http://researchspace.auckland.ac.nz

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author’s right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author’s permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage. http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form and Deposit Licence.

Note: Masters Theses

The digital copy of a masters thesis is as submitted for examination and contains no corrections. The print copy, usually available in the University Library, may contain corrections made by hand, which have been requested by the supervisor.
A Diatom Stable Isotope Paleolimnology of Lake Pupuke, Auckland, New Zealand

Thomas William Stephens

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy in Geography

The University of Auckland
2011
ABSTRACT

High-resolution, continuous environmental records spanning the late Quaternary are scarce from the mid-latitudes of the SW Pacific sector of the Southern Hemisphere. However, detailed sedimentary records of the late Quaternary exist in Auckland’s volcanic crater (maar) basins. The purpose of this study is to reconstruct a continuous, high-resolution record of paleoclimate from an Auckland maar, Lake Pupuke, through: (1) the construction of a detailed tephra and radiocarbon-based chronology; (2) application of a suite of proxies for environment including novel diatom stable isotopic proxies (δ\(^{18}\)O\(_{\text{Diatom}}\) and δ\(^{30}\)Si\(_{\text{Diatom}}\)); and (3) a multi-proxy reconstruction of paleolimnology from ~48 cal. kyr BP until today.

A mixed-effect regression age-depth model was constructed from tephra and radiocarbon age-markers (n = 11, 13 respectively), permitting reconstruction of paleoclimate at Lake Pupuke during the last ~48 kyrs (~14 m) from biological (diatom), geochemical (TOC, TN, TS, δ\(^{13}\)C, δ\(^{15}\)N, ITRAX) and physical (magnetic-susceptibility, particle-size distribution) proxies for environmental and limnological change. Paleoclimatic inferences are made from δ\(^{18}\)O\(_{\text{Diatom}}\) and δ\(^{30}\)Si\(_{\text{Diatom}}\) proxies following a novel approach to tephra-contaminant removal involving physical separation and geochemical mixture modeling. Estimates of the Oxygen and Silicon contributed by basalt and rhyolite contaminants were combined with representative δ\(^{18}\)O and δ\(^{30}\)Si signatures to yield a basaltic and rhyolitic isotope effect. Once removed, this yielded tephra-free estimates of δ\(^{18}\)O\(_{\text{Diatom}}\) and δ\(^{30}\)Si\(_{\text{Diatom}}\) for the Pupuke paleo-record from ~48 cal. kyr BP until today.

A synthesis of multi-proxy inferences on erosion, biological productivity, mixing and lake level generates robust dates for the onset of reduced effective precipitation and cooling in the Last Glacial Coldest Phase (LGCP; ~28.5-18.5 cal. kyr BP), a return to warmer, wetter climate in the Last Glacial-Interglacial Transition (LGIT; 18.5-10.2 cal. kyr BP), and warmest conditions in the Holocene (post-10.2 cal. kyr BP). The LGCP, LGIT and Holocene exhibited marked paleoclimatic variation at Lake Pupuke, including harshest paleoclimate near the onset and termination of the LGCP (~27.6-26.0 and ~21.0-19.0 cal. kyr BP), a Late Glacial Reversal in climate amelioration (LGR; ~14.5-13.6 cal. kyr BP) and a Holocene rise in seasonality (from ~5.7 cal. kyr BP, intensifying from ~3.2 cal. kyr BP).
This thesis/desk weight/example of how to remain in student debt (delete as appropriate) is dedicated to Rachael Pentney for her endless support, home-brew for its improving taste, and to the Burgess, Pentney, Greer and Stephens families without which this PhD could not have been submitted.
ACKNOWLEDGEMENTS

Collaboration

This study of Lake Pupuke was performed in conjunction with a fellow doctoral candidate, Daniel Atkin (University of Auckland). All bulk sediment analyses within Chapter 4 were carried out in a collaborative effort between Dan and myself, and he deserves my thanks for this work and discussion of the Lake Pupuke dataset.

Supervision and Advice

Paul Augustinus (University of Auckland) has provided critical insight and valued advice throughout this research at the University of Auckland. His (legible) comments on drafts of this thesis have improved it substantially. Likewise his comments on grant and scholarship applications have rewarded the author with significant funding. Thank you for providing the opportunity to conduct this research.

Alayne Street-Perrott (University of Wales, Swansea) sowed the seed to undertake this doctorate at the University of Wales, Swansea through her extensive knowledge of Quaternary paleoclimate. Thank you for all your help in securing NERC funding as well as forging links with truly exceptional academics, notably Philip Barker and Melanie Leng.

Philip Barker (University of Lancaster) has provided countless hours of guidance, practical experience and the opportunity to conduct research at the University of Lancaster. Thank you especially for access to the SPLITT-fractionation equipment and for addressing so many of my queries and concerns on diatom stable isotope geochemistry.

Melanie Leng (National Isotopes Geosciences Laboratory) has offered exceptional guidance and a critical insight to diatom isotope geochemistry at the National Isotope Geosciences Laboratory (Natural Environment Research Council). Thank you especially for your support of our NERC-grant throughout the application process and subsequently in this research, especially when faced with the daunting challenge of cleaning the samples.

Phil Shane (University of Auckland) has provided specialist insight and advice throughout the doctoral process at the University of Auckland, also offering support and a critical review of aims, methodologies and findings.

Ursula Cochran (Geological and Nuclear Sciences) has provided invaluable diatom advice throughout this doctorate and is to be thanked especially for fitting this around a hectic personal schedule. Thank you for identifying diatom taxa and providing abundance/concentration estimates. Congratulations on your new family and thank you.
Discussion

The following people provided invaluable information and discussion. Thank you for the willingness to share your knowledge, expertise and experience.

Andrew Lorrey (National Institute of Water and Atmospheric Sciences) has proven a truly remarkable advisor, offering critical insight, review and settling the doctoral boat when the crew threatened to mutiny. Thank you especially for offering critical feedback at a busy time for yourself, when under no obligation, and more importantly, with none of the supervisor’s reward. By rights you deserve to be the third supervisor in this project.

George Swann (National Isotopes Geosciences Laboratory) offered countless insights to the methodological constraints on diatom isotope geochemistry as well as guidance on limiting the impact of uncertainties. Thank you for also directing me to key literature on contemporary studies of diatom isotope systematics.

Mike Reid (University of New England) kindly supplied the diatom calibration dataset for application of his diatom transfer function in this research. Thank you very much for the opportunity to demonstrate its capacity to reconstruct past environment at Lake Pupuke as well as the critical insights to its application.

Russell Frew (University of Otago) graciously supplied several months of stable isotopes in precipitation data for the North and South Island of New Zealand. The latter was critical in observing the isotopic behavior of Lake Pupuke and therefore underpins the novel proxy development contained in this thesis. Thank you.

Martin Neale (Auckland Council) proved exceptional at supplying a lengthy monitoring dataset of water quality at Lake Pupuke as well as aiding its interpretation. Thank you.

Field Assistance

Thank you to all the field and technical staff at the University of Auckland for their willingness to get cold and wet for the sake of a decent water quality specimen, muddy sample bag or lost sediment trap. In particular, thanks to:

David Jenkinson, Brendan Hall, David Wackrow and Russell Clarke.

In addition thanks to several of the doctoral candidates at the University of Auckland for also offering to get muddy at the lakeside, including:

Daniel Atkin, Hiroki Ogawa and Aleksandra Zawalna-Geer.

Special thanks is also needed for Ian Snowball and Andreas Nilsson at the University of Lund for aiding collection of sediment cores at Lake Pupuke and keeping the author amused in Wellington and Vienna.
Technical Assistance

This thesis required the expert guidance and supervision of laboratory staff across the world, at NIGL (UK), the University of Auckland (NZ), the University of Lancaster (UK) and GNS (NZ). Thank you to all involved but especially:

Hilary Sloane (National Isotopes Geosciences Laboratory) for your expertise in stable isotope geochemistry and for shouldering so much of the “life affirming” laboratory work at NIGL. Thank you also for persevering when others would have refused my samples.

Andy Quin (University of Lancaster) for permitting my access to the facilities at the University of Lancaster’s School of Geography and continued help to clean the SPLITT fractionation equipment.

David Jenkinson, Ritchie Sims and John Wilmshurst (University of Auckland) for permitting me continued access to the laboratory facilities in the School of Environment, even after the numerous mishaps and incident reports.

Ursula Cochrane (Geological and Nuclear Sciences) for counting the innumerable (poorly manufactured) diatom slides during this thesis.

Catherine Molloy (University of Auckland) for describing the geochemistry of the tephra employed in this thesis.

Auckland Council was also instrumental in permitting access to monitor and sample Lake Pupuke.

Kristian Saethers for printing and binding this thesis when he could have been at Old Government House.

Financial Support

Thank you to the numerous organizations that made this research possible through their support of the author.

The New Zealand Vice-Chancellor’s Committee in conjunction with the Commonwealth Scholarship and Fellowship Program awarded a Commonwealth Doctoral Scholarship to the author.

The Scholarships Sub-committee (UoA) for awarding a further 6-month doctoral stipend to cover the extended duration of research.

The Royal Society of New Zealand awarded a Marsden Fund grant (UOA0517) to Paul Augustinus which funded much of the analytical research undertaken by the author.

The Natural Environment Research Council (NERC) graciously awarded a competitive research grant (IP/995/1107) to the author (c/o Prof. Alayne Street-Perrott and Prof. Melanie Leng) to fund the cost of high-resolution stable isotope analyses of biogenic silica extracted from the Lake Pupuke sediment.

The Scholarships Council (UoA) awarded a Universitas 21 Doctoral Mobility Scholarship to support research exercises in the UK aimed at developing novel diatom stable isotope approaches to paleolimnology.
Education New Zealand (NZ) awarded a competitive grant to support research exercises in the UK aimed at developing novel diatom stable isotope approaches to paleolimnology.

The School of Environment (UoA) has provided several competitive grants to attend conferences (INQUA 2007, EGU 2010) and an advanced statistical short-course in paleoecological data at University College London (UCL, 2009).

The Faculty of Science (UoA) awarded a doctoral scholarship to the author to permit publication of this thesis.

A special word of thanks is directed at Patrick Stephens for generously tiding the author through his student loan obligations.

Personal Support

By far the biggest thanks of all are reserved for those who over the past four years have shared their humour and conversation with the author (despite his slightly Baldric-like undertones) especially at the darkest hours. Thanks to Dan, Ola, Kris, Amy, Hiroki, Corina, Francis, Steve, Murray, Nat, Joe, Lou, Lucy, Ritchie and last but not least, Barry.

I would also like to thank Rachael Pentney for politely smiling through every inane conversation about possible causes of diatom isotope fractionation, sedimentary age-depth models, Quaternary paleoclimate and the joys of neon lit, dirty laboratories. You’re exceptional and although less than by comparison, this thesis could not have been completed without you.

I must also thank all those who upon reading this believe they have been omitted whether by accident, for which I am truly sorry because without your help this would not have been made possible, or not. Please consider yourself in the first category. Thank you.
# TABLE OF CONTENTS

ABSTRACT.................................................................................................................. ii  
DEDICATION................................................................................................................ iii  
ACKNOWLEDGEMENTS.............................................................................................. iv  
TABLE OF CONTENTS ............................................................................................... viii  
LIST OF FIGURES ......................................................................................................... xliii  
LIST OF TABLES .......................................................................................................... xxii  
GLOSSARY ................................................................................................................... xxxv  

CHAPTER ONE: INTRODUCTION ................................................................................. 1  
1.1 The INTIMATE Project ....................................................................................... 1  
1.2 The NZ-INTIMATE Project .............................................................................. 2  
1.3 Research Objectives ......................................................................................... 8  
1.4 Research Approach ............................................................................................ 8  
1.4.1 Paleolimnology .............................................................................................. 9  
1.4.2 Stable Isotope Paleolimnology ..................................................................... 10  
1.4.3 Thesis Organization ....................................................................................... 12  

CHAPTER TWO: LIMNOLOGY OF LAKE PUPUKE ..................................................... 13  
2.1 Introduction ........................................................................................................ 13  
2.2 Geology .............................................................................................................. 13  
2.3 Bathymetry and Morphometry .......................................................................... 16  
2.4 Climatology (Regional and Local) .................................................................... 16  
2.5 Hydrology ........................................................................................................... 20  
2.5.1 Hydrologic Balance and Residence Time .................................................... 20  
2.5.2 Temperature and Thermal Stratification ....................................................... 21  
2.5.3 Dissolved nutrients (DO, TN, TP) ................................................................. 23  
2.5.4 pH ................................................................................................................. 26  
2.6 Modern Ecology of Lake Pupuke ...................................................................... 27  
2.6.1 Aquatic Microflora ....................................................................................... 27  
2.6.2 Land Use and Anthropogenic History ....................................................... 30  
2.6 Summary ............................................................................................................. 31  

CHAPTER THREE: SEDIMENT CORING, COMPOSITE CORE CORRELATION, AGE-DEPTH  
MODELLING AND COMPOSITE STRATIGRAPHY ....................................................... 33  
3.1 Introduction ........................................................................................................ 33  
3.2 Sediment Coring ................................................................................................ 33  
3.3 Core Description, Sampling and Preliminary Analyses ................................... 36  
  3.3.1.1 Magnetic Susceptibility ......................................................................... 37  
  3.3.1.2 High-resolution Imaging ....................................................................... 38  
  3.3.1.3 Chemical Fingerprinting of Tephra ....................................................... 38  
3.3.2 Wet Bulk Density, Water Content and Dry Bulk Density .......................... 41  
3.3.3 Sediment Core Logs ...................................................................................... 41
CHAPTER FOUR: PALEOLIMNOLOGY OF LAKE PUPUKE INFERRED FROM BULK GEOCHEMICAL AND PHYSICAL ENVIRONMENTAL PROXIES ........................................ 62

4.1 Introduction to Geochemical and Physical Paleolimnology ........................................ 62
4.2 The Modern Geochemical Framework of Lake Pupuke (TOC, TN, TS and $\delta^{13}$C) .......... 63
   4.2.1 Modern Sampling, Methods and Analyses ...................................................... 64
      4.2.1.1 Sediment Sampling ........................................................................................ 64
      4.2.1.2 Total Organic Carbon (TOC), Total Nitrogen (TN) and Total Sulphur (TS) Analyses 65
      4.2.1.3 Bulk Stable Carbon Isotope Analyses ............................................................... 66
   4.2.2 Modern Sediment Results ...................................................................................... 66
      4.2.2.1 Correction for Inorganic Nitrogen .................................................................... 66
      4.2.2.2 TOC, TN and TS ............................................................................................. 67
      4.2.2.3 Bulk OM $\delta^{13}$C ............................................................................................ 67
      4.2.2.4 Implications for Sedimentary Proxy Indicators .................................................. 69
4.3 Paleolimnologic Methods .............................................................................................. 70
   4.3.1 Magnetic Susceptibility ......................................................................................... 70
   4.3.2 Grain Size Analyses ............................................................................................... 70
   4.3.3 Elemental Analyses ............................................................................................... 71
      4.3.3.1 Bulk TOC, TN and TS Analyses ......................................................................... 71
      4.3.3.2 Analytical Methods .......................................................................................... 75
         4.3.3.2.1 Flux Calculation (CAR, NAR and SAR) ............................................................. 75
      4.3.3.3 Bulk XRF (ITRAX) Analyses .............................................................................. 75
   4.3.4 Bulk Stable Isotopic Analyses .................................................................................. 77
      4.3.4.1 Bulk $\delta^{13}$C ..................................................................................................... 77
      4.3.4.2 Bulk $\delta^{15}$N ..................................................................................................... 80
      4.3.4.3 Analytical Methods .......................................................................................... 82
   4.3.5 Data Analysis and Presentation ............................................................................... 82
      4.3.5.1 Zonation ............................................................................................................ 82
4.4 Paleolimnologic Results ................................................................................................. 83
   4.4.1 Magnetic Susceptibility (MS) ................................................................................. 83
   4.4.2 Grain Size Analyses ............................................................................................... 83
   4.4.3 Elemental Analyses ............................................................................................... 86
      4.4.3.1 Correction for Inorganic Nitrogen ..................................................................... 86
      4.4.3.2 Total Organic Carbon, Nitrogen and Sulphur ..................................................... 87
      4.4.3.3 Elemental Fluxes ............................................................................................... 88
CHAPTER FIVE: THE PALEOLIMNOLOGY OF LAKE PUPUKE INFERRED FROM DIATOM FOSSIL ASSEMBLIES

5.1 Introduction to Paleoecology ................................................................. 125
  5.1.1 Diatoms as Paleoecologic Indicators ............................................... 125
  5.1.2 Interpretation of Fossil Diatom Assemblages ...................................... 127
  5.1.3 Reconstruction of Physical Habitat from Diatom Life-Forms: Ecological Preferences and Indices (Qualitative and Semi-Quantitative Approaches) ................................................................. 128
  5.1.3.1 Species Diversity ........................................................................... 130
  5.1.3.2 Autecologies of Dominant Taxa ...................................................... 132
  5.1.4 Reconstruction of Water Chemistry from Diatom Abundance: Transfer Functions (Quantitative Approaches) .................................................................................. 133
  5.1.4.1 Quantitative Paleoenvironmental Reconstruction Approaches ...... 134
  5.1.4.2 A New Zealand Transfer Function ............................................... 135
5.2 Diatom Methodology ............................................................................ 138
  5.2.1 Laboratory Methods .......................................................................... 138
  5.2.1.1 Identification and Abundance ....................................................... 139
  5.2.1.2 Concentration and Flux ................................................................ 139
  5.2.2 Numerical and Graphical Methods .................................................... 140
  5.2.2.1 Diversity and Habitat Preference .................................................. 140
  5.2.2.2 Morphotype Agglomeration ........................................................ 140
  5.2.2.3 Diatom Zonation ......................................................................... 140
  5.2.2.4 Diatom Ordination ....................................................................... 141
  5.2.2.5 Diatom Transfer Function ............................................................ 141
5.3 Diatom Results and Interpretation ....................................................... 142
  5.3.1 Preservation ...................................................................................... 142
  5.3.2 Influx ................................................................................................. 142
  5.3.3 Diversity ........................................................................................... 143
  5.3.3.1 Habitat Preference ....................................................................... 145
  5.3.3.2 Community Water Quality Indicators ........................................... 145
CHAPTER SIX: PALEOLIMNOLOGY OF LAKE PUPUKE INFERRED FROM DIATOM STABLE ISOTOPES

6.1 Introduction ........................................................................................................................................ 176
6.1.1 Diatom Oxygen Isotopes in Paleolimnology .................................................................................. 176
  6.1.1.1 Non-lacustrine Controls on δ18O_{Diatom} .................................................................................. 180
  6.1.1.2 Lacustrine Controls on δ18O_{Diatom} .................................................................................. 181
  6.1.1.3 Summary .................................................................................................................................. 182
6.1.2 Diatom Silicon Isotopes in Paleolimnology .................................................................................... 182
  6.1.2.1 Controls on δ^{30}Si_{Diatom} ........................................................................................................ 183
  6.1.2.2 Data assessment: Relationship of δ^{29}Si to δ^{30}Si ................................................................. 186
  6.1.3 Uncertainty and Error in Diatom Stable Isotope Paleolimnology .................................................. 187
6.2 Modern Stable Isotope Systematics of Lake Pupuke: Evaporation-dominated Basin ...................... 189
6.2.1 Methods .......................................................................................................................................... 189
  6.2.1.1 Precipitation and Lake Water Sampling .................................................................................. 189
  6.2.1.2 Modern Diatom Sampling ........................................................................................................ 190
  6.2.1.3 Lake Water and Diatom Stable Isotope Analyses .................................................................. 190
6.2.2 Results and Interpretations .............................................................................................................. 191
  6.2.2.1 Modern Isotope Hydrology (Precipitation and Lake Water Composition) ................................ 191
  6.2.2.2 Temporal Variability in δ^{18}O_{Precipitation} ............................................................................ 194
  6.2.2.3 Thermal (‘Dansgaard’) and Amount Relationships in δ^{18}O_{Precipitation} ............................. 196
  6.2.2.4 Spatial and Temporal Variability in δ^{18}O_{Lake} ..................................................................... 198
  6.2.2.5 Diatom Isotope Seasonality ..................................................................................................... 201
  6.2.3 Summary of Modern Stable Isotope Systematics ......................................................................... 202
6.3 Paleolimnologic Methods .................................................................................................................... 203
  6.3.1 Sample Selection ............................................................................................................................ 203
  6.3.2 Chemical and Physical Separation ............................................................................................... 203
  6.3.3 SPLITT Separation ........................................................................................................................ 205
  6.3.4 Stable Isotope Analysis ................................................................................................................ 207
  6.3.5 Contaminant Analysis .................................................................................................................. 207

5.3.4 Multivariate Paleoenvironmental Reconstruction ............................................................................ 147
5.3.4.1 Zonation ...................................................................................................................................... 147
5.3.4.2 Zonal Taxonomic Change .......................................................................................................... 147
  5.3.4.2.1 Zone 1 (~44.0 to 22.5 cal. kyr BP) ......................................................................................... 150
  5.3.4.2.2 Zone 2 (~22.5 to 15.3 cal. kyr BP) ......................................................................................... 150
  5.3.4.2.3 Zone 3 (~15.3 to 3.3 cal. kyr BP) ............................................................................................ 151
  5.3.4.2.4 Zone 4 (~3.3 cal. kyr BP to today) .......................................................................................... 151
5.3.4.3 Diatom Ordination Results ......................................................................................................... 152
5.3.4.4 Diatom Transfer Function Results .............................................................................................. 155
  5.3.4.4.1 No Analogue ......................................................................................................................... 155
  5.3.4.4.2 DI-pH .................................................................................................................................... 155
  5.3.4.4.3 DI-EC .................................................................................................................................... 155
  5.3.4.4.4 DI-DRP and DI-TP ................................................................................................................ 156
  5.3.4.4.5 DI-Chl a ................................................................................................................................. 157
5.4 Discussion ............................................................................................................................................ 160
5.4.1 Paleoerosion ..................................................................................................................................... 162
5.4.2 Paleoproductivity ............................................................................................................................. 166
5.4.3 Paleo-REDOX and Mixing ............................................................................................................ 170
5.5 Summary ............................................................................................................................................ 175
CHAPTER SEVEN: THE COMBINED PALEOLIMNOLOGY OF LAKE PUPUKE AND COMPARISON TO THE NZ-INTIMATE CLIMATE EVENT STRATIGRAPHY ........................................ 236

7.1 Introduction .................................................................................................................. 236
7.2 A Paleoclimate Event Stratigraphy for Lake Pupuke .................................................. 236
7.2.1 Pre-LGCP (~48.2 to 28.5 cal. kyr BP) ........................................................................ 240
7.2.2 LGCP (~28.5 to 18.5 cal. kyr BP) .............................................................................. 240
7.2.3 LGIT and Holocene (~18.5 cal. kyr BP to today) ...................................................... 241
7.3 Regional Comparison with Northern North Island paleoclimate records ................ 244
7.4 Comparison with the NZ-INTIMATE Climate Event Stratigraphy .............................. 251
7.4.1 Palynological Records ................................................................................................. 251
7.4.2 Glacial Records ......................................................................................................... 254
7.4.3 Marine Records ......................................................................................................... 257
7.4.4 Speleothem Records .................................................................................................. 260

CHAPTER EIGHT: CONCLUSION AND FUTURE RESEARCH ........................................ 262

8.1 Conclusion ..................................................................................................................... 262
8.2 Future Research and Improvement .............................................................................. 264

APPENDICES .................................................................................................................... 266

A Sediment Core Logs ........................................................................................................ 266
B Auteologies of subdominant (30%> n >5%) diatom taxa in the Pupuke composite sequence 267
C Diatom Species List ........................................................................................................ 269
D Uncertainty and Error in Diatom Isotope Paleolimnology ................................................ 271
E Modern Isotope Hydrological Modeling .......................................................................... 276
F SPLITT Fractionation Approach .................................................................................... 278
G Cellulose Purification Approach .................................................................................... 280

BIBLIOGRAPHY ................................................................................................................ 283
LIST OF FIGURES

Figure 1.1: Oceanographic setting, topography, glaciers and vegetation zones during the Last Glacial Maximum (LGM) and today, and location of high-resolution climate record sites in the NZ-INTIMATE program (Source: Alloway et al., 2007: 11).............................................................................................................4

Figure 1.2: The Auckland Volcanic Field (AVF) showing the location of volcanic maars in the NZ-Maar project: Lake Pupuke, Hopua, Onepoto and Orakei Basin, and Pukaki crater (Modified from Newnham et al 2007a: 518).........................................................................................................................5

Figure 1.3: Mean rainfall anomalies (% normal) associated with New Zealand weather regimes of Kidson (2000) who undertook climatology calculations for 1958-1997. Note the distinct spatial response of differing climate zones to similar dominant regimes (e.g., anti-phase response of NNI and WSI to zonal or blocking regimes) (Modified from: Lorrey et al., 2007: 413)........................................................................................................................................7

Figure 2.1: The Auckland Volcanic Field (AVF) is a region of late-Quaternary active volcanism covering 140 km² and centred on a narrow isthmus of Miocene deep water Waitemata Group sediments. The steep-sided bathymetry of Lake Pupuke is typical of a phreatomagmatic crater maar (Modified from: Kermode [1992]; Allen et al., [1996]; Horrocks et al., [2005])......................................................15

Figure 2.2: Map of New Zealand and Australia along with simplified features of ocean and atmospheric circulation that affect New Zealand. Right: expanded map of New Zealand showing regional climate districts after Kidson (2000) and high axial relief above 1000 m. NNI = Northern North Island; SWNI = Southwestern North Island; ENI = Eastern North Island; NSI = Northern South Island; ESI Eastern South Island; WSI = Western South Island (Source: Lorrey et al., 2007:408)..................................................17

Figure 2.3: Average monthly air temperature (ºC), evaporation (mm), precipitation (mm) and precipitation/evaporation recorded at the ARC’s North Shore weather station (Agent No. A64775) from January 2006 to January 2010 ..................................................................................................................18

Figure 2.4: Average monthly variation in water column temperature (ºC) by depth (m) over the period 1976-2009 ..................................................................................................................................................22

Figure 2.5: Average monthly variation in DO (%), TN (mg L), NH₄⁺ (mg L) and TP (mg L) by depth (m) within Lake Pupuke (1976-2009) ........................................................................................................24

Figure 2.6: Average monthly variation in pH by depth within Lake Pupuke (1976-2009) ..........................................................................................................................26

Figure 2.7: Seasonal variation in microalgal community structure by count in Lake Pupuke and averaged over the period 01/2004-01/2009. Note the absence of data available in July ...........................................................................28

Figure 2.8: Seasonal variation in diatom community structure by count in Lake Pupuke and averaged over the period 01/2004-01/2009. Note the absence of data available in July ...........................................................................29

Figure 3.1: Coring locations within Lake Pupuke during the 2007 field exercise ...............................................................................................................................34

Figure 3.2: UWITEC percussion fixed-piston coring system and mobile drilling platform (Modified from: UWITEC, 2007a,b)........................................................................................................................................35

Figure 3.3: A summary of the teprochrono logical framework for Lake Pupuke and Auckland Crater Maar tephra deposits. Tephra are described in Table 3.2 (Source: Molloy et al, 2009: 1671)......40
Figure 3.4: A summary of the Pupuke composite sediment sequence demonstrating overlap and correlation between cores to construct a continuous sequence of ~1420 cm.............................................43

Figure 3.5: Calibrated radiocarbon and tephra age-markers sampled in the Pupuke composite series, highlighting those radiocarbon age-markers excluded following comparison to reliable tephra age-markers (circled in red). Error bars are for 2σ.................................................................46

Figure 3.6: Linear segment inferred sediment accumulation rate (SAR) for the Pupuke composite series. Note the presence of ‘plateaux’ in SAR due to the fixed, linear trend between paired age-markers which fails to capture smooth changes to SAR. .................................................................47

Figure 3.7: Linear-segment, power \(y = 1.9235 * x^{0.6048}\), exponential \(y = 319.8 * e^{0.0005x}\), 3rd order polynomial age-depth models \(y = -1*10^5 * x^3 + 0.0342 * x^2 +7.0856 * x - 57\) and cubic spline age-depth models for the Pupuke composite sequence. Note the presence of bends in the cubic spline model to accommodate closely spaced isochrons that result in negative accretion and infinite SAR . 48

Figure 3.8: A constant variance mixed effect regression (MER) age-depth model for the Pupuke composite sequence with 95% confidence intervals (red dashed lines). Diagnostic plots are shown for constant and µ-variance models beneath (from left to right: residuals vs. fitted values, square root of absolute residuals vs. fitted residuals; observed vs. fitted, and a qq-normplot. Note the greater residuals attached to µ-variance making the constant-variance model more robust at predicting age from depth for age-markers.................................................................52

Figure 3.9: Mixed effect regression (MER) inferred sediment accumulation rate (SAR) for the Pupuke composite series. Note SAR maxima between 9.0-10.0 cal. kyr BP, 13.2-14.0 cal. kyr BP and 20.6-22.6 cal. kyr BP. Lesser maxima occur between ~28.4-30.4 cal. kyr BP and ~32.3-34.5 cal. kyr BP . 56

Figure 3.10: Variation in WBD, \(W_c\) and DBD throughout the Lake Pupuke 2007 composite sediment series. Variation in \(W_c\) and DBD reveals 3 distinct zones of changing sediment compaction and density: Zone 1 (today to ~18.2 cal. kyr BP); Zone 2 (~18.2-22.8 cal. kyr BP); and Zone 3 (~22.8-48.2 cal. kyr BP).................................................................58

Figure 3.11: Variation in Mass accumulation rate (MAR), Water Content (\(W_c\)) and Dry Bulk Density (DBD) throughout the Lake Pupuke 2007 composite sequence. An initial peak in MAR (~2.0 cal. kyr BP to today) is attributed to increased organic sedimentation (e.g., low DBD, high \(W_c\)), a later peak (~14.8-12.7 cal. kyr BP) is a complex of initially highly inorganic, eroded sediment followed by a peak in biological productivity, whilst the oldest peak in MAR (~18.4-23.5 cal. kyr BP) is of highly inorganic, eroded sediment (e.g., high DBD, low \(W_c\)).................................................................60

Figure 4.1. Sediment traps manufactured for this project and located at 40 m depth beneath the lake surface by attachment to a 20 kg weight and 20 kg buoy. Depth was maintained by use of a guard fixed at 40 m depth from the surface of Lake Pupuke. Fluctuations in lake level over the annual cycle are ~1.5 m (ARWB, 1990). Thus variation in depth would not be sufficient to allow oxidation of sedimentary organic matter (e.g., <20-25 m depth [beneath oxycline]).................................................................64

Figure 4.2: TN-TOC regression plot for sediment trap collected samples within Lake Pupuke (2008-2009). Note the presence of 0.425 wt.% inorganic Nitrogen amongst total Nitrogen. Sediment trap estimates of TN have been corrected accordingly to yield total organic Nitrogen (e.g., Talbot, 2001) 66

Figure 4.3: Seasonal variation in TOC, TN, TS and \(^{13}\)C within Lake Pupuke over the period 15/03/2008-22/07/2009. Note that the red bar represents period of overturn in Lake Pupuke (July to August). Solid lines extend over the period of sediment trap deployment.................................................................68

Figure 4.4: Sources of dissolved Nitrogen and stable isotopic signatures within lacustrine systems (Modified from: Talbot, 2001).................................................................73

Figure 4.5: Schematic presentation of the Sulphur cycle in freshwater sediments (Source: Holmer and Storkholm, 2001:432).................................................................74
Figure 4.6: An idealised carbon isotope cycle in a stratified lake. OM Carbon isotope signatures are a function of terrestrial and lacustrine influx, dissolved inorganic carbon (DIC), and the rates of primary production and respiration within the water column. Isotope enrichment factors (ε) are listed here as the difference between product and substrate δ13C, and vary with the form of DIC that lake algae assimilate (e.g., CO2(aq) or HCO3\(^-\)). Inorganic carbonate (CaCO3 or CO3\(^2-\)) typically forms in isotopic equilibrium with DIC and is indirectly affected by OM sources, primary production and respiration (Modified from: Meyers and Teranes, 2001: 247 and Leng and Marshall, 2004: 821)..............................79

Figure 4.7: Idealised Nitrogen isotope cycle in a small stratified lake. The isotopic composition of sedimentary OM is determined by sources of nitrogen, rates of primary production and respiration, and the types of denitrification processes. Isotopic values for external sources of atmospheric and combined forms of Nitrogen are from Kendall (1998). Isotope enrichment factors (ε) are from Foel and Cifuentes (1993) and vary with the form of inorganic Nitrogen that lake algae assimilate. Note that Nitrogen isotopes are not fractionated by algal fixation of atmospheric N2 and that the importance of Nitrogen fixation can vary greatly from lake to lake (Modified from: Meyers and Teranes, 2001: 249)81

Figure 4.8: Magnetic susceptibility (κL-E), volume-weighted mean particle size (μm), the proportions of clay, silt and sand-sized particles (%), sediment accumulation rate (SAR) and mass accumulation rate (MAR) of Lake Pupuke composite sediments. Note κL-E have been filtered to exclude tephra contamination, please refer to core log files in Appendix 3.1 for κL-E including tephra. Further note that the series mean of ~23.43 μm is highlighted on volume-weighted mean particle size (dashed line)...85

Figure 4.9: Stratigraphic plot of percentage grains within defined size-class intervals throughout the Pupuke composite sequence ..................................................................................................................................86

Figure 4.10: A regression of sample TOC on TN. Note the negative intercept on the TN axis demonstrating the absence of inorganic Nitrogen within TN estimates and affording greater reliability to sedimentary TN and TOC/TN proxy interpretation ..................................................................................................................................................86

Figure 4.11: Stratigraphic variation in total organic Carbon (TOC; wt. %), total Nitrogen (TN; wt. %), total Sulphur (TS; wt. %), C/N (atomic ratios), sediment accumulation rate (cm/yr), mass accumulation rate (g cm\(^-2\) yr\(^{-1}\)), Carbon accumulation rate (CAR; g cm\(^-2\) yr\(^{-1}\)), Nitrogen accumulation rate (NAR; g cm\(^-2\) yr\(^{-1}\)) and Sulphur accumulation rate (SAR; g cm\(^-2\) yr\(^{-1}\)) for the Lake Pupuke composite sequence. Note TN values correspond to TON and have not undergone correction ...........................................................................................................................................90

Figure 4.12: Selected micro-XRF elemental integrals within the Pupuke composite sequence ~48 cal. kyr BP to today). Changes in core settings are indicated by dashed horizontal lines. Note the distinct changes to lighter atomic elements (e.g., Al-Cl) at ~17.0 cal. kyr BP coincident with a change in ITRAX settings and indicative of an analytical artefact ......................................................................................................................................92

Figure 4.13: Normalised elemental ratio (element peak count/incoherent peak count) and Compton Scattering integrals for the interval ~17 cal. kyr BP to today within the Lake Pupuke composite sediment series. Note the dotted line in represents average Mn/Fe ratios for the composite sequence .........................................................................................................................................93

Figure 4.14: EA-TS and incoherent peak-normalised XRF-TS content of bulk sediment throughout the Lake Pupuke composite sequence. Note the lack of a strong correlation between inferred estimates of TS concentration preclude the use of XRF-TS because the latter has suffered interference from other lighter atomic elements in ITRAX core scans (e.g., strong correlation to lighter elements [Table 4.4]) .................................................................................................................................................95

Figure 4.15: Normalised Ti abundance and TOC (wt. %) within the Lake Pupuke composite sequence demonstrating periods of greater erosive input associated with declines in OM content (e.g., lower TOC........................................................................................................................................96

Figure 4.16: Normalised Mn/Fe ratios indicative of changing REDOX potential by sedimentary TOC (wt. %) within the 2007 Lake Pupuke composite sequence. Relative Mn-enrichment and -depletion records lesser and greater oxygen availability respectively. Note instances of reduced Mn/Fe possess lower TOC demonstrating a mixing rather than productivity related effect upon REDOX.................97
Figure 4.17: Carbon and Nitrogen stable isotope signatures ($\delta^{13}$C, $\delta^{15}$N [%o]), elemental concentration (TOC, TN [wt. %]), sediment accumulation rate (SAR [cm/yr]), mass accumulation rate (Mar [g cm$^{-2}$ yr$^{-1}$]) and elemental flux (CAR, NAR) reconstructed throughout the Lake Pupuke composite sequence. Note the division of the Carbon stable isotope series into 3 broad intervals: (1) depletion prior to ~30.0 cal. kyr BP (~24.69 ± 1.48‰ [μ ± 1σ, n = 87]); (2) enrichment between ~30.0 cal. kyr BP and ~18.2 cal. kyr BP (~18.54 ± 1.86‰ [μ ± 1σ, n = 46]); and (3) depletion beginning ~18.2 cal. kyr BP to today (~23.67 ± 1.79‰ [μ ± 1σ, n = 133]). Note the division of the Nitrogen stable isotope series into 2 broad intervals: (1) depletion prior to ~6.0 cal. kyr BP (2.96 ± 0.46‰ [μ ± 1σ, n = 32]); and (2) enrichment after ~6.0 cal. kyr BP (5.04 ± 0.55‰ [μ ± 1σ, n = 13])

Figure 4.19: Erosional event stratigraphy for the Pupuke composite sequence highlighting changes in multiple erosional proxies that correspond to several peaks in sediment and mass accumulation rate (SAR, MAR): water content (Wc), dry bulk density (DBD), Titanium concentration (Ti), magnetic susceptibility (MS), coarse particle abundance (> 32μm) and Carbon/Nitrogen atomic ratios (C/N). Increased erosion occurs from ~31.5-18.5 cal. kyr BP, 15.5-13.8 cal. kyr BP, 7.8-5.7 cal. kyr BP and from 0.6 cal. kyr BP to today

Figure 4.20: Biological productivity event stratigraphy for the Pupuke composite sequence highlighting increased biomass from ~18.5 cal. kyr BP until today from total organic Carbon (TOC), Nitrogen (TN), C/N (atomic ratios), sediment accumulation rate (SAR), mass accumulation rate (MAR), Carbon accumulation rate (CAR) and Nitrogen accumulation rate (NAR). Millennial-scale variability in biomass is also highlighted, including biomass peaks that drove coeval increases to SAR and MAR during the last ~18.5 cal. kyr BP

Figure 4.21: Trends in composite TS-concentration and flux (SAR) record three broad zones of change: increased TS and SAR from ~48.2 to 31.7 cal. kyr BP; reduced TS and SAR from ~31.7 to 16.5 cal. kyr BP; and greater TS and SAR from ~16.5 cal. kyr BP to today. The concentration and flux of organic Carbon (TOC, CAR) and Nitrogen (TN, NAR) are plotted for comparison to identify changes in TS or SAR most likely to reflect changing REDOX and biological productivity

Figure 4.22: Variation in sedimentary indicators of mixing and benthic REDOX in the Pupuke composite sequence highlighting the likely onset of intense thermal stratification at ~5.6 cal. kyr BP resulting in greater oxygenation of deeper water during overturn than occurred previously, through wave-induced mixing alone (e.g. by greater Mn/Fe ratio), and marked enrichment of composite $\delta^{15}$N-values through denitrification under intensely anoxic conditions generated by isolation of the hypolimnion during stratification. Increased autochthonous Fe-abundance records the coeval natural eutrophication and greater supply of organic-S to the hypolimnion in Lake Pupuke (e.g., increased biological productivity supplies greater dissolved Sulphate which can be reduced under anoxia, during stratification, to iron pyrite)

Figure 4.23: Biplot of TN by TOC (wt. %) for composite sediment highlighting a greater intercept on TN by linear regression, in samples younger than ~5.6 cal. kyr BP and ~3.2 cal. kyr BP. Note the significant relationship in the latter implying the presence of inorganic Nitrogen. Ammonia is the most common source of inorganic Nitrogen within anoxic freshwater and is generated in the hypolimnion during seasonal thermal stratification at Lake Pupuke, suggesting the onset of intense thermal stratification and ammonification from ~5.6 cal. kyr BP and intensifying from ~3.2 cal. kyr BP until today

Figure 4.24: Variation in the Pupuke composite $\delta^{13}$C-series highlighting the effects of altered pCO$_2$, biological productivity and mixing upon the availability of dissolved inorganic Carbon (DIC).
Enrichment of δ\textsuperscript{13}C from ~28.8 to 18.3 cal. kyr BP records the global drop in pCO\textsubscript{2} during Marine Oxygen Isotope Stage II, whilst enrichment events from ~13.8 to 13.6 cal. kyr BP and ~9.3 to 8.0 cal. kyr BP record reduced DIC-availability by greater biological demand. Changes in δ\textsuperscript{13}C from the middle Holocene are driven by varying intensities of thermal stratification, moreover overturn, limiting the recirculation and availability of DIC in the epilimnion.

Figure 5.1: A schematic diagram illustrating the three main classes of diatom and their diagnostic morphology: (A) a typical centric form, Coscinodiscophyceae, showing radial symmetry (e.g., Stephanodiscus) and pattern of areolae radiating from the centre of the valve; (B) a typical pennate diatom without a raphe, Fragilariphycaceae (e.g., Staurosira) with areolae are usually arranged in rows or striae, in this case striae are parallel; (C) a typical pennate diatom with a raphe, Bacillariophycaceae (e.g., Pinnularia) with a cnaviculoid raphe running along the central axis of the valve which is divided into two separated by the central area; (C1) a pennate diatom, Bacillariophycaceae (e.g., Nitzschia) with an eccentric raphe (Source: Jones, 2007: 477).

Figure 5.2: Plots of observed vs. predicted values and observed vs. residual (predicted-observed) values for TF models of (a) pH\textsubscript{ALL}; (b) EC\textsubscript{ISO}; (c) DRP\textsubscript{ISO}; (d) TP\textsubscript{ALL}; and (e) Chl a\textsubscript{ISO}. Note each variable met requirements for TF development by Reid (2005) (e.g., \(A_1/A_2 > 0.5\); explain >5 % of total species variation). With the exception of TP\textsubscript{ALL}, each also performed well at predicting calibration water chemistry. There are also notable trends in residuals of pH\textsubscript{ALL}, EC\textsubscript{ISO} and DRP\textsubscript{ISO} which reveal the TF to over-estimate variables at lower gradient values. Reid (2005) notes these trends were not significant in Chl a\textsubscript{ISO} or TP\textsubscript{ALL}. (Source: Reid, 2005: 28).

Figure 5.3: Diatom laboratory procedure employed for Pupuke composite samples.

Figure 5.4: Mass accumulation rate (MAR), diatom concentration, influx, alpha diversity (Shannon-Weaver H and Hill’s N2) and beta diversity (Sørensen’s dissimilarity and Hoagland et al’s [1982] similarity indices). Higher alpha diversity scores record greater species richness. Lower Sørensen and higher (~1) Hoagland values record greater community similarity between paired samples. Vice-versa denotes lesser between-sample similarity.

Figure 5.5: Diatom habitat preference and water quality indicator scores (as per Van Dam et al., 1994) reconstructed from the Lake Pupuke composite sequence.

Figure 5.6: Constrained incremental sum of squares (CONISS) cluster analysis and broken stick results for diatom assemblages within Lake Pupuke composite sediment series. Note the red line represents the random variance explained by a broken stick model and the black the actual variance explained by CONISS clusters.

Figure 5.7: Dominant (>30 %) and sub-dominant (>20 %) diatom taxonomic change and influx within the Lake Pupuke composite sequence.

Figure 5.8: DCA biplot of Axis 1 and 2 scores centred by 62 species. Taxa appearing at abundances of >5 % in any one sample are printed whilst ‘stars’ correspond to important rare taxa. Beginning clockwise from top left these are Cymbella delicatula, Tabellaria fenestrata, Caloneis bacillum and Cymbella minutum. Species data were square root transformed.

Figure 5.9: DCA biplot of Axis 1 and 2 scores centred by 73 samples. Axis 1 and 2 explain 15.83 % and 5.82 % of taxonomic variation respectively. Species data were square root transformed. Samples have been highlighted if found outside cluster boundaries (e.g., anomalous assemblage compared to prior and subsequent communities). Arrows indicate the general trend of increasing nutrient loading (Axis 1) and increasing Oxygen saturation prior to a reversal at ~7.0 cal. kyr BP (Axis 2).

Figure 5.10: Diatom-inferred water chemistry and boot-strapped predictive error, complemented by measures of structure and change in the diatom assemblages. (a) Diatom-inferred pH (DI-pH); (b) conductivity (DI-EC); (c) dissolved reactive Phosphate (DI-DRP); (d) total Phosphate (DI-TP); (e) chlorophyll a (DI-Chl a); (f) percentage of no-analogue taxa; (g) DCA ordination Axis 1; and (h) DCA ordination Axis 2. DCA Axis 1 presents the primary diatom structural changes and is broadly aligned...
to changing trophic status from oligotrophy (negative values) to eutrophy (positive values). DCA Axis 2 is a compound axis likely to be driven by changes to Oxygen availability.

Figure 5.11: Diatom paleoerosion event stratigraphy for the Pupuke composite sequence highlighting coeval changes to productivity and geochemical indicators (water content [Wd], dry bulk density [DBD], particles >32 μm (>32 μm) and mass accumulation rate [MAR]). Changes in productivity record variation in lake level and mixing.

Figure 5.12: Diatom paleoproductivity event stratigraphy for the Pupuke composite sequence highlighting coeval changes to physical and geochemical indicators (total organic Carbon [TOC], Nitrogen [TN], Sulphur [TS] and mass accumulation rate [MAR]). Changes in productivity record variation in lake level and mixing.

Figure 5.13: Diatom paleo-REDOX and mixing event stratigraphy for the Pupuke composite sequence highlighting the onset of thermal stratification at ~5.6 cal. kyr BP coeval with changes in sediment geochemistry (total organic Carbon [TOC], Nitrogen [TN], Sulphur [TS], C/N, stable N-isotopes [δ15N]) and diatom community structure, stability (Hoagland et al. 1982 SIMI-index), nutrient availability (DI-DRP), conductivity (DI-EC).

Figure 5.14: DCA sample biplot for the Pupuke composite sequence. Note several recent assemblages whose sample score (e.g., composition) is nearer that of glacial, oligotrophic communities (circled in red). Corresponding organic Carbon is relatively 13C enriched (circled in red).

A mechanism to explain the enrichment of organic Carbon and return to oligotrophic diatom assemblages involves lesser mixing at overturn during a period of particularly stable thermal stratification. Lesser mixing would return fewer nutrients to the productive epilimnion such that the dissolved inorganic Carbon reservoir would become relatively exhausted in 12C through productivity and sedimentation, whilst other dissolved nutrients would also become more limited, favouring the dominance of oligotrophic diatom taxa producing 13C enriched organic sediment.

Figure 6.1: The distribution of an inner tetrahedrally bonded internal silica node (Si-O-Si) with an outer, hydrous layer (Si-OH) where Q₄ and Q₆ are Si-O-Si and Si-OH species respectively.

Figure 6.2: Dependency of the Oxygen isotope fractionation in biogenic opal on temperature for three different size classes of freshwater diatoms from Lake Holzmaar. Each symbol represents the average of up to 4 measurements. Error bars represent 1ζ. Centre lines are regression lines; neighbouring curves express 95% confidence intervals. Regression coefficients are identical at P<0.05.

Figure 6.3: Schematic diagram explaining the principal controls on lacustrine δ18O_Diatom: Changes in δ18O_Diatom incorporate variation in δ18O_Lake and δ18O_Precipitation. The former is subject to spatial and seasonal variation that is buffered in larger lakes by greater residence time. The latter is subject to changes in source water δ18O (e.g., through changes in oceanic δ18O) as well as changes to airmass δ18O by altered trajectory (e.g., altitude effect of ~2‰/km increased elevation above sea level; distance to source effect of ~+0.0002 ‰/km increased distance; a variable amount effect) and seasonality. In addition to a thermodynamic effect, vital effects might exist in biogenic silica (Modified from Leng and Marshall, 2004: 812).

Figure 6.4: Schematic diagram explaining the principal controls on lacustrine δ30Si_Diatom: Changes to δ30Si_Diatom record changes to diatom productivity (e.g., competition for dissolved Silicon [DSI]) and availability of DSI principally by changes to mixing (e.g., thermal stratification) and runoff (e.g., changes in effective precipitation, vegetation cover and soil water dynamics). The DSI-signature of runoff is also affected by precipitation/dissolution dynamics of soil water: (1) secondarily bound Si in newly formed Al silicates (enriching DSI); (2) amorphous silica precipitates on mineral surfaces (enriching DSI); (3) plant uptake, formation of phyrogenic Si (phytoliths) (enriching DSI); (4) dissolution or desilication of soils (depletion of DSI) (Modified from Leng et al., 2009: 67).

Figure 6.5: Plot of δ30Si versus δ29Si of 582 samples analysed by De La Rocha (2002). The gradient is defined as 1.93 (R² = 0.99) (Source: De La Rocha, 2002: 6).
Figure 6.6: The δD and δ18O stable isotope framework for Lake Pupuke generated from climatic data in conjunction with precipitation and lake water stable isotopic composition for the period 05/2008-04/2009. Model parameters are described in the text and Appendix 6.2. Briefly, δP is the amount-weighted annual precipitation, δSS is the steady state isotopic composition of a terminal basin, δ* is the limiting isotopic composition and δLake is the modern isotopic composition of Lake Pupuke. Diamonds mark monthly precipitation δD and δ18O samples ...........................................192

Figure 6.7: Monthly variation in the stable isotopic composition and deuterium excess (D-excess) of precipitation at Lake Pupuke (05/2008-01/2010) highlighting seasonal enrichment and depletion in winter and summer months respectively .............................................195

Figure 6.8: Thermal or 'Dansgaard' relationship for precipitation collected in Auckland (05/2008-01/2010) ..........................................................197

Figure 6.9: Amount relationship for precipitation collected in Auckland (05/2008-01/2010) ...............198

Figure 6.10: Monthly stable isotopic composition of Lake Pupuke by depth (05/2008-01/2010) ........199

Figure 6.11: The 6-stage methodology employed to extract purified biogenic silica stable isotopic (δ18O_Diatom, and δ30Si_Diatom) signatures from the Lake Pupuke composite sequence .........................204

Figure 6.12: Cross-section of a SPLITT cell (not to scale). ISP = inlet splitter plane; OSP = outlet splitter plane. Height and length apply to the University of Lancaster SPLITT cell used (Modified from Leng and Barker, 2007; Rings et al., 2004) ..................................................206

Figure 6.13: Scanning Electron Microscopy (SEM) images of purified diatom extracts recovered from the Pupuke composite sequence. Scale bars represent 20, 50, 100 and 200 μm from top to bottom rows ..............................................................211

Figure 6.14: XRF-inferred abundance of basaltic (% Basalt) and rhyolitic glass (% Rhyolite), light-microscope inferred tephra contamination (% Tephra [light microscope]), and light-microscope inferred sponge spicule abundance (% Sponge [light microscope]) for purified diatom silica extracts. Note the weak/moderate but significant correlation between XRF and light microscope inferred tephra abundance (r = 0.42, R² = 0.18, P < 0.01, n = 63), and that XRF-inferred estimates of tephra subsequently underwent correction for variable %O and %Si by mass within basalt and rhyolite compared to clean diatom silica. Hence, XRF-inferred estimates of % Basalt are multiplied by a correction factor of 0.83 and 0.49 to yield the respective % of O and Si basaltic-contamination of total sample O and Si (e.g., basalt contains ~17% less O and ~51% less Si than pure diatom silica per unit mass). Rhyolite O and Si correction factors are 0.93 and 0.78 respectively (e.g., rhyolite contains ~7% less O and ~22% less Si than pure diatom silica per unit mass) ..........................................................214

Figure 6.15: Raw and modelled tephra-free δ18O_Diatom signatures throughout the Pupuke composite sequence. XRF-inferred basalt and rhyolite abundance are also presented. Note the presence of 3 broad zones of enriched (~0.5 to 18.5 cal. kyr BP), depleted (~19.1 to 28.6 cal. kyr BP) and enriched δ18O_Diatom signatures (~30.5 to 48.2 cal. kyr BP). Basalt and rhyolitic tephra is depleted in δ18O hence modelled tephra-free signatures are relatively enriched over uncorrected δ18O_Diatom ........................................216

Figure 6.16: Uncorrected (raw) and tephra-free (corrected) δ30Si_Diatom signatures in the Pupuke composite sequence. XRF-inferred basalt and rhyolite abundance are also presented. Note the presence of 3 broad zones of enriched (~0.6 to 5.0 cal. kyr BP), depleted (~9.4 to 14.0 cal. kyr BP) and enriched δ30Si_Diatom signatures (~18.5 to 48.2 cal. kyr BP). Downcore δ30Si/δ29Si ratio scores are also presented for 23 samples analysed for δ30Si_Diatom and δ29Si_Diatom (dotted line marks ~1.93). Note a single sample at ~1.7 cal. kyr BP has been excluded from further interpretation owing to an anomalously high δ30Si/δ29Si ratio, whilst another at ~14.0 cal. kyr BP has been included because the tephra-contaminant effect has been modelled and removed from δ30Si_Diatom ........................................218

Figure 6.17 Modelled tephra contamination of stable isotope samples and location of major tephra in the Pupuke composite sequence. Macroscopic tephra have been identified: (1) dotted lines represent tephra ~1-5 mm; and (2) solid lines represent tephra >5 mm in thickness. Labelled tephra are widespread throughout the North Island of New Zealand and have thickness noted in brackets ......220
Figure 6.18: Tephra-free (corrected) and uncorrected (raw) $\delta^{18}$O$_{\text{Diatom}}$, $\delta^{30}$S$_{\text{Diatom}}$ and diatom silica maturity values downcore in the Pupuke composite sequence .................................................. 223

Figure 6.19: Diatom taxonomic (interpolated) and stable isotopic variation in the Pupuke composite sequence. Diatom taxonomic data is portrayed for actual sample depths and frequency though in the text, correlation analyses have been performed with interpolated data to match the composite depths of diatom stable isotopic samples. There are no significant relationships between diatom stable isotopic composition and beta or alpha diversity (e.g., measures of community richness and turnover). Only the abundance of A. granulata var. ambigua strongly correlates with stable isotopic composition ($\delta^{30}$S$_{\text{Diatom}}$) and records the onset of thermal stratification from ~5.6 cal. kyr BP with consequent changes in the availability of DSI that thereby suggests both the abundance of A. granulata var. ambigua and $\delta^{30}$S$_{\text{Diatom}}$ signatures are dependent on the changes to mixing and nutrient availability mediated by changes in the intensity of thermal stratification, rather than a taxonomic vital effect in $\delta^{30}$S$_{\text{Diatom}}$ .......................................................... 225

Figure 6.20: Paleoclimatic shifts in effective precipitation are recorded by changes to $\delta^{18}$O$_{\text{Diatom}}$ within the Pupuke composite sequence. Three broad zones of (1) greater (~18.5 cal. kyr BP to today), (2) reduced (~28.6 to 18.5 cal. kyr BP) and (3) greater effective precipitation are recorded (~48.2 to 28.6 cal. kyr BP). Zone 1 corresponds to the Holocene and Last Glacial Interglacial Transition (LGIT), Zone 2 the Last Glacial Coldest Phase (LGCP) and Zone 3 the earlier Moerangi Interstadial (MIS 1, 2 and 3 respectively). Zone 3 is characterised by the most heavily enriched $\delta^{18}$O$_{\text{Diatom}}$ values of the composite sequence indicating that despite a cooler, climate than today, the Moerangi interstadial exhibited high rates of evaporation and precipitation to permit an increase in the residence time of Lake Pupuke . 229

Figure 6.21: Paleoclimatic shifts in Si-cycling, uptake and availability recorded by changes to $\delta^{30}$S$_{\text{Diatom}}$ within the Pupuke composite sequence. Three broad zones of (1) greater (~5.0 cal. kyr BP to today), (2) lower (~18.5 to 5.0 cal. kyr BP) and (3) greater enrichment are recorded (~48.2 to 18.5 cal. kyr BP). Zone 1 corresponds to the mid-to-late Holocene, Zone 2 the early Holocene and Last Glacial Interglacial Transition (LGIT) and Zone 3 the Last Glacial Coldest Phase (LGCP) and earlier Moerangi Interstadial. Zone 2 is interrupted by enriched $\delta^{30}$S$_{\text{Diatom}}$ between ~14.0 and 13.6 cal. kyr BP indicative of an LGIT peak in diatom and total productivity .......................................... 234

Figure 7.1: A schematic representation of the paleoclimate event stratigraphy for Lake Pupuke from ~48.2 cal. kyr BP to Present. Arrows indicate the direction of lake level change ................................................. 237

Figure 7.2: Summary of paleolimnological proxy variation in the Pupuke composite sequence including mass accumulation rate (MAR), dry bulk density (DBD), magnetic susceptibility (MS), abundance of particles >32 μm, total organic Carbon (TOC), Nitrogen (TN), Sulphur (TS), Carbon/Nitrogen atomic ratio (C/N), Carbon stable isotope ($\delta^{13}$C), Nitrogen stable isotope ($\delta^{15}$N), Hoagland similarity index scores (SIMI), diatom taxa (planktic, tychoplanktic, meroplanktic, benthic and aerophilic), diatom-inferred dissolved reactive Phosphate (DI-DRP), diatom sample DCA Axis 1 scores, diatom Oxygen isotope ($\delta^{18}$O$_{\text{Diatom}}$) and diatom Silicon isotope composition ($\delta^{30}$S$_{\text{Diatom}}$) ...... 239

Figure 7.3: Prominent pollen taxa for the upper part of the Okarito-Pakiri record (indicating vegetation succession during the last deglaciation), pollen and chironomid taxa for the Boundary Stream Tarn record (including WA-PLS and PLS mean summer air temperature model reconstruction for which a LOWESS smoother is represented by the dark line [sample specific errors are indicated by shading]), and geochemical profiles for the Pupuke composite sequence. Grey shading represents a Late Glacial Reversal in climatic amelioration during which early montane forest development gave way to subalpine shrubs and grasses at Okarito-Pakiri and Boundary Stream Tarn. (Modified from Newnham et al., 2007b: 532 and Vandergoes et al., 2008: 596) ................................................. 252

Figure 7.4: Holocene glacial advances near Mount Cook in New Zealand’s Southern Alps, together with published $^{14}$C ages on soils buried by Mount Cook glacier expansion events over the past 4000 years (probability plots are derived from $^{14}$Be moraine ages with the arithmetic mean highlighted in blue), and evidence for increased seasonality at Lake Pupuke during the mid-to-late Holocene (e.g., greater beta diversity [lower SIMI score] and variable $\delta^{15}$C. Although tentative, a link to the Southern Alps could be offered by the influence of westerly circulation on zonal regime frequency in the
Northern North Island, manifest in patterns of enrichment and depletion of δ\(^{13}\)C at Lake Pupuke. (Modified from Schaefer et al., 2009: 625)

Figure 7.5: Geochemical proxy variation in the Pupuke composite sequence (including the Pupuke climate event stratigraphy) and marine sediment core paleoclimatic proxy variation during the last ~50 cal. kyr BP. Grey shading represents the Antarctic Cold Reversal while brown shading represents the Younger Dryas (as per Barrows et al., 2007b). MD97-2120 includes an Oxygen isotope record for Globerigerina bulloides (Pahnke et al., 2003) (line represents a three-point running mean), sediment lightness (Michel and Turon, 2006) and estimates of SST from Mg/Ca (Pahnke et al., 2003). SO136-GC3 includes an Oxygen isotope record for Gg. bulloides (Barrows et al., 2007b) (line is a three-point running mean), estimates of SST from the \(^{237}\)U index (Pelejero et al., 2006) and planktonic foraminifera (Barrows et al., 2007b). DSDP Site 594 includes an Oxygen isotope record for Uvigerina sp., (Nelson et al., 1993) (line represents a three-point running mean), tree and shrub pollen, and estimates of SST from planktonic foraminifera (Barrows et al., 2007b). (Modified from Barrows et al., 2007b: 5, 7 and 11)

Figure 7.6: Geochemical proxy variation in the Pupuke composite sequence (including the Pupuke climate event stratigraphy) and speleothem proxy variation during the last ~30 cal. kyr BP. The Waitomo district (Southwest North Island) and Northwest South Island speleothem records incorporate the extended and improved ages of Williams et al (2010). Speleothem δ\(^{18}\)O has been corrected for ice-volume effects on δ\(^{18}\)O\(_{\text{Precipitation}}\). (Modified from Williams et al., 2010: 103-104)

Figure 8.1: Preliminary δ\(^{18}\)O\(_{\text{Cellulose}}\) (CUAM extract) plotted by δ\(^{18}\)O\(_{\text{Diatom}}\) demonstrating marked differences in stratigraphic variation and suggesting the presence of vital effects in δ\(^{18}\)O\(_{\text{Cellulose}}\) distorting the link to δ\(^{18}\)O\(_{\text{Lake}}\) within the Pupuke sediment record
LIST OF TABLES

Table 1.1: Details of the three dominant weather regimes in contemporary New Zealand (Source: Lorrey et al., 2007: 413) .......................................................... 6

Table 2.1: Contemporary diatom taxa and preference for nutrient, suspension conditions within Lake Pupuke (compiled from Cassie, 1989: 44-45; Holmes, 1994: 98-102) .......................................................... 29

Table 3.1: Coordinates, depths and recovery of sediment cores within Lake Pupuke during the 2007 field exercise .......................................................... 34

Table 3.2: Depths, thickness and estimated ages of tephra discovered within Lake Pupuke sediment cores. Estimated ages have been provided from a linear segment approach in Molloy et al (2009) except those in bold which represent independently dated isochrons (e.g., Lowe et al, 2008; Molloy et al, 2009). Bold and underlined tephra offer reliable independent ages that are used in subsequent age-depth modelling (Source: Molloy et al., 2009: 1669) ........................................................................................................ 39

Table 3.3: Calibrated (OxCal v.4.1) age-markers employed in the Pupuke composite sediment sequence .......... 46

Table 3.4: The input information to the Agedepth function (Heegaard et al., 2005) for construction of a mixed effect regression age-depth model for the Pupuke composite series .......................................................... 51

Table 3.5: Calibrated (OxCal v.4.1) age-markers employed in the Pupuke composite sediment sequence and corresponding MER-inferred ages .................................................................................................. 54

Table 4.1: Seasonal variation in TOC, TN, TS and δ¹³C within Lake Pupuke over the period 15/03/2008-22/07/2009 .......................................................................................................................... 67

Table 4.2: Elemental integrals and ratios informative of paleoenvironment together with their sensitivity to ITRAX detection (using a Mo X-ray Tube). Elements and element ratios highlighted in bold are applied to the Pupuke composite sequence (Source: Rothwell et al., 2006: 87) .......................................................................................................................... 76

Table 4.3: Equilibrium (a) and kinetic (b) isotopic fractionation factors (α) of importance to Nitrogen cycling in lakes (Collister and Hayes, 1991). As a first approximation, an α value of, for example, 1.020 implies a difference in δ¹⁵N of ca. 20‰ between the reactant and product. In the case of N₂ gas dissolution therefore, δ¹⁵N differs by less than 1‰ between the gaseous and aqueous phases, whereas gaseous ammonia liberated during ammonia volatilisation will be ca. 34‰ lighter than the aqueous ammonia (Source: Talbot, 2001: 407) .......................................................................................................................... 81

Table 4.4: Correlation coefficients among ITRAX elemental profiles (bold are significant at P < 0.001) (Pearson’s r, n = 671) .......................................................................................................................... 94

Table 4.5: Geochemical and physical evidence of paleoenvironment from the Pupuke composite sequence ........ 103

Table 4.6: Intervals of heightened erosion within the Pupuke composite sequence. Note average values for the Pupuke composite sequence excluding those intervals below, are: MS, 23.20 x 10⁻⁶ (SI); >32 μm, 18.15 %; and Ti-abundance, 0.0075 cps/inc .......................................................................................................................... 107

Table 4.7: Intervals of heightened biological productivity within the Pupuke composite sequence .................... 112

Table 5.1: Classification of diatom taxa by habitat (Barker, 1990; Round et al., 1990; Cochran, 2009) ............ 128

Table 5.2: Classification of diatom taxa by trophic and pH status (modified from Van Dam et al., 1994) ........ 129
Table 5.3: Classification of ecological indicator values (Source: Van Dam et al., 1994: 120) ........................................130

Table 5.4: Summary of ecological tolerances amongst dominant (>5 % count) diatom taxa in the Lake Pupuke composite series. Indicators are: (R) pH; (N) Nitrogen uptake mechanism; (O) Oxygen requirements; (S) saprobity; (T) trophic state; and (M) moisture requirements (for identification of code scores refer to Table 5.3) (modified from Pienitz et al., 1991: 172-174; and Van Dam et al., 1994: 122-127) ........................................133

Table 5.5: Water quality properties of the 53 lakes used in Reid’s (2005) New Zealand diatom transfer function ...............................................................................................................................136

Table 5.6: Summary of transfer function model performance for Reid (2005: 27 and 31) ........................................136

Table 5.7: Summary of outlying lakes excluded from diatom transfer function reconstructions of water quality parameters at Lake Pupuke (Modified from Reid, 2005:27). ..................................................................................142

Table 5.8: Definition of diatom zones according to dominant taxa........................................................................147

Table 5.9: Summary of DCA sample and site scores for diatom abundance (% count, square-root transformation and downweighting of rare species [73 samples, 62 species]) ........................................................................152

Table 5.10: Summary of DCA scores by diatom ordination cluster identified from Figure 5.8 .........................154

Table 5.11: Presence of no analogue taxa by Lake Pupuke composite diatom series ........................................155

Table 5.12: Diatom-inferred pH, EC, TP, DRP and Chl a with CONISS-defined zonation for the Lake Pupuke composite series ........................................................................................................158

Table 5.13: Diatom inferred paleoenvironment from the Pupuke composite sequence ..................................161

Table 6.1: Features of lakes likely to produce temperature, δ18O or precipitation/evaporation reconstructions from isotopic composition of primary precipitates within lake sediment (Source: Leng and Marshall, 2004: 814) ......182

Table 6.2: The values of isotopic framework parameters used in generation of the stable isotope framework for Lake Pupuke (05/2008-01/2010). Note: all values used for calculations with appropriate equations and references are listed in Appendix 6.2 ..................................................................................................................192

Table 6.3: Correlation matrix of climatic/hydrologic factors by lake water and precipitation stable isotope composition for Lake Pupuke (05/2008-01/2010). Samples underscored are significant at the P < 0.01 level (n = 11) ..................................................................................................................200

Table 6.4: Variation in monthly isotopic composition between epilimnetic (surface), thermocline (15 m) and hypolimnetic (28 m) water in Lake Pupuke (05/2008-01/2010) ........................................................................200

Table 6.5: Explorative correlations between whole-lake water chemistry and stable isotope composition of sedimentary diatom silica ........................................................................................................201

Table 6.6: Experimental settings for SPLITT fractionation steps adopted in this study. Diatom outlet refers to the outlet preferentially collecting diatom frustules over contaminants: a and b referring to the same SPLITT step number in different samples; a, b referring to different SPLITT step numbers in different samples ..................................................................................206

Table 6.7: Representative geochemistry of tephra and diatom end members for use in assessing contribution to sample mass by mixture modelling. Mean abundance is bracketed by a standard deviation (nDiatom = 3; nBasalt = 2; nHydolite = 2) ............................................................................................................209

Table 6.8: Sediment trap biogenic silica maturity and stable isotope composition (δ18O and δ30Si) ...213
Table 6.9: Correlation matrix of inferred tephra abundance between individual geochemical indicators within rhyolite and basalt

Table 6.10: Correlation coefficients between $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}\text{Si}_{\text{Diatom}}$ variation, and dominant diatom flora as well as habitat preference. All correlations are insignificant ($P < 0.01$)

Table 7.1: A paleoclimate event stratigraphy for Lake Pupuke from ~48.2 cal. kyr BP to Present. The boundary of the Holocene and LGIT (dashed line) is tentative due to the transitional paleoclimatic trends exhibited from ~12.8 to 10.2 cal. kyr BP

Table 8.1: Preliminary $\delta^{16}O_{\text{Cellulose (CUAM extract)}}$ variation in laboratory cellulose standards suggesting the CUAM method introduces marked variation to the isotopic composition of cellulose extracts
# GLOSSARY

<table>
<thead>
<tr>
<th>ACR</th>
<th>Antarctic Cold Reversal</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVF</td>
<td>Auckland Volcanic Field</td>
</tr>
<tr>
<td>BSi</td>
<td>Biogenic Silica</td>
</tr>
<tr>
<td>CONISS</td>
<td>Constrained Incremental Sum of Squares</td>
</tr>
<tr>
<td>C/N</td>
<td>Ratio of organic carbon relative to nitrogen</td>
</tr>
<tr>
<td>DBD</td>
<td>Dry Bulk Density</td>
</tr>
<tr>
<td>DCA</td>
<td>Detrended Correspondence Analysis</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>DIC</td>
<td>Dissolved Inorganic Carbon</td>
</tr>
<tr>
<td>DI-Chl a</td>
<td>Diatom-Inferred Chlorophyll a</td>
</tr>
<tr>
<td>DI-DRP</td>
<td>Diatom-Inferred Dissolveable Reactive Phosphorus</td>
</tr>
<tr>
<td>DI-EC</td>
<td>Diatom-Inferred Electrical Conductivity</td>
</tr>
<tr>
<td>DI-pH</td>
<td>Diatom-Inferred pH</td>
</tr>
<tr>
<td>DI-TP</td>
<td>Diatom-Inferred Total Phosphorus</td>
</tr>
<tr>
<td>DSI</td>
<td>Dissolved Silica</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infra-Red</td>
</tr>
<tr>
<td>GMWL</td>
<td>Global Meteoric Water Line</td>
</tr>
<tr>
<td>LEL</td>
<td>Local Evaporation Line</td>
</tr>
<tr>
<td>LGCP</td>
<td>Last Glacial Coldest Period</td>
</tr>
<tr>
<td>LGM</td>
<td>Last Glacial Maximum</td>
</tr>
<tr>
<td>LGR</td>
<td>Late Glacial Reversal</td>
</tr>
<tr>
<td>LGIT</td>
<td>Last Glacial-Interglacial Transition</td>
</tr>
<tr>
<td>LMWL</td>
<td>Local Meteoric Water Line</td>
</tr>
<tr>
<td>MAR</td>
<td>Mass Accumulation Rate</td>
</tr>
<tr>
<td>MER</td>
<td>Mixed Effect Regression</td>
</tr>
<tr>
<td>MIS</td>
<td>Marine Isotope Stage</td>
</tr>
<tr>
<td>MS</td>
<td>Magnetic-susceptibility</td>
</tr>
<tr>
<td>OM</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Components Analysis</td>
</tr>
<tr>
<td>RMSEP</td>
<td>Root mean squared error of prediction</td>
</tr>
<tr>
<td>SAR</td>
<td>Sediment Accumulation Rate</td>
</tr>
<tr>
<td>SPLITT</td>
<td>Split-flow laminar fractionation</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>TP</td>
<td>Total Phosphorus</td>
</tr>
<tr>
<td>TS</td>
<td>Total Sulphur</td>
</tr>
<tr>
<td>WA-tol</td>
<td>Weighted Averaging with tolerance down-weighting</td>
</tr>
<tr>
<td>WA-PLS</td>
<td>Weighted Averaging partial least squares</td>
</tr>
<tr>
<td>WBD</td>
<td>Wet Bulk Density</td>
</tr>
<tr>
<td>$W_c$</td>
<td>Water Content</td>
</tr>
<tr>
<td>YD</td>
<td>Younger Dryas</td>
</tr>
</tbody>
</table>