristomatal respiration than xerophyllic mature leaves (Walcroft, 1994). The likely result is that juvenile leaves restrict stomatal conductance to maintain their leaf-water potential, thereby decreasing the relative pressure of intercellular to ambient CO$_2$, meaning that the carboxylation process must make do with the available CO$_2$, reducing fractionation and raising $\delta^{13}C$ (Francey and Farquhar, 1982).

While leaf morphology may contribute to the decreasing trend in DK $\delta^{13}C$ but we suggest there is another possible cause. One frequently postulated cause of the ‘juvenile effect’ is the gradual release of young trees from the shading of the canopy (Francey and Farquhar, 1982); as they receive more sunlight their photosynthetic rate increases, lowering the relative pressure of intercellular to ambient CO$_2$, causing $\delta^{13}C$ to rise. A related hypothesis is that there is a corresponding reduction in the amount of sub-canopy $^{13}C$ depleted, respired CO$_2$ utilised during photosynthesis (Schleser and Jayasekera, 1985). However, in the plantation environment at DK the situation may be reversed; seedlings, planted in a clearing had little competition for light and were in a well mixed, rather than stratified, atmosphere. As the kauri have grown, however, their dense plantation layout means that they have effectively competed with each other, shading one-another’s canopies. Canopy shading reduces photosynthesis (Walcroft et al., 2002) and results in lower $\delta^{13}C$ (Francey and Farquhar, 1982), so this plantation-specific situation of increased competition with height may be chemically represented in the tree-ring cellulose $\delta^{13}C$.

Unfortunately, at this stage our data cannot provide a conclusive answer to this question, as they only cover the period of decreasing ring-width so we are unable to assess whether tree-ring $\delta^{13}C$, like ring-width, was relatively constant prior to 1983. However, we tentatively suggest that this ‘reverse juvenile effect’ may be a chemical analogy for the decrease in ring-width over the same time period, caused by the same increased light competition. Whether leaf morphology, canopy shading, or a combination of the two are responsible for the ‘reverse juvenile effect’ documented, a potentially valuable avenue of inquiry for dendroclimatic study of kauri chemistry is to establish whether this plantation situation finds similarities
in natural kauri stands, where saplings grow into dense ricker-thickets. Such a finding would require
researchers to consider disregarding multi-decadal (or longer) trends in any juvenile trees/rings. Although
this cautionary approach has already been adopted by some researchers (Leavitt, 2010), the relatively
minor age effects associated with dendrochemistry compared with ring-width study is seen as one of its
major strengths (Loader et al., 2013).

**8.7.4 Conclusions**

Beyond their remarkable history, the Wairongoa Springs kauri provide a unique botanical opportunity
to better understand the ecology and forestry potential of one of New Zealand’s iconic species, growing
essentially untended well outside its current natural range. Ring-width patterns show the stand responding
to its environment in a cohesive manner. The average growth rate of DK trees is comparable to other
plantations, an exceptional result given the site is >20% cooler, >40% drier and receives >200 less
sunshine hours each year than most of kauri’s current natural range. After a period of continuous, rapid
growth, the kauri’s growth-rate has consistently slowed since 1983 to the present, probably reflecting
competition for a combination of root space, nutrients and light. This may suggest the onset of the ‘self
thinning’ process, well documented for kauri. A corresponding decrease in tree-ring δ¹³C over the same
time-period could also be explained by increased light competition, creating a ‘reverse juvenile effect’
which serves as a dendrochemical analogy for the self-thinning evident ring-width signal. The onset of
growth decline is much earlier (26 ± 5.6 years) than modelling predicts, which may reflect site specific
influences related to enhanced light competition and/or climatic stress due to the reduced temperature,
rainfall and sunshine hours for DK compared North Island locations. Nonetheless, the success of the
Wairongoa Springs plantation suggests that kauri can be successfully grown in sheltered sites far south of
its natural range, although stand density may need to be slightly lower than northern plantations to avoid
early onset self-thinning.

**8.7.5 Acknowledgements**

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their support of the research.

**8.7.6 Author Contributions**

THB co-designed the dendrochronological research, conducted fieldwork, processed and analysed
samples for carbon isotope determination, statistically analysed data and conceived and prepared
the manuscript. GAS developed and contributed the kauri forestry modelling, conducted the PSP
measurements and contributed to the writing of the corresponding sections of the manuscript. JGP
co-designed the dendrochronological research, conducted fieldwork and revised the manuscript. PF
conducted all dendrochronology and revised the manuscript. AHB facilitated fieldwork, provided historical background to the site and revised the manuscript. TWH contributed to project design, stable isotope analysis and manuscript preparation. All authors read and approved the final manuscript.
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8.8 Detailed Extraction Protocols

The following text, unchanged other than pagination and formatting, is taken from supplemental information to:


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8.8.1 Canterbury Stable Isotope Laboratory α-cellulose Processing Method

Prepared by Tom Brookman, January 2011

This laboratory procedure is based on the Standard Brendel (Evans and Schrag, 2004) and modified (for resinous wood) based on our experiences at the University of Canterbury. We homogenise our samples using an ultrasonic probe, as documented in Laumer et al. (2009)

8.8.1.1 Sample preparation procedure:

For this study 0.5g ponderosa and huon pine core sections were powdered using a dremel rotary drill. New Zealand kauri was powdered using a wood saw on a thick chunk of wood. The powder was then sieved into <355μm and >355μm fractions and the <355μm fraction homogenised in de-ionised water using an ultrasonic probe for a number of minutes. The powder was then dried in a low (50°C) oven and broken into sub samples for processing.

For tree ring samples we slice <3mg wood by hand into slivers of ~0.5x0.5x2-3mm.

8.8.1.2 Procedure as standard for tree ring material (experiment #7 in the manuscript):

1. Using 1000μL pipette, add 360 μL 80% acetic acid into sample tubes.

2. Using 100 μL pipette, add 36 μL 69% nitric acid into sample tubes.

3. Cap securely, ensure all wood is submerged and insert tubes into heating block (at 120°C) and extract for 30 minutes.

4. Remove heating blocks from heat plate and set aside to cool (~10 minutes)
5. Using 1000 µL pipette, add 1ml ethanol to tubes. Shake, centrifuge for 4 minutes at 12, 000 RPM. Using the same pipette, remove as much supernatant as possible and discard into dedicated beaker (Ethanol, Acetic, Nitric). Discard pipette tip.

6. Add 1ml de-ionised water to tubes. Shake, centrifuge for 4 minutes at 12, 000 RPM. Using the same pipette, remove as much supernatant as possible and discard into dedicated beaker (ethanol, de-ionised water). Discard pipette tip.

7. Add 1ml ethanol to tubes and let tubes rest while cellulose settles to the bottom (usually 10+ minutes). Using same pipette, remove as much supernatant as possible and discard into dedicated beaker (ethanol, de-ionised water). Discard pipette tip.

8. Add 1ml acetone to tubes and let tubes rest while cellulose settles to the bottom (usually 10+ minutes). Using same pipette, remove as much supernatant as possible and discard into dedicated beaker (acetone). Discard pipette tip.

9. Place samples in warm (50-60°C) oven until dry (usually 30+ minutes). Leave caps in a safe place in order that tubes are in micro-tube rack.

10. Add ~1ml de-ionised water to each sample and refrigerate overnight.

11. Pack refrigerated samples into an ice-tray to keep cool and individually homogenise using ultrasonic probe until cellulose is no longer fibrous in appearance (~½-1 minute).

12. Return samples to low (50-60°C) oven until dry (~2 days). Cellulose should be a fine, white powder.

8.8.1.3 Further preparation for Isotope analysis:

1. Mass samples into 5x3.5mm capsules (silver for oxygen, tin for carbon) and fold capsules into small cubes.

2. For oxygen only: place massed, boated samples into a nunc tray and secure a kimwipe over the top with rubber bands. Place in the vacuum dessicator for a minimum of 24hrs prior to analysis. Samples should be transferred directly from the nunc tray to the autosampler and flushed with helium with the purge valve open for a minimum of 10 minutes followed by ~30 minutes with the purge valve closed.

8.8.2 University of New Mexico Department of Earth and Planetary Sciences α-cellulose Preparation Method

Prepared by Thomas Whittaker, January 2011
8.8.2.1 Sample preparation procedure:

For this study 0.5g samples of each of ponderosa pine, huon pine and New Zealand kauri were diced into slivers approximately 1x0.5x3 mm in size. These slivers were then freeze milled. The freeze milling process involved packing slivers and a steel ball bearing into a steel canister before immersing the canister in liquid nitrogen until vigorous bubbling ceased. The canister was then quickly transferred to a Crescent™ WiggleBug and vibrated at maximum speed for 2 minutes. Powder produced by freeze milling was then sifted into <355μm and >355μm fractions. The >355μm fraction was then freeze milled again, and the sifting process also repeated. The <355μm fractions were homogenized further by stirring and shaking.

8.8.2.2 Single amount (½ hr boil) mBrendel (experiment #1 in manuscript):

1) Enter 1.00 ± 0.02 mg of powdered wood into a flip-top 1.5ml microcentrifuge tube.

2) Into the microcentrifuge tube pipette 120 µL 80% acetic acid and 12 µL 69% nitric acid.

3) Cap the microcentrifuge tube, place in an aluminum heating block and heat at 115°C for 30 minutes.

4) After 30 minutes turn off heat and allow to cool to room temperature (~1 hour).

5) Pipette 400 µL of 100% ethanol into the microcentrifuge tube.

6) Re-cap the tube and centrifuge at 9000 rpm for 6 minutes.

7) Remove supernatant from centrifuge tube using a pipette.

8) Pipette 300 µL of distilled de-ionized water into the microcentrifuge tube, cap the tube, and centrifuge at 9000 rpm for 6 minutes.

9) Remove supernatant from centrifuge tube using a pipette.

10) Pipette 150 µL 100% ethanol into the microcentrifuge tube, cap the tube, and centrifuge at 9000 rpm for 6 minutes.

11) Remove supernatant from centrifuge tube using a pipette.

12) Pipette 300 µL of general purpose grade acetone into the microcentrifuge tube, cap the tube, and centrifuge at 9000 rpm for 6 minutes.

13) Remove supernatant from centrifuge tube using a pipette.

14) Dry in a warm (~80°C) oven for 45-60 minutes.
15) Store overnight in a vacuum desiccator.

References


8.9 A Brief Overview of Dual Element Low-Temperature Pyrolysis

8.9.1 Introduction/Background

The large number of samples needed to conquer individual variability within palaeo-records, particularly tree-rings, means that studying extended and/or high resolution records using stable isotopes is a time and resource intensive process. Consequently, even small advances in methodological procedure/efficiency, whether in sample preparation (Dodd et al., 2008; Wieloch et al., 2011), processing (Boettger et al., 2007; Brendel et al., 2000; Evans and Schrag, 2004; Li et al., 2011; Loader et al., 1997), homogenisation (Laumer et al., 2009) or analysis (Knöller et al., 2005; Leuenberger and Filot, 2007; Saurer et al., 1998; Woodley et al., 2012; Young et al., 2011) can have significant repercussions for scientific progress.

Another hurdle for stable isotope dendroclimatology is the lack of a certified reference material (CRM) for organic δ^{18}O, an issue that has long been recognised (Saurer et al., 1998) and has been the subject of extensive interlaboratory comparisons, debate and research (Boettger et al., 2007; Brand et al., 2009; Saurer et al., 1998). The major issue with cellulose as an international standard is its hydroscopic nature, which means that adsorbed H_{2}O of local atmospheric composition almost always alters the apparent δ^{18}O (Brand et al., 2009). At odds with the need to use a CRM is the need to use standards that match the chemical/crystalline composition of the samples.

Early researchers in the field of on-line pyrolysis methods, both low temperature (LT) (Saurer et al., 1998; Werner et al., 1996) and high temperature (HT) (Kornexl et al., 1999) saw potential for dual analysis of δ^{18}O and δ^{13}C from CO, effectively doubling analytical efficiency. However, the idea lost favour and until recently the prevailing thinking was that the two should be analysed separately (Woodley et al., 2012; Young et al., 2011). In recent years, however, experimentation with dual analysis of CO has been revisited with varying levels of success (Knöller et al., 2005; Leuenberger and Filot, 2007), culminating in a promising and comprehensive study by the Swansea University Tree Ring Group (Woodley et al., 2012; Young et al., 2011).

On-line pyrolysis commonly takes two forms: 1) HT (~1400+ °C) conversion in a TC/EA (Thermal Conversion Elemental Analyser) or 2) LT (1000-1090 °C) conversion in a modified EA (Elemental Analyser). For cellulose, the benefit of HT pyrolysis is the quantitative conversion of sample C and O into CO (Leuenberger and Filot, 2007; Loader and Buhay, 1999). The disadvantage is the relatively time consuming and expensive process of running a TC/EA.

LT pyrolysis generates products other than CO (CO_{2}, H_{2}O, H_{2}) (Leuenberger and Filot, 2007; Loader and Buhay, 1999). The fractionation during creation of these extra products also potentially biases results; as little as <60% of sample O and 40-50% of sample C may be analysed as CO (Leuenberger and Filot, 2007). Provided these challenges can be overcome through sufficient correction using cellulose standards, the LT conversion has the significant long term advantage of requiring less maintenance and using cheaper consumables, both significant factors in a field that demands large sample numbers.
No matter the temperature, pyrolysis of cellulose results in the deposition of at least one carbon atom from each molecule as cellulose has a 6:5 ratio of carbon-to-oxygen (C6H10O5); one carbon atom must remain un-bonded during even quantitative CO conversion (Woodley et al., 2012; Young et al., 2011). The result appears to be a bias towards the mean δ¹³C of the sample set, reducing the natural variance within the data. This effect is less prominent in LT systems making the ‘raw’ data serviceable for long-term climatic reconstruction whereas HT data may require ‘pyrolysis correction’ (Nakatsuka et al., 2004; Woodley et al., 2012; Young et al., 2011).

Recent literature generally agrees that high temperature pyrolysis provides usable δ¹⁸O and δ¹³C from a single analysis (Knöller et al., 2005; Leuenberger and Filot, 2007; Nakatsuka et al., 2004; Woodley et al., 2012). On the subject of low temperature pyrolysis, however, there is less certainty: Leuenberger and Filot (2007) argue that some carbon in analysed CO is contributed by glassy carbon and suggest that pyrolysis/reduction should only be performed at temperatures >1450°C. In contrast, Young et al. (2011) suggest that LT pyrolysis includes no contribution from glassy carbon and that the data are sound; they may require less correction than HT (Woodley et al., 2012). The reinvestigation of ideas explored a decade ago is limited to a small number of specialist laboratories and a broader data-set is required before the methodologies can be applied to main-stream research. In particular, the careful use of standards to correct data requires further consideration.

8.9.2 The UC Setup

Chapter 5 details the UC Dual C and O low temperature pyrolysis analytical setup and resultant precision and accuracy (seen in Fig. 8.14 below). The results demonstrate that, in agreement with Young et al.’s (2011) findings, Dual C and O low temperature determinations on α-cellulose are as precise as traditional separate high temperature and pyrolysis (O) and combustion (C) methods. The accuracy of δ¹³C results from low temperature determinations, however, remains an issue without sufficient correction, ideally using a two-point/stretch and shift/mean and variance bias approach based on two isotopically disparate standards. The development of such standards is a time-intensive process due to the lack of commercial and/or certified material; it is an ongoing process at UC.

Aside from small accuracy concerns, generally considered negligible for palaeoclimate reconstruction (Young et al., 2011), dual element low-temperature pyrolysis provides a time and cost effective means of analysing cellulose. The analytical setup on a Costech 4010 ECS (Elemental Analyser) is essentially an oxygen configuration per the Costech user manual, with the potential modification of an additional heating system to improve ‘bake out’ the gas chromatographic column (GC). Early early trials used heat tape attached to a thermocouple to bring the column, usually restricted to 110°C within the inbuilt oven, up to 270°C. The rudimentary UC setup, however, resulted in increased laboratory ‘clutter’ and when trials without the additional heating showed no appreciable reduction in precision, the standard GC column oven was run continuously at 110°C. Provided dilution is not used, samples under 100μg can be analysed (Fig. 8.15), although ~250μg samples are desirable as they allow equivalent sample and reference gas peak heights, while maintaining reliable reference gas delivery pressure.
Fig. 8.14: UC LT Pyrolysis schematic on a Costech 4010 ECS.

Fig. 8.15: Isodat 2.0 Workspace view of a 116µg MtC α-cellulose sample, showing that despite the small sample size, all CO isotopologues recorded intensities (voltages) >2000mV. Early experimentation showed that even intensities of ~1000mV provided reliable reference standard replication.
References


8.10 Distribution of Sample and Outlier Residuals – implications for system improvement

In order to assess whether there was a bias in the sample set or outliers we plotted sample and standard residuals (sample/standard value, minus median value for that series) and plotted histograms to assess kurtosis and skew (Fig. 8.17). Residuals data for standards’ δ\(^{13}\)C and δ\(^{18}\)O have highly leptokurtic distributions, which is encouraging as it shows the bulk of values are clustered tightly about the median. δ\(^{18}\)O residuals have a slight negative skew while δ\(^{13}\)C residuals have a positive skew (Fig. 8.17a). However, the skew is reversed in the all-sample residuals (Fig. 8.17b), suggesting that outliers caused by poor sample drops or other analytical faults do not have a particular isotopic signature as that would result in a consistent, pronounced skew. Encouragingly, the outlier-stripped sample data (Fig. 8.17c) show an almost normal distribution with minimal skew or kurtosis and means and medians of very close to zero for both δ\(^{13}\)C and δ\(^{18}\)O. A normal distribution means that statistical tests that assume normality can be readily applied and is also often a good approximator of variability in natural systems, suggesting outlier removal was both effective and justified.

At this stage we believe that the system can be improved in two major ways: firstly, visual observation of ‘drops’ from the autosampler showed a small number of samples sticking to the inside of the quartz tube, well above the glassy carbon chips. These samples presumably pyrolised at lower temperature and, we believe, are the most likely cause of occasional unexplained outliers in our standards. We hypothesise that the lower temperature pyrolysis of samples stuck to the quartz tube above the glassy carbon alters the conversion of cellulose to CO (Leuenberger and Filot, 2007), influencing the δ values without influencing the spectra. The outliers seemed more frequent during a reactor’s middle-age; LT pyrolysis results in a solid ball of silver building on top of the glassy carbon, which may gradually alter the He flow pattern. Further investigation is needed in this area but it seems that modification of the He flow (either amount or positioning) into the reactor is a potential solution.

The second improvement is the introduction of a retrofitted heating system for the gas chromatograph column (GC), allowing heating to ~250-270°C may improve δ\(^{18}\)O precision by ensuring that all H\(_2\)O is driven out of the GC. From our brief experiment it certainly reduces the length of bake-out required before running/after maintenance. Michael Evans has consistently achieved better analytical precision than we present here, on smaller samples, and the modified GC within his system is a likely contributor to that.
Fig. 8.17: Distribution of residuals from LT pyrolysis standards (column a), all LT pyrolysis samples (column b) and LT pyrolysis samples after box and whisker outlier stripping (column c).

References

### 8.11 DK δ¹⁸O Data

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Appendices

13C Core-Stripped Dataset
### 8.15 DKHR Data - ‘Binned’ and Resampled Series

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| 34   | June     | 6     | 33.79| 33.80| 34.81| 33.21| 1.95  | 1.13  | 1.37 |
| 33   | May      | 5     | 33.09| 31.03| 31.45| 35.50| 33.28| 1.97  | 0.98 | 2.59 |
| 32   | April    | 4     | 31.01| 30.75| 31.29| 32.54| 31.00| 1.47  | 0.74 | 1.12 |
| 31   | March    | 3     | 32.31| 29.02| 30.60| 29.92| 30.59| 1.52  | 0.76 | 1.71 |
| 30   | February | 2     | 31.24| 28.83| 30.62| 34.67| 31.58| 2.13  | 1.07 | 3.01 |
| 29   | January  | 1     | 31.00| 29.83| 30.95| 32.08| 30.83| 1.03  | 0.51 | 1.14 |
| 28   | December | 12    | 31.22| 29.60| 31.45| 31.11| 31.08| 0.12  | 0.06 | 1.08 |
| 27   | November | 11    | 30.78| 31.05| 30.82| 32.27| 31.97| 1.13  | 0.56 | 1.36 |
| 26   | October  | 10    | 31.77| 33.39| 32.39| 32.80| 32.25| 1.21  | 0.60 | 0.96 |
| 25   | September | 9     | 33.94| 33.60| 33.01| 33.19| 33.28| 0.67  | 0.33 | 0.56 |

1982

| 48   | August   | 8     |      |      |      |       |       |       |      |
| 47   | July     | 7     |      |      |      |       |       |       |      |
| 46   | June     | 6     |      |      |      |       |       |       |      |
| 45   | May      | 5     | 30.68| 30.70| 30.28| 30.49| 0.29  | 0.21  | 0.25 |
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Appendices

8.16 DKHR Binning Spreadsheet

See excel spreadsheet available from http://library.canterbury.ac.nz/

8.17 Compiled Isotope Time-Series

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### 8.18 VCSN Data Details

Due to data usage permissions, copyright I was unable to directly include the climate data used here.

However, readers can access the data at no cost using CLIFLO, a database maintained by NIWA, by registering at [http://www.cliflo.niwa.co.nz/](http://www.cliflo.niwa.co.nz/) and using the following information.

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### 8.19 Barbour et al. 2004 Mechanistic Model

See excel spreadsheet available from [http://library.canterbury.ac.nz/](http://library.canterbury.ac.nz/)