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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

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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 (Δ18O_Diatom and Δ30Si_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, Δ13C, Δ15N, ITRAX) and physical (magnetic-susceptibility, particle-size distribution) proxies for environmental and limnological change. Paleoclimatic inferences are made from Δ18O_Diatom and Δ30Si_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 Δ18O and Δ30Si signatures to yield a basaltic and rhyolitic isotope effect. Once removed, this yielded tephra-free estimates of Δ18O_Diatom and Δ30Si_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).
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# TABLE OF CONTENTS

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

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 δ¹³C) ..................... 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 δ¹³C .................................................................................................. 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 δ¹³C .................................................................................................... 77
         4.3.4.2 Bulk δ¹⁵N ................................................................................................... 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

3.4 Composite Core Construction .............................................................................................. 42
   3.4.1 Tephra Correlation and Removal ................................................................................. 42
   3.4.2 Composite Core Correlation ....................................................................................... 42
   3.5 Chronology ....................................................................................................................... 44
      3.5.1 Tephra .................................................................................................................. 44
      3.5.2 Radiocarbon Dating and Calibration .................................................................... 45
      3.5.3 Age-Depth Model Construction ....................................................................... 47
      3.5.4 Age-Depth Model Evaluation and Selection ...................................................... 53
   3.6 Lithology and Stratigraphy .............................................................................................. 54
      3.6.1 Lithology .............................................................................................................. 55
      3.6.2 Sediment Accumulation Rate .............................................................................. 56
      3.6.3 Wet and Dry Bulk Density ............................................................................... 57
      3.6.4 Mass Accumulation Rate ..................................................................................... 59
   3.7 Summary of Stratigraphic Framework .............................................................................. 60
4.4.3.4 Bulk XRF (ITRAX) Analyses ................................................................. 91
4.4.4 Comparison of EA-TS and XRF-TS ......................................................... 95
4.4.5 Paleoerosion Profile (Ti) ........................................................................ 96
4.4.6 Paleo-REDOX Profile (Mn/Fe) ................................................................. 97
4.4.7 Bulk Stable Isotopic Analyses ................................................................. 98
   4.4.7.1 Bulk δ¹³C ...................................................................................... 98
   4.4.7.2 Bulk δ¹⁵N ............................................................................. 100
4.4.8 Geochemical Zonation Analyses ............................................................ 100
4.5 Discussion .................................................................................................. 102
   4.5.1 Paleoerosion ...................................................................................... 104
   4.5.2 Paleoproductivity ............................................................................. 109
      4.5.2.1 Changes to catchment vegetation ............................................... 109
      4.5.2.2 Changes to biological productivity .......................................... 110
   4.5.3 Total Sulphur: A Novel Proxy for Paleoproductivity and Mixing .......... 114
   4.5.4 Change to Mixing and Benthic REDOX ............................................ 117
   4.5.5 Carbon Stable Isotopes: A Complex Story of Changing pCO₂ productivity and mixing ... 121
4.6 Summary .................................................................................................. 124

CHAPTER FIVE: THE PALEOLIMNOLOGY OF LAKE PUPUKE INFERRED FROM DIATOM FOSSIL ASSEMBLIES ............................................................................................................. 125

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
5.3.4 Multiivariate 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 cal. kyr BP) .............................................................. 150
    5.3.4.2.2 Zone 2 (~22.5 cal. kyr BP) .............................................................. 150
    5.3.4.2.3 Zone 3 (~15.3 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 SIX: PALEOLIMNOLOGY OF LAKE PUPUKE INFERRED FROM DIATOM STABLE ISOTOPES ......................................................................................................................... 176

6.1 Introduction ..................................................................................................... 176
  6.1.1 Diatom Oxygen Isotopes in Paleolimnology ............................................... 178
    6.1.1.1 Non-lacustrine Controls on \( \delta^{18}O_{\text{Diatom}} \) ....................................... 180
    6.1.1.2 Lacustrine Controls on \( \delta^{18}O_{\text{Diatom}} \) .............................................. 181
    6.1.1.3 Summary .......................................................................................... 182
  6.1.2 Diatom Silicon Isotopes in Paleolimnology .................................................. 182
    6.1.2.1 Controls on \( \delta^{30}Si_{\text{Diatom}} \) ............................................................... 183
    6.1.2.2 Data assessment: Relationship of \( \delta^{29}Si \) to \( \delta^{30}Si \) ...................... 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 \( \delta^{18}O_{\text{Precipitation}} \) ..................................... 194
    6.2.2.3 Thermal (‘Dansgaard’) and Amount Relationships in \( \delta^{18}O_{\text{Precipitation}} \) .......................................................... 196
    6.2.2.4 Spatial and Temporal Variability in \( \delta^{18}O_{\text{Lake}} \) ............................. 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
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 Autecologies 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
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 km$^2$ 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), NH$_4$$^+$ (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 tephrachronological 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 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).

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 N\(_2\) and that the importance of Nitrogen fixation can vary greatly from lake to lake (Modified from: Meyers and Teranes, 2001: 249).

Figure 4.8: Magnetic susceptibility (κ\(_{LF}\)), 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 κ\(_{LF}\) have been filtered to exclude tephra contamination, please refer to core log files in Appendix 3.1 for κ\(_{LF}\) including tephra. Further note that the series mean of ~23.43 μm is highlighted on volume-weighted mean particle size (dashed line).

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

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.

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.

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.

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.

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])

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).

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.
Figure 4.17: Carbon and Nitrogen stable isotope signatures ($\delta^{13}C$, $\delta^{15}N$ [‰]), 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 = 40]); 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 4.18: Biplots of paired elemental (total organic Carbon [TOC] and Nitrogen [TN]) and stable isotopic data ($\delta^{13}C$ and $\delta^{15}N$) from the Lake Pupuke composite sequence. Note that C/N ratios did not require correction for inorganic Nitrogen. Four clusters of geochemically similar sediment samples (e.g., deposited under similar limnological and diagenetic conditions) are apparent in a biplot of $\delta^{13}C$ by $\delta^{15}N$ (~47.8-28.8 cal. kyr BP, ~27.3-17.0 cal. kyr BP, ~15.5-6.5 cal. kyr BP and from ~5.5 cal. kyr BP until today). Two clusters are apparent in a biplot of $\delta^{15}N$ by C/N atomic ratios (~47.8 cal. kyr BP and ~3.8 cal. kyr BP until today). Anomalous samples are highlighted in green. A single sample (~6.5 cal. kyr BP) belongs to separate geochemical clusters depending on which biplot is selected and is highlighted in green.

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 authothonous 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 δ¹³C from ~28.8 to 18.3 cal. kyr BP records the global drop in pCO₂ 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 δ¹³C 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, Fragilariphycceae (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, Bacillariophycceae (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, Bacillariophycceae (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_ALL, (b) EC_ALL, (c) DRP_ISO, (d) TP_ALL and (e) Chl_a_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 variance). With the exception of TP_ALL each also performed well at predicting calibration water chemistry \( (r^2_{j,cal} > 0.7) \). Thus the latter was excluded from application to the Lake Pupuke composite sequence. There are also notable trends in residuals of pH_ALL, EC_ALL and DRP_ISO which reveal the TF to over-estimate variables at lower gradient values. Reid (2005) notes these trends were not significant in Chl_a_ISO or TP_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 minatum. 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..................................................159

Figure 5.11: Diatom paleoerosion event stratigraphy for the Pupuke composite sequence highlighting coeval changes to physical and geochemical indicators (water content [Wd], dry bulk density [DBD], particles >32 μm (>32 μm) and mass accumulation rate [MAR]). Shading denotes periods of increased erosion..................................................................................165

Figure 5.12: Diatom paleoproduction 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.................................................................169

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) .................................................................173

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 δ13C 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 dominance of oligotrophic diatom taxa producing 13C enriched organic sediment..................................................174

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 Qn are Si-O-Si and Si-OH species respectively (Source: Leng et al., 2009: 69)..................................................................................................................................................177

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 1σ. Centre lines are regression lines; neighbouring curves express 95% confidence intervals. Regression coefficients are identical at P<0.05 (Source: Moschen et al 2005, 32, L07708) .........................................................................................................................178

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)........................................................................................................................179

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 phytogenic Si (phytoliths) (enriching DSi); (4) dissolution or desilication of soils (depletion of DSi) (Modified from Leng et al., 2009: 67)..................................................................................................................184

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) .........................................................................................................................187
erwent correction for variable %O and %Si by mass within basalt and rhyolite -

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 δ29Si_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 6.6: 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 6.14: 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) δ29Si_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 δ29Si_Diatom signatures (~18.5 to 48.2 cal. kyr BP). Downcore δ29Si/30Si ratio scores are also presented for 23 samples analysed for δ29Si_Diatom and δ30Si_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 30Si/29Si ratio, whilst another at ~14.0 cal. kyr BP has been included because the tephra-contaminant effect has been modelled and removed from δ29Si_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. ambiguca 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. ambiguca 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 $^{14}C$ and $^{10}Be$ 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 $\delta^{13}C$. 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 $\delta^{13}$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 Globigerina 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 $U^{37}$ 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 $\delta^{18}$O has been corrected for ice-volume effects on $\delta^{18}$O_precipitation. (Modified from Williams et al., 2010: 103-104)

Figure 8.1: Preliminary $\delta^{18}$O_Cellulose (CUAM extract) plotted by $\delta^{18}$O_Diatom demonstrating marked differences in stratigraphic variation and suggesting the presence of vital effects in $\delta^{18}$O_Cellulose distorting the link to $\delta^{18}$O_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 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 $\delta^{30}Si_{\text{Diatom}}$ 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 $\delta^{18}O_{\text{Cellulose}}$ (CUAM extract) variation in laboratory cellulose standards suggesting the CUAM method introduces marked variation to the isotopic composition of cellulose extracts...
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACR</td>
<td>Antarctic Cold Reversal</td>
</tr>
<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 Dissolvable 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>SPLITTT</td>
<td>Split-flow laminar fractionation</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</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>Wc</td>
<td>Water Content</td>
</tr>
<tr>
<td>YD</td>
<td>Younger Dryas</td>
</tr>
</tbody>
</table>
CHAPTER ONE

Introduction

Terrestrial paleoclimatic records from Australasia have highlighted the sensitivity of Southern Hemisphere land masses to late glacial changes in oceanic/atmospheric circulation (e.g., Turney et al., 2003; Shulmeister et al., 2006, 2010; Putnam et al., 2010). Despite this impetus to research the late Quaternary paleoclimatic history of Australasia, there are few lacustrine or paleolimnological records and a dearth of high-resolution chronologies available to further improve our understanding of climate change processes within New Zealand (Alloway et al., 2007). This thesis responds to this demand by producing a high-resolution (<500 yr resolution) paleoclimatic event stratigraphy for a phreatomagmatic maar crater lake (Lake Pupuke, Auckland), at a critical location for evaluating late Glacial palaeoenvironmental change in the North Island of New Zealand (e.g., Newnham et al., 2007a). This introduction explores an existing framework for conducting Quaternary paleoclimatic research in Australasia (the AUS-INTIMATE program), which helps to frame the goals of this research as well as its approach. This research also contributes to an increasing demand for novel paleolimnological proxies by the first application of a dual diatom stable Oxygen and Silicon isotope approach to a Southern Hemisphere lake paleo-record (including development of a novel approach for removing tephra contaminant isotopic effects), complementing traditional biological (diatom), geochemical (TOC, TN, TS, δ¹³C, δ¹⁵N, ITRAX) and physical (magnetic-susceptibility, particle-size distribution) paleolimnogical inferences. The fundamentals of paleolimnology including stable isotope paleolimnology are also covered in this chapter, to more easily outline the paleolimnological approach and structure of this thesis.

1.1 The Intimate Project

The Quaternary is a period of repeated mid-latitude glaciation and deglaciation accompanied by altered oceanic/atmospheric circulation covering the last ~2.68 Myr driven by the changes in orbital parameters of the Earth (i.e., the precession, eccentricity and obliquity components of Milankovitch cycles) (Bowen and Gibbard, 2007). Quaternary paleoclimatic change occurred largely under present boundary conditions (i.e., oceanographic and atmospheric circulation, insolation and landmass distribution) ensuring the Quaternary offers valuable potential to model future climatic scenarios (Bowen and Gibbard, 2007). Accordingly, paleoclimatic researchers are increasingly focussed on reconstructing past environments of the Quaternary, in particular the last glacial cycle (last ~120 kyrs), and especially the Last Glacial-Interglacial Transition (LGIT) (Alloway et al., 2007; Hoek et al., 2008).
The Northern Hemisphere has benefitted from a regional drive to generate a coherent record of late Quaternary environmental change through an INQUA-funded paleoclimate commission, the INTegration of Ice-core, MArine and TErrestrial program (INTIMATE [Bjorck et al., 1998]). INTIMATE is a core project of the INternational QUaternary Association (INQUA) Paleoclimate Commission whose primary goal is the synthesis of marine, terrestrial and ice-core records within the North Atlantic for the late Quaternary, initially for the LGIT (last ~15 kyrs) but recently extended to cover the period of heightened glacial climate during the Last Glacial Maximum (LGM; 23 to 19 cal. kyr BP) (Hoek et al., 2008).

The INTIMATE project has pursued approaches that overcome the limitations of precision and accuracy routinely achievable using contemporary chronological methods, namely through an event stratigraphy approach (i.e., the definition of key climatic events within a region from the inter-comparison of numerous environmental records) (e.g., Lowe et al., 2001; Turney et al., 2006). This has proven essential to better constrain the timings of events and the ‘leads’ or ‘lags’ between terrestrial, marine, cryospheric and atmospheric realms (Lowe et al., 2001). In particular, the application of time-parallel marker horizons including tephra layers, stable isotope stratigraphy, paleomagnetic stratigraphy and radiocarbon wiggle-matching have permitted the correlation of events throughout the North Atlantic during the LGIT (e.g., Lowe et al., 2001; Turney et al, 2006; Rasmussen et al, 2008). In contrast, there is a conspicuous absence of continuous, high-resolution and well-dated Quaternary terrestrial records from the low- and mid-latitude Southern Hemisphere (Alloway et al., 2007). Thus a subsidiary INTIMATE program, AUS-INTIMATE, was established at the XVIth INQUA Congress (2003) for the integration of Australasian paleoclimate records of the late Quaternary (~8-30 cal. kyr BP) within the Southern Hemisphere (Turney et al., 2004). Nevertheless as noted, the timing, magnitude and drivers of Southern Hemisphere Quaternary change remain poorly understood, and records extending beyond the LGM rare, with the notable exception of Antarctic ice cores (McManus, 2004). Reasons for this include technological limitations, the need to develop novel proxies tailored to Southern Hemisphere archives, and a paucity of high-resolution, continuous, long-term records (e.g., Alloway et al., 2007). A high-resolution and multi-proxy study of past climate at Lake Pupuke, Auckland, can therefore extend knowledge of the nature and driving forces behind mid-latitude Southern Hemisphere climate and environment during the late Quaternary.

1.2 The NZ-INTIMATE Project

The Australasian INTIMATE project (AUS-INTIMATE) comprises the Australian (OZ-INTIMATE) and New Zealand (NZ-INTIMATE) research centres, whose aim is to develop a coherent climate event stratigraphy for the Australasian region from ~30 to 8 cal. kyr BP (Turney et al., 2006). However, AUS-INTIMATE publications have highlighted marked variability in responses to and dates associated with the last Termination (T1) in Australasia (Turney et al., 2006; Alloway et al., 2007; Lowe et al., 2008). Consequently, conflicting evidence has been presented for the nature of inter-hemispheric teleconnections and the principle forcing mechanism(s) (Turney et al., 2006). Turney et al. (2006) note that in addition to a paucity of high-resolution paleoclimatic records in the Southern Hemisphere, the wide dispersal of archive sites have compounded this problem (Turney et al., 2006).
Independently and precisely dated, robust investigations of paleoclimate over the last ~30 kyrs within Australasia are therefore urgently needed to better define regional paleoclimate (Turney et al., 2003; Williams et al., 2009).

New Zealand has a wealth of terrestrial archives of paleoclimate which in conjunction with a maritime climate offer a sensitive record of interactions between sub-tropical surface water (STW) and sub-Antarctic surface water (SAW) at the nearby subtropical front (STF) (Figure 1.1) (Alloway et al., 2007). The STF is believed to have migrated through ocean-atmosphere induced changes to the extent of Arctic and Antarctic sea ice (Denton et al., 2010), thereby driving marked changes to paleoclimate in New Zealand (Shulmeister et al., 2006). Other important regional climatic drivers include the position of the Inter-Tropical Convergence Zone (ITCZ), which governs precipitation patterns as far south as 30 °S and is modulated by the Interdecadal Pacific Oscillation (IPO), and changes to El Niño Southern Oscillation (ENSO) (Salinger et al., 2001; Turney et al., 2006). The relatively small size and maritime climate of New Zealand afford its terrestrial archives the capacity to accurately record changes in ocean-atmosphere circulation (McGlone et al., 1993). For instance, Denton et al., (2010) have recently employed paleoclimatic data gathered in New Zealand to propose a comprehensive mechanism for global climate change experienced during T1. The distinct nature of two-step deglacial patterns in Antarctica and Greenland during the LGIT, including an earlier Antarctic Cold Reversal (ACR; 14.5 to 12.7 cal. kyr BP) than the Younger Dryas in Greenland (YD; 12.9 to 11.6 cal. kyr BP) (Alloway et al., 2007), permitted the role of Atlantic Meridional Overturning Circulation (AMOC) and Southern Ocean circulation, in regulating LGIT global climate to be identified (e.g., Denton et al., 2010).

The application of paleoclimatic data from New Zealand by Denton et al., (2010) to late Quaternary climate models, coupled to ongoing research by NZ-INTIMATE aimed at improving chronologies for the late Quaternary (e.g., Newnham et al., 2008), demonstrates the capacity for paleoclimatic studies of New Zealand to provide high-value data. New Zealand’s sensitivity to regional atmospheric/oceanic circulation changes has also been used to develop insights into glacial-interglacial climate from which to test competing hypotheses on inter-hemispheric climate teleconnections (e.g., McGlone et al., 2004, 2010; Vandegoes et al., 2005; Shulmeister et al., 2006; Turney et al., 2006; Williams et al., 2009). The absence of a large ice-sheet during the LGM has also aided preservation of paleo-archives permitting Alloway et al., (2007) the opportunity to conduct the most exhaustive review of late glacial paleoclimate within New Zealand using diverse paleoclimatic archives (e.g., marine sediment cores, speleothems, terrestrial sediment cores, glacial and fluvial sequences). Three major climate phases were identified: (1) a Last Glacial Coldest Period (~28.0 to 18.0 cal. kyr BP); (2) Late Glacial-Interglacial Transition (~18.0 to 11.6 cal. kyr BP); and (3) the Holocene (~11.6 cal. kyr BP to present). However, the authors note a paucity of continuous, high-resolution records from which to address the debate surrounding a possible Late Glacial Reversal (LGR) believed to record the ACR through an Antarctic teleconnection (e.g., Turney et al., 2003; Williams et al., 2005), or alternatively, the YD through an Arctic teleconnection (e.g., Denton and Hendy, 1994). A paucity of well-dated sequences also restricts the precise identification of other millennial-scale climate events (e.g., Dansgaard-Oeschger [DO] and Antarctic Isotope Maxima [AIM]) with which to assess climate teleconnections (Alloway et al., 2007; Augustinus et al., 2011a). Thus a principal goal of the NZ-INTIMATE project is the analysis of novel high-resolution, continuous terrestrial sequences with precise chronologies (Alloway et al., 2007).
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).
Within the Auckland Volcanic Field (AVF; Figure 1.2), a series of sediment cores extracted from volcanic maars that constitute the NZ-Maar project (e.g., Augustinus, 2007) contain lacustrine records of paleoclimate. The Auckland maars are subject to proximal ashfall (tephra) from the active AVF as well as distal sites in the central North Island of New Zealand (Sandiford et al., 2002, 2003; Horrocks et al., 2005; Newnham et al., 2007a,b; Augustinus et al., 2011a). The distinct geochemistry and known ages of tephra permit robust chronologies for the maar sediment sequences to be developed (e.g., Shane and Hoverd, 2002; Molloy et al., 2009). Moreover, widespread tephra deposits offer links to other high-resolution archives throughout New Zealand (e.g., 21 tephras have been selected for use in NZ-INTIMATE projects spanning the last ~30 kyrs [e.g., Newnham et al., 2008]). Auckland is also situated close to the Tasman Front and experiences greater sub-tropical influxes of warm water than more southern locations meaning that even subtle changes to the STF can become manifest as marked changes to regional paleoclimate (refer to Figure 1.1) (Alloway et al., 2007). For instance, prior investigations of Onepoto maar demonstrated the region’s sensitivity to global oscillatory climate systems including ENSO and the IPO (Pepper et al., 2004; Shulmeister et al., 2006). Other nearby maars also contain a detailed record of late Quaternary paleoclimate (Sandiford et al., 2002, 2003; Newnham et al., 2007b; Augustinus et al., 2011a). However, Lake Pupuke is the only maar crater to have not either in-filled or become breached and subject to wave and tidal mixing of sediment (Horrocks et al., 2005). Lake Pupuke was drilled for sediments in February 2007, in order to provide the most detailed and continuous record of climatic change affecting the Auckland region for the last ~48 kyrs and is the subject of the analyses described in this thesis.

Figure 1.2: The Auckland Volcanic Field (AVF) showing the location of volcanic maars in the NZ-Maar project: Lake Pupuke, Hopua, Onepoto and Oraeki Basin, and Pukaki crater (Modified from Newnham et al 2007a: 518).
A recent development of the NZ-INTIMATE programme is extending our understanding of modern synoptic patterns to the paleoclimatic records. Lorrey et al., (2007) have employed the findings of Kidson (2000) to demonstrate that New Zealand possesses six distinct regional climate zones, which can behave in- or out-of-phase with other regional climate zones (Figure 1.3). The interaction of moisture-laden sub-tropical and sub-Antarctic airmasses within these generate three dominant regimes: (1) trough; (2) zonal; and (3) blocking. Long-term climate can therefore record the dominant effects of trough, zonal and/or blocking regimes with shifts resulting in a distinct spatial structure for temperature and precipitation throughout New Zealand due to the marked orographic and latitudinal gradients occupied by each of the six regional climate zones (Table 1.1). A recent investigation of the Eastern North Island and Southwest South Island confirmed that distinct modern spatial patterns of precipitation and temperature can be applied to paleoclimate records to infer past climate regime shifts (e.g., altered atmospheric circulation and associated synoptic types) and permits different paleoclimate in regional climate zones to arise simultaneously by common forcing (Lorrey et al., 2008). Application of a regional paleoclimate zone classification including knowledge of climate regime shifts is therefore essential to further improvement in understanding of late Quaternary terrestrial paleoclimate within New Zealand (Lorrey et al., 2007).

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

<table>
<thead>
<tr>
<th>Weather Regime</th>
<th>Precipitation</th>
<th>Temperature</th>
<th>Winds</th>
<th>Average position of regional high pressure</th>
<th>Modern % occurrence</th>
<th>Association with the Southern Oscillation Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trough</td>
<td>Wetter across all of New Zealand, 109% to 118% normal; cloudy.</td>
<td>Colder than average for entire country; negative temperature gradient increases southward and westward.</td>
<td>Mixed</td>
<td>N/A</td>
<td>38</td>
<td>More common during positive SOI (La Nina)</td>
</tr>
<tr>
<td>Zonal</td>
<td>Dry for the North Island; dry east and north of South Island; wet western and southern South Island; anticyclones in the north.</td>
<td>Usually results in cooler temperatures for western and southern regions and warmer northern and eastern regions.</td>
<td>Westerly and south-westerly</td>
<td>30° S – 39° S</td>
<td>25</td>
<td>More common during negative SOI (El Niño)</td>
</tr>
<tr>
<td>Blocking</td>
<td>Wetter in northern and eastern areas; drier in southwest of both North and South Islands.</td>
<td>Warmer than average for entire country; warmest in north and western regions.</td>
<td>Northerly and easterly</td>
<td>39° S – 50° S</td>
<td>37</td>
<td>More common during positive SOI (La Nina) but at expense of synoptic types in Trough regime, and primarily during summer</td>
</tr>
</tbody>
</table>
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).
1.3 Research Objectives

The goal of the NZ-INTIMATE project is to improve our knowledge of climate in New Zealand during the last 30 cal. kyr BP (Alloway et al., 2007). This knowledge is critical to the debate regarding inter-hemispheric climate teleconnections (e.g., Turney et al., 2003, 2006; Shulmeister et al., 2006; Denton et al., 2010; McGlone et al., 2010). The NZ-Maar project can contribute data to NZ-INTIMATE though with a focus on rapid climate change events, as well as the development of novel paleoclimate proxies (Augustinus, 2007).

The presence of a continuous, high-resolution lacustrine sedimentary record containing well-dated tephra isochrons, gives Lake Pupuke the capacity to precisely and accurately record the terrestrial paleoclimate of mid-latitude New Zealand. This thesis encompasses a high-resolution multiple-proxy approach to extract a continuous record of paleoclimate from ~48 cal. kyr BP to today from Lake Pupuke. In conjunction with a detailed chronology, this permits the robust determination of the timing, duration and direction of major climatic changes at Lake Pupuke during the late Quaternary. The principal aim of this thesis is to add to our understanding of the sensitivity of mid-latitude Southern Hemisphere landmasses to late Quaternary climate change, by:

1. Development of a robust chronology in keeping with INTIMATE protocols on improved precision for paleoclimate events at Lake Pupuke from ~48 cal. kyr BP to today;
2. Application of novel Oxygen and Silicon stable isotopes of diatom silica proxies to the Lake Pupuke sequence including, by:
   a. Improvement of existing techniques for the purification of diatom silica and contaminant effect modelling;
   b. Comparison of modelled diatom isotope proxies for past environment with more established indicators of change.
3. Reconstruction of past climate at Lake Pupuke from ~48 cal. kyr BP to today.

In the regional paleoclimate approach of Lorrey et al., (2007), Lake Pupuke offers the longest record of terrestrial paleoclimate for the Northern North Island (NNI). To meet the third aim above, this thesis concludes by development of a climate event stratigraphy for the Auckland region from ~48 cal. kyr BP to today.

1.4 Research Approach

To meet aims (2) and (3) above in this thesis, the past environment (paleolimnology) of Lake Pupuke, Auckland is examined using a paleolimnological approach (e.g., Last and Smol, 2001). Briefly this includes:

1. Understanding the present controls on lacustrine processes and ecology ('the present is the key to the past');
Chapter One

2. Coring the lacustrine archive;
3. Analysing the sediment sequence for stratigraphy to create a single continuous sequence;
4. Establishing an age-depth model to infer timings and duration of changes in paleolimnology;
5. Analysing proxies for past environment;
6. Compiling a multiple-proxy climate event stratigraphy.

1.4.1 Paleolimnology

Lakes contain a record of past biological, chemical and physical change either in isolation as a closed basin (endorheic), or integrated with a fluvial system as an open basin (exorheic) (Smol et al., 2001). Organic and inorganic matter within lake sediment preserve this record of past environment either from within the lake (autochthonous) or external to it (allochthonous) (Smol et al., 2001). For instance, lacustrine ecosystem structure can be reconstructed from the biological remains of aquatic organisms (Sayer et al., 2010). Geochemical information contained within these microorganisms and the bulk sediment offer a complimentary record of past lacustrine processes and environment (Talbot, 2001).

Advances in analytical techniques, as well as innovations in statistical approaches, have meant that the field of paleolimnology has grown rapidly in the last 15 years to become one of the principal pathways for reconstruction of terrestrial paleoclimates across a range of spatial and temporal scales (Birks and Birks, 2006). Multivariate statistical interpretation of the wealth of proxy environmental data capable of being recovered from lake sediment is now commonplace and an important aid to data interpretation (Birks and Birks, 2006). Consequently, the field of paleolimnology has been critical in elucidating mid- and low latitude records of past climate, environment and anthropogenic activity (Smol et al., 2001). However, application of paleolimnology to past climate change has raised numerous issues, namely the challenges of identifying: (1) the spatial scale of change (e.g., local versus regional); (2) temporal rates of change (e.g., resolution permissible by age model, effect of seasonality); and (3) extent of proxy changes (e.g., errors attached to single proxies) (Fritz, 2008).

The NZ-Maars project aims to prevent (1) by analysing several Auckland maar craters although the present project is limited to a single site (Lake Pupuke) so it will inevitably incorporate some local events (alleviated by comparison to similar paleo-records from the Northern North Island in Chapter 7). Previous investigations of Lake Pupuke have focussed on discrete time slices and with insufficient resolution or proxies to reliably meet the aims listed above (e.g., Pepper et al., 2004; Horrocks et al., 2005; Striewski et al., 2009) but have demonstrated the presence of numerous fine laminae including seasonal couplets that contribute to a relatively high sedimentation rate (Augustinus et al., 2008). The high sedimentation rate in conjunction with a detailed tephra and radiocarbon-based chronology will reduce the impact of (2). Likewise the application of multiple proxies for past environments is now a standard approach used to avoid the errors or uncertainty inherent in a single proxy (e.g., Smol et al., 2001). Furthermore, a multi-proxy approach is also essential to be able to successfully apply diatom stable isotope proxies ($\delta^{18}$O, $\delta^{30}$Si) to the Pupuke sediment sequence as these are often limited by
significant uncertainties (e.g., diagenetic, taxonomic and other vital effects as well as complications due to changes in effective moisture, air mass circulation, rain-out, and seasonality across catchment to regional spatial scales [e.g., Leng and Barker, 2006; Leng et al., 2009]). Within this multiproxy approach, advances in statistical techniques permit truly quantitative paleoenvironmental inferences to be made (e.g., use of transfer functions [Birks, 1998]). For instance, a diatom transfer function (Reid, 2005) is applied to the Pupuke diatom record in this thesis (Chapter 5) to model quantitative water quality changes (e.g., pH, conductivity, chlorophyll-a, dissolved nutrients), thereby reducing (3) and increasing the reliability of climate reconstructions.

Successful modelling of paleolimnology requires an understanding of modern limnological controls on environmental indicators (Sayer et al., 2010). More importantly, modern hydrology and their seasonal variations are critical in bracketing proxy changes in the sedimentary record, thereby removing the capacity for local short term events to obscure longer term trends in paleoclimate. Consequently, the modern limnology of Lake Pupuke is assessed in Chapter 2 emphasizing the controls on the environmental proxies employed later in the thesis.

1.4.2 Stable Isotope Paleolimnology

Paleolimnological proxies offer an indirect record of past lake environment (Smol et al., 2001). Each can be classified by origin: biogenic, geochemical or physical (Smol et al., 2001). Recent paleolimnological advances in biogenic and geochemical proxies have included the application of stable isotopes to lacustrine archives (Leng and Barker, 2006). Changes in the relative abundance of heavier isotopic forms of an element relative to a lighter equivalent can provide an insight to a range of climatic and environmental processes, in particular the stable isotopes of Hydrogen, Carbon, Nitrogen, Oxygen and Silicon given their abundance in organic and inorganic matter (Hoefs, 1997; Talbot, 2001). Stable isotopic changes are reported as δ values and expressed as per mil (‰) variations between a sample and standard in ratio format. For instance, for Oxygen:

$$\delta^{18}O \text{ (‰)} = [(R_{\text{sample}}/R_{\text{std}})-1] * 1000$$

where \(R_{\text{sample}}\) and \(R_{\text{std}}\) are the ratios of \(^{18}\text{O}/^{16}\text{O}\) present in the sample and standard respectively.

The control of lake water geochemistry by climatic processes enables the isotopic composition of lacustrine precipitates to record paleoclimate (Leng and Barker, 2006). Natural variations in the isotopic composition of lacustrine precipitates can be attributed to two isotopic effects: physical and chemical (Talbot, 2001). Physical effects are those attributed to phase-state changes (e.g., freezing, sublimation, melting, evaporation), diffusion and adsorption, whilst chemical effects occur through inorganic exchanges and biochemical reactions (Kaplan, 1983; Owens, 1987; Talbot, 2001). Physical and chemical isotope effects can further be defined as one of two types: equilibrium and kinetic (Talbot, 2001). Equilibrium fractionation describes the isotopic exchange between product and reactant at a rate that maintains equilibrium and is bidirectional with the free exchange of isotopes in both directions (Clark and Fritz, 1997). Although the rate process is in equilibrium, the rate of exchange in any
direction might be different so that the result is a shift to heavier isotopes or an enrichment of the reactant. The corresponding product will be relatively lighter or depleted in heavier isotopes. For instance, the equilibrium fractionation of water vapour to precipitation in a closed system can be explained as:

$$H_2^{18}O (gas) \rightleftharpoons K^{18} H_2^{18}O (liquid)$$

$$H_2^{16}O (gas) \rightleftharpoons K^{16} H_2^{16}O (liquid)$$

Where K is the rate of exchange which is constant in both directions but whose rate value is different between isotope forms. Thus K18 ≠ K16, in fact K18 < K16 such that liquid water and vapour become enriched and depleted respectively in a change of state from vapour to liquid or vice versa (Clark and Fritz, 1997).

A fractionation factor (α) describes the ratio difference between parent and daughter (α_{Gas-liquid} = [^{18}O/^{16}O]_{Gas} / [^{18}O/^{16}O]_{Liquid}). The cause of fractionation is the relatively lower bond strengths and higher zero point energies needed to utilise lower atomic weight isotopes (e.g., lower bond strength of ^{16}O relative to ^{18}O) (Hoefs, 1997). In equilibrium processes, at lower temperature, lighter isotopes diffuse more rapidly and evaporate whilst a higher temperature will reduce the difference in zero point energies resulting in a lower equilibrium fractionation rate (Hoefs, 1997). In kinetic processes, complex, one-way isotope reactions occur, either as systematic or non-linear fractionations (e.g., evaporation, diffusion, biological processes) (Clark and Fritz, 1997). Kinetic isotope effects are often expressed in biogenic precipitates thereby obscuring equilibrium, thermodynamic processes (Leng and Barker, 2006). However, some biogenic precipitates offer a stable isotope proxy with limited non-linear or kinetic fractionation, most notably diatom silica (Leng and Marshall, 2004). As diatom silica contains Oxygen and Silicon precipitated in equilibrium from lake water, δ^{18}O_{Diatom} and δ^{30}Si_{Diatom} can provide an indirect proxy for changes to δ^{18}O_{Lake} and δ^{30}Si_{Lake} (Leng and Marshall, 2004).

The presence of Oxygen in dissolved forms throughout the global water cycle permits changes to lacustrine signatures (δ^{18}O_{Lake}) to trace variability in meteorological parameters and atmospheric circulation (Dansgaard, 1964; Rozanski et al., 1993). Values of δ^{18}O_{Lake} reflect the water sources so that open lakes possess a δ^{18}O_{Lake} signature closely aligned to δ^{18}O_{Precipitation} (closed lakes undergo greater kinetic fractionation leading to highly dissimilar values) (Leng and Barker, 2006). Values of δ^{18}O_{Precipitation} are principally dependent upon the oceanic source region and temperature in a positive relationship (Clark and Fritz, 1997). For instance, global δ^{18}O_{Precipitation} observes a linear relationship to temperature varying ~0.67-0.90‰/ºC (at high latitude) to ~0‰/ºC (at the Equator) (Dansgaard, 1964; Rozanski et al., 1993; Fricke and O’Neil, 1999). The most commonly cited relationship is that derived for coastal locations in the North Atlantic by Dansgaard (1964), where T is mean annual temperature (ºC):

$$δ^{18}O = 0.69 \times T - 13.6$$
Changes to $\delta^{18}\text{O}_{\text{Lake}}$ can therefore be employed as a ‘paleothermometer’ of moisture vapour (e.g., Leng and Barker, 2006). However, records of $\delta^{18}\text{O}_{\text{Lake}}$ can also provide information on changes to atmospheric circulation (a source effect), distance from source through the preferential loss of enriched moisture via ‘rain-out’ or Rayleigh distillation (a continentality effect), sea-level (an altitude effect), and seasonality of precipitation (an amount effect) (Clark and Fritz, 1997; Hoefs, 1997). This then forms the basis for application of $\delta^{18}\text{O}_{\text{Diatom}}$ to paleolimnological sequences (Leng and Marshall, 2004).

The precipitation of dissolved Silicon into diatom silica is also linked to paleoclimate because $p\text{CO}_2$ governs the dissolution of terrestrial silicates (Street-Perrott et al., 2008), and precipitation governs the supply of dissolved Silicon in runoff and throughflow to lakes (Leng et al., 2009). There is no thermodynamic relationship in $\delta^{30}\text{Si}$ precluding its use beyond modelling supply and uptake of dissolved Silica (DSi) by siliceous organisms (e.g., diatoms, sponges, higher plants, chrysophytes) (Leng et al., 2009). However, uptake of DSi is a proxy for biological productivity which is determined by several factors including climate (Leng et al., 2009).

It is essential to monitor the seasonal and spatial variation in dissolved Oxygen and Silicon isotopic pools as well as any corresponding ‘vital’ effect incorporated during precipitation of biogenic silica, and its burial, especially in deep crater lakes, where complex patterns of mixing and nutrient availability can arise (e.g., Lamb et al., 2007). The isotopic controls on modern diatom silica precipitated in Lake Pupuke are therefore assessed prior to $\delta^{18}\text{O}_{\text{Diatom}}$ and $\delta^{30}\text{Si}_{\text{Diatom}}$ paleo-reconstructions in Chapter 6.

1.4.3 Thesis Organisation

In this chapter, the INTIMATE and subsidiary NZ-INTIMATE programs have been described, highlighting the need for further high-resolution, well-dated and continuous reconstructions of past climate from New Zealand. The aims of this thesis fall within the remit of NZ-INTIMATE (e.g., the development of a precise chronology and reconstruction of paleoclimate from a high-resolution climate record, the Pupuke sediment sequence) but extend to meet the NZ-Maar project through the development of novel stable isotopic proxies of paleolimnology. To enable these to be achieved, this thesis adopts a paleolimnological approach with each chapter following the sequential order outlined earlier (Section 1.3. Research Approach). To better elucidate the major controls on paleoenvironmental indicators applied later, the neolimnology of Lake Pupuke is described next (Chapter 2). This is followed by a description of the coring process, sediment stratigraphy, construction of a single composite sediment sequence from Lake Pupuke and development of an age-depth model (Chapter 3). The proxies for past climate are distinguished by their type and applied in three chapters: physical and geochemical indicators explored first in Chapter 4, followed by biological (diatom) indicators in Chapter 5, and novel diatom stable isotope proxies in Chapter 6. This approach permits the first aim to be met in Chapter 3, second aim to be met in Chapter 6 and the third aim to be met by a multi-proxy reconstruction of late Quaternary paleoclimate in the Auckland region in Chapter 7. Conclusions and future research are described in Chapter 8.
CHAPTER TWO

Limnology of Lake Pupuke

2.1 Introduction

Lake sediments can provide an accurate, resolute and continuous means to assess and infer changes to past climate (Smol et al., 2001). However, the sensitivity of lakes to climate varies according to their physicochemical and biological characteristics (Wetzel, 2001). Changes to meromixis, surface water residence time and hydrochemical properties are all reflected in sedimenting organic and inorganic matter (Telford et al., 1999; Telford and Lamb, 1999). Crater maar lakes can provide the most suitable sedimentary records for reconstructing past environments because of their deep morphology, restricted catchment and short fetch (Williams et al., 1993). A high depth/width ratio also affords maars better potential for preserving continuous records of paleoclimate, particularly where lake volume and biochemical characteristics are linked to changes in the precipitation to evaporation balance ($P/E$) (Leng and Marshall, 2004). However, without an understanding of modern seasonality and its effects on lacustrine cycles (e.g., physicochemical, nutrient and biomass) environmental inferences derived from a sedimentary record will be liable to considerable error.

Subsequent chapters utilise recent sedimentation in water-column traps to calibrate paleolimnologic change with reference to contemporary seasonality. To facilitate the reconstruction of paleolimnology at Lake Pupuke the limnology of the maar lake (e.g., geology, climatology and hydrology) is explored focussing on the fundamental role of stratification in contemporary nutrient cycling and productivity. Seasonal release of deep nutrients during overturn is likely to be characteristic of much Holocene sedimentation at Pupuke and is thus a fundamental control on the proxy data.

2.2 Geology

Lake Pupuke (36°78.30'S, 174°76.70'E) lies within a phreatomagmatic explosion crater (maar), at the heart of New Zealand’s largest city, Auckland (Figure 2.1). Auckland sits astride a narrow isthmus of Miocene and Pleistocene sedimentary and igneous rock. Indeed, a range of active volcanic systems exist across the North Island of New Zealand from larger, arc-related volcanoes of the central North Island (andesitic and rhyolitic) to the small-scale basaltic, intraplate Auckland Volcanic Field. The AVF exists north of the extinct South Auckland volcanic field which remained active throughout the early to middle Quaternary (~500 cal. kyr BP [Cook et al., 2005]). The AVF comprises ~50 Late-Quaternary mono- and digenetic volcanoes within the City of Auckland, a
region covering ~140 km² (Figure 2.1) (Searle, 1964; Kermode, 1992; Allen and Smith, 1994; Cassidy et al., 1999; Shane and Hoverd, 2002). Local AVF volcanic deposits record a range of eruption styles from explosive phreatomagmatic to Strombolian event types and comprise a combined volume of 3.4 km³ dense rock equivalent (DRE) of magma (Allen et al., 1996). A single volcanic centre alone accounts for ~59% of total DRE ejecta, namely the youngest, Rangitoto volcano (Magill and Blong, 2005; Cassidy et al., 2007). Of the remaining ~49 volcanic centres, 13 comprise maars whose sediments preserve records of late Quaternary paleoenvironment (e.g., Shane and Sandiford, 2003 [Onepoto Maar]; Sandiford et al., 2003 [Pukaki Maar]; Horrocks et al., 2005 [Pupuke Maar]).

Pupuke maar is the northernmost and possibly the oldest in the AVF, formed 200-250 kyr ago in a 1.1 km² crater through the eruption of 0.045 km³ DRE magma (Cassidy et al., 1999). Maar catchment lithology is characterised by basaltic lava, ash and lapilli (Allen et al., 1996). Crater formation and interactions with the local groundwater table led to the excavation of the ~57 m deep modern crater, a ~3 km lava apron up to ~15 m thick and inner and outer tuff-ring deposits (Searle, 1981). Indeed, Pupuke is one of eleven AVF volcanoes with tuff-rings whilst a further twenty four retain scoria cones (Kermode, 1992). Tuff rings comprise a minor component of the AVF (<0.05 km³ DRE) (Searle, 1981). Despite this, the tuff ring of Pupuke volcano has provided an effective barrier to the nearby Hauraki Gulf from early in its formation until today. Lake Pupuke is the only AVF crater maar lake to have retained its freshwater status (Kermode, 1992). Another 8 including Pukaki and Onepoto Maars had their sills overtopped by rising sea levels during the marine transgression after the Last Glacial Period Maximum (LGM) (particularly between 9.0 and 7.0 cal. kyr BP [Gibb, 1986]). Consequently they were inundated with marine waters leading to rapid estuarine sedimentation and infilling (e.g., Hayward et al., 2002).

Until recently no studies had been conducted into the sediment fill and post-eruptive history of the AVF maar lakes. Horrocks et al (2005) and Augustinus et al (2006) provide some of the first evidence for reconstructed paleolimnology in the AVF. These and other studies have noted that AVF crater maar lakes have received both proximal and distal tephra, sourced from several major volcanic fields including those mentioned above (e.g., Taupo Volcanic Zone [TVZ], Tongariro Volcanic Zone [ToVZ], and Taranaki Volcanic Zone [TaVZ] as well as the smaller Okataina, Mayor and White Island centres) (Molloy et al., 2009). For instance, cores of Onepoto maar paleolake, revealed the presence of well-dated tephra, of which 4 originated locally from the AVF: Rangitoto (0.62 ± 0.07 cal. kyr BP); Mt. Wellington (9.16 ± 0.32 cal. kyr BP); Panmure Basin (26.63 ± 0.17 cal. kyr BP); and Crater Hill (29.10 ± 0.80 cal. kyr BP) (Allen and Smith, 1994; Shane and Hoverd, 2002).
Chapter Two

Figure 2.1: The Auckland Volcanic Field (AVF) is a region of late Quaternary active volcanism covering 140 km$^2$ 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]).
Chapter Two

2.3 Bathymetry and Morphometry

Lake Pupuke exhibits typical bathymetry and morphometry for a volcanic maar lake (Figure 2.1) (Horrocks et al., 2005; Augustinus et al., 2006, 2008). The lake occupies a large proportion of its 1.85 km$^2$ catchment (~58%; lake surface area [$A_0$] 1.1 km$^2$) (ARWB, 1979). The modern lake level fluctuates between 5.09 m and 5.86 m a.s.l. with a maximum ($Z_{\text{max}}$) and mean water depth ($Z$) of ~58.0 m and ~28.9 m respectively (Barker, 1970). Maximum lake diameter ($b_{\text{max}}$), shoreline length ($L$) and volume ($V$) are 1.3 km, 4.3 km and $2.9 \times 10^7$ m$^3$ (Holmes, 1994). As noted, the crater rim and underlying lava flows encircling the tuff deposit (15 m above sea level [a.s.l.]) have provided a natural barrier to the ocean less than 200 m away at its narrowest (refer to Figure 2.1) (Main and Barnes, 1989).

Basin morphology is a product of its volcanic provenance with shallow (<12 m deep) shelves that grade rapidly into very steep crater walls and a broad flat bottom (Figure 2.1). The lake sediments are composed of loose silty clay bound on the shelves by luxurious aquatic macrophytes (see below; ARWB, 1990). Basin sides are composed of exposed basalt (Salter et al., 2005). The high depth/width ratio favours paleolimnological approaches by reducing sediment disturbance through fetch-induced wave activity by limiting the wave base to ~20-30m depth, well above the central benthic zone (Barker, 1970). Limited mixing results in extended periods of benthic hypoxia within the hypolimnion under stable thermal stratification (see below).

2.4 Climatology (Regional and Local)

Regional climate affecting Auckland and within northern New Zealand (34-40 °S) is sub-tropical with warm, humid summers (December-February) and mild winters (June-August) driven by westerly migrating anticyclones and troughs (Coulter, 1975). Anticyclonic blocking regimes frequently occur in winter and result in mild conditions whilst changes to zonal trough circulation account for most of the variance in inter-annual precipitation (Salinger, 1980). Changes to seasonal and inter-annual regimes arise through changes to the position of the South Pacific Convergence Zone (SPCZ) – the confluence of Divergent Easterlies (DE) and Southeast Trade Winds (STW) (Figure 2.2) (Kidson, 2000). Climatic connections between the SPCZ and the equatorial Pacific cause changes to the SPCZ through El Nino Southern Oscillation (ENSO) and Inter-Pacific Decadal Oscillation (IPO) variation (Lorrey et al., 2007). For instance, ENSO modulation of regional precipitation and temperature occurs by changes to zonal circulation: El Niño events result in weakened STW, more frequent blocking systems and drier conditions in the Northern North Island (NNI); La Nina years result from greater easterly circulation and result in wetter, warmer conditions in the NNI (Mullan, 1995; Salinger et al., 1995). Likewise the IPO modulates ENSO behaviour on a decadal and multi-decadal time scale: positive phases are characterised by reduced precipitation in the NNI; and negative phases by reduced southwest circulation and wetter conditions in the NNI (Salinger and Mullan, 1999; Salinger et al., 2001). Importantly, changes to regional climate through ENSO and the IPO can induce changes to dominant circulation regime (e.g., trough, zonal and blocking) affecting the NNI and either in-phase or opposing responses to the other 5 regional climate zones (e.g., Lorrey et al., 2007). Thus a comparison of paleo-climate at Lake Pupuke and other regional datasets can reconstruct past circulation regimes in New Zealand.
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).
An understanding of contemporary climate effects upon hydrology is required for the successful reconstruction of paleoclimate from paleolimnological changes in Lake Pupuke. Local climate has therefore been investigated from January 2007 to December 2009 through data available from meteorological stations monitored by the National Institute for Water and Atmospheric Research (NIWA; http://www.niwa.co.nz [last accessed 16/01/2010). The nearest stations are the Auckland Regional Council’s North Shore electronic weather station (Agent Number A64775; 36°78.60’S, 174°74.00'E) and Albany weather station (Agent Number 1412; 36°74.96’S, 174°75.56'E) <10 km from the basin and capable of recording air temperature, wind speed, gust strength, wind direction, open-water evaporation and rainfall at daily and hourly intervals. Air temperature, precipitation and precipitation to evaporation ratios (P/E) for the interval 01/01/2006 until 01/01/2010 are presented in Figure 2.3 and interpreted below.

Figure 2.3: Average monthly air temperature (°C), 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.
Auckland’s temperate climate and location in the South Pacific Ocean result in mild seasonal temperature variation. For instance, between January 2006 and January 2010 mean monthly air temperature ranged 8.83 °C from a Winter low (July 10.97 °C) through to a Summer high (January 19.80 °C) with an annual average of 15.06 ± 3.15 °C (μ ± σ, n = 535). Daily air temperature ranges were highly similar between months (8.85 ± 0.33 °C [μ ± 1σ, n = 535]) with daily extremes occurring in January (24.2 °C) and July (6.6 °C). Average monthly wind speed also demonstrates limited variability characterised by a winter low (May 1.44 ms⁻¹) and Spring high (October 2.96 ms⁻¹). Nevertheless annual average wind speed is relatively high at 2.29 ms⁻¹ from a predominantly southwesterly direction (196 ± 19 ° [μ ± σ, n = 535]). Winter months (June, July and August) also demonstrate greater gusting speeds (winter μ = 20.08 ms⁻¹, annual μ = 18.44 ms⁻¹). High and consistent wind speeds across Lake Pupuke result in greater mixing depths (up to 30 m [ARWB, 1979]) whilst the seasonal range in temperature permits development of thermal stratification throughout the months of September to June (Holmes, 1994). Thereafter, greater wind speed and gustiness in the months of July and August result in more energetic waves whose bases, in conjunction with lower monthly temperatures, result in a breakdown of thermal stratification and overturn (Holmes, 1994). Thus seasonality (e.g., in air temperature and windiness) is an important parameter for consideration when interpreting the paleoenvironmental record contained in Lake Pupuke sediments, as the latter will dictate the strength of thermal stratification, and insodoing, indirectly determine dissolved nutrient availability and productivity (see below).

Auckland precipitation between January 2006 and January 2010 also exhibited marked seasonality varying from a monthly average low of 49 mm (November) to a high of 152 mm (July). Annual and monthly averages were 1161 ± 34 mm (1σ) and 97 ± 34 mm (1σ) respectively. Over the study period, total deposition over the winter and spring months (June to August and September to November) accounted for 35% (405 mm) and 27% (314 mm) respectively. Summer and autumn months (December to February and March to May) contributed a further 16% (190 mm) and 22% (252 mm) of annual precipitation. Thus summer periods of peak air temperature also correspond to a prominent reduction in precipitation (Figure 2.3), which it is important to note, will influence the availability and isotopic composition of dissolved nutrients including Oxygen (DO) and Silicon (DSi) (e.g., by isolating surface waters favouring equilibrium and/or kinetic fractionation by evaporation/biological uptake from a meteoric water line [Leng and Marshall, 2004]). DO and DSi are then assimilated as diatomaceous silica which contributes to the sediment record and offers a proxy for past variations in seasonality (Section 1.3.2. Stable Isotope Paleolimnology).

Seasonal air temperature, windiness and precipitation regimes also result in significant changes to the balance of precipitation and evaporation (P/E) – an important climatic parameter capable of altering the chemistry of lake waters (Wetzel, 2001). Surface water evaporation rates within Lake Pupuke were estimated from the North Shore electronic weather station (Agent Number A64775) using an open pan Class A evaporimeter. Meteorological pans provide an upper estimate of evaporation as thermal conduction from the base and sides enhance observed values beyond corresponding lake estimates (Dunne and Leopold, 1978 in Ladd, 1997). Values have been reduced by a factor of 0.69 in line with the empirical relationship observed between lake and Class A pan evaporimeters (e.g., Finklestein, 1961 in Ladd, 1997). Seasonal extremes of evaporation are driven by insolation
(e.g., maximum daily 4.4 mm [January] and minimum daily 1.3 mm [July]) with an average annual total of 707 mm (note: this figure refers only to direct evaporation from the lake surface and is likely to be conservative as it excludes evapotranspiration from the catchment). Comparing direct surface precipitation and evaporation yields an annual precipitation excess of 455 mm. Presumably this component is accounted for by groundwater losses as the basin contains effluent springs on its northern edge at Thorne Bay (Figure 2.1). Inspection of direct, seasonal P/E demonstrates that the months of November to February exhibit a precipitation deficit.

Seasonal thermal stratification occurs from September through to June so that the period of excessive evaporation coincides with isolation of the surface waters, meaning that surface waters are likely to become more saline through concentration of dissolved solutes produced and recycled by plankton but incapable of physical mixing with deeper waters. Isolation of DO and DSi reservoirs within the epilimnion coupled to evaporative enrichment will also enrich dissolved stable isotope reservoirs within the productive photic zone. Any siliceous microfossils precipitated within the epilimnion will therefore record enriched isotopic signatures.

### 2.5 Hydrology

Lake Pupuke has been sampled in the central water column at a range of depths and across a seasonal gradient for water quality (and stable isotope hydrology: see Chapter 6.0. Paleolimnology of Lake Pupuke inferred from Diatom Stable Isotopes). Hydrochemical data included here comprise monthly sampling to 50 m depth by the author over the interval May 2008 to April 2009 (DO, conductivity, pH and temperature) and Auckland Regional Council for the period 1976 to 2008 (DO, Biological total Nitrogen [TN], Ammonia [NH₄⁺], total Phosphate [TP], temperature and pH). These are discussed below owing to their importance in biogeochemical cycles, notably productivity, and which can alter physical and geochemical proxies of past environment (e.g., Last and Smol, 2001).

#### 2.5.1 Hydrologic Balance and Residence Time

The water balance of Lake Pupuke has been investigated by Hoare and Associates (1990), Holmes (1994), Ladd (1997) and Salter et al (2005). A limited catchment (land surface = 0.85 km²; lake = 1.10 km²) of relatively impermeable basalt with low hydraulic conductivity (K = 2 x10⁻⁵ to 2 x 10⁻⁷ m/s) results in gentle horizontal and steep vertical hydraulic gradients (e.g., low vertical permeability leads to stratified recharge pathways along faulted basalt) (Salter et al., 2005). Corresponding seepage velocities are also low (0.040 to 0.054 m/day) suggesting limited groundwater input (~1.1% of precipitation in 2005 [4.26 x 10⁻⁴ m³ s]) (Salter et al., 2005). Instead, the basin is effectively closed with precipitation and runoff the major inflows and evaporation and groundwater efflux the major outflows (Barker, 1970; Holmes, 1994). Here again, limited catchment permeability prevents much groundwater outflow except along discharge pathways to the Thorne Bay Springs (~0.020 to 0.057 m³ s [Holmes, 1994]). By way of comparison to earlier estimates of direct precipitation gains and evaporative losses from Lake Pupuke this represents 574 to 1635 mm (e.g., flux per year = 0.63 to 1.80 x 10⁶ m³ which per
unit lake surface area \(110000 \text{ m}^2\) = 0.574 to 1.635 m per year) (Salter et al., 2005). From January 2006 to January 2010 annual precipitation excess was in fact 454 mm which closely approximates the more conservative value for groundwater outflow (note: differences would arise from differences in precipitation during groundwater monitoring in 2005 and the corresponding interval of 2006 to 2010 used in this thesis, and failure to model catchment runoff and evapotranspiration which would alter annual input). This simple exercise stresses the important role of groundwater outflow to the Thorne Bay Springs in regulating hydrologic balance within Lake Pupuke. Indeed groundwater outflow is thought to have given the lake its Maori name *Pupukemoana* ("overflowing sea") in reference to the welling up of the lake and its overflowing coastal freshwater springs (ARWB, 1990). Likewise Salter et al (2005:43) report that groundwater efflux varies in response to changes in stage height (e.g., to hydraulic head) varying from peak rates of 0.057 m\(^3\) s at a stage height of 5.9 m a.s.l. to 0.020 m\(^3\) s at a lower lake level of 5.6 m a.s.l. (seasonal lake levels fluctuate by ~0.8 m; 5.1 to 5.9 m a.s.l. [ARWB, 1990; Hoare et al., 1990]). Thus past changes to lake level (e.g., through altered sea level and P/E balance) would result in changes to spring discharge. As the latter is thought to cause hydraulic drawdown of the thermocline (ARWB, 1990), such changes might significantly impact upon the intensity of past thermal stratification. Thermal stratification alters nutrient availability and productivity meaning any changes to groundwater efflux might very well result in changes to proxies for paleoproductivity.

The relatively small scale of hydrologic fluxes compared to total lake volume results in unusually long residence times \(t_w\) for Lake Pupuke (e.g., annual direct precipitation \(1.28 \times 10^6 \text{ m}^3\), evaporation \(0.78 \times 10^6 \text{ m}^3\) and P-E excess assumed to be groundwater flow \(0.50 \times 10^6 \text{ m}^3\) = 4.23, 2.58 and 1.65 % respectively of total lake volume \(3.02 \times 10^7 \text{ m}^3\)). Using the steady state mass balance approach outlined in Hoare et al (1990), the lake currently possesses a theoretical residence time of approximately 30 years (corresponding value for January 2006 to January 2010 is 24 years; equivalent to total volume / annual sum of outflow \(3.02 \times 10^7 \text{ m}^3 / 1.28 \times 10^5 \text{ m}^3\)). The lake is therefore flushed very weakly and can accumulate evaporative effects upon dissolved solutes and stable isotope reservoirs, a characteristic important to proxy reconstructions of water chemistry (see Chapters 4 to 6).

### 2.5.2 Temperature and Thermal Stratification

The seasonal thermal regime by depth for Lake Pupuke from April 1976 to April 2009 is presented in Figure 2.4. The thermal regime is typical of deep water lakes in temperate latitudes with an average lake water temperature of 14.22 ± 2.69 °C (\(\mu \pm \sigma, n = 602\)) and warm, monomictic pattern of seasonal thermal stratification between the months of September and June. Thermal stratification is a property of many deep lakes whereby water is of greatest density at ~4.0 °C, above and below which density decreases (Wetzel, 2001). High thermal inertia gives water the capacity to develop distinct stratified layers of successively higher density from surface to benthos thereby separating a well mixed surface layer (epilimnion) from a poorly ventilated bottom later (hypolimnion) by a region of rapid temperature and density change (metalimnion) (Wetzel, 2001). An average temperature range of 5.15 °C operates between surface and bottom waters (0 to 50 m) in Lake Pupuke. Surface water temperatures do not exceed 23.22 °C with highest temperatures recorded in February and coldest in August (12.59 °C). Coldest overall water temperatures were recorded at 50 m depth during July (12.00 °C) during overturn. Seasonal
differences reflect overlying air temperature but are complicated by thermal stratification. Due to the stability of bottom water layers, bottom water temperature varies only 0.64 °C over the course of a year.

Figure 2.4: Average monthly variation in water column temperature (°C) by depth (m) over the period 1976-2009.
Lake Pupuke does not experience seasonal ice cover so only between July and September does bottom water approach surface water temperatures during holomixis (combined temperature July to August = 12.66 ± 0.20 °C [μ ± σ, n = 92]). Mixing is so strong that in this interval only 0.97 °C variation occurs between the surface and 50 m depth. Consistent moderate wind and reduced air/water temperature are the probable causes of such strong overturning (see above). However, from onset to decay of thermal stratification the hypolimnion and epilimnion are physically separated by a stable and defined thermocline whose upper limit is relatively fixed at ~10 m depth and whose lower limit varies from ~20 m at initial stratification (November to April) to ~30 m prior to decay (May to June). This point must be stressed as stratification plays an important role on present nutrient and biomass cycles such that it’s impact will likely be expressed in the paleolimnological record.

Rather unusually, under contemporary climatology the great depth of the thermocline necessitates at least 20-30 m of standing water prior to the onset of thermal stratification. Seasonal water temperatures would also likely need to exceed ~14 °C (temperature of upper 10 m water during weakest stratified months [June and September] = 14.27 ± 0.36 °C [μ ± σ, n = 22]). The appearance of seasonal stratification within the sedimentary record can thereby offer valuable information on likely minimum summer water temperatures and depth (to overcome wind induced mixing and hydraulic outflow). Please note this point which will be discussed in later chapters to explain Holocene shifts in several nutrient proxies particularly sensitive to sediment anoxia and productivity. In Lake Pupuke these currently result from stratification-induced isolation of bottom, nutrient-rich waters (e.g., organic matter elemental and isotopic content [Chapter 4], microalgal productivity [Chapters 4 and 5], and microalgal isotope signatures [Chapter 6]).

2.5.3 Dissolved Nutrients (DO, TN, TP)

There are seasonally-defined patterns in the abundance of dissolved nutrients in Lake Pupuke that reflect the development of thermal stratification (Holmes, 1994). Thermal stratification effectively seals hypolimnetic waters from the atmosphere, allowing biota within the sediment benthos and water column to exhaustively consume dissolved Oxygen (DO) and nutrients (e.g., Nitrogen [DN], Phosphorus [DP], dissolved Silica [DSi]). For instance, seasonal DO concentrations vary markedly in the bottom waters (>25 m) as a consequence of the seasonal isolation from the atmospheric O₂ pool (Figure 2.5). From October DO levels begin to drop until a DO minimum (1.51 mg L⁻¹) is reached in the hypolimnion from February to June. The gradient between hypolimnetic and surface epilimnetic waters is particularly strong between October and June (0.17 mg L⁻¹ m⁻¹) underscoring the strength of seasonal thermal stratification. Surface waters are saturated with DO throughout the year (Figure 2.5). Water column DO profiles demonstrate that only ~10-20 m of upper surface water remains saturated with >50% DO due to thermal stratification. The thermocline migrates with changing air temperature but from Figure 2.5 it is apparent that a gradient of ~1.0 mg m⁻¹ is typical over ~5-10 m. OM mineralisation is evident at the oxy- and thermocline, where DO profiles decline to 4 mg L⁻¹. The interface between greater dissolved nutrients in the hypolimnion and greater availability of DO in the epilimnion is an ideal location for planktonic algae to photosynthesize (Wetzel, 2001). Organic compounds synthesised in this way are likely to therefore undergo decay and aerobic respiration, rapidly consuming DO (e.g., drop in DO coincident with ~10-20 m depth throughout November to June).
Figure 2.5: Average monthly variation in DO (%), TN (mg L), $NH_4^+$ (mg L) and TP (mg L) by depth (m) within Lake Pupuke (1976-2009).
Total Nitrogen (TN) and total dissolved ammonia (NH$_4^+$) profiles demonstrate the effects of stratification particularly by the observed peak in TN content amongst hypoxic bottom water during summer and autumnal months (January to May) (Figure 2.5). Peaks of TN and NH$_4^+$ are 0.61 mg L and 0.45 mg L respectively. The two are strongly correlated ($r_{\text{TN,NH}_4} = 0.83$, $p < 0.01$, $n = 19$) suggesting variation in TN and NH$_4^+$ is driven by the same mechanism. Reduction of oxidised nitrate and nitrite is the most probable cause of abundant NH$_4^+$ within the hypoxic hypolimnion, a significant process in many lacustrine Nitrogen cycles (Wetzel, 2001). Denitrification affects TN incorporation to lake sediment, releasing organically bound Nitrogen to the water column for recycling (favouring discrimination against the heavier $^{15}$N isotope) and loss of TN to the atmosphere as gaseous ammonia (Talbot, 2001). Genera of bacteria responsible for nitrate reduction and denitrification (e.g., *Pseudomonas* spp., *Achromobacter* spp., *Escherichia* spp., *Bacillus* spp., and *Micrococcus* spp.) are known to increase in concentration with trophic content and benthic anoxia (Wetzel, 2001). Hence, under conditions of thermal stratification, sedimentary TN will therefore be reduced and bulk $\delta^{15}$N signatures will be artificially enriched by taphonomic processes, complicating interpretation of the sedimentary record. Anoxic or hypoxic conditions are necessary as even minor DO availability halts denitrification (e.g., Talbot, 2001) and so the current regime of denitrification likely has continued since the onset of intense thermal stratification in the ontogeny of Lake Pupuke which generated highly reduced benthic conditions.

Total Phosphate (TP) levels follow a similar pattern of seasonal abundance by depth to TN (Figure 2.5). Greater TP concentrations are present in hypolimnetic waters (>40 m) during thermal stratification (January to June; 0.05 mg L). These likely reflect benthic hypoxia and sedimenting organic matter (OM). Benthic hypoxia results in greater reducing potential at the active bacterial microzone (interface of water and sediment) releasing base alkalises including Phosphate (Wetzel, 2001). Reducing bacteria (e.g., *Pseudomonas* spp., *Bacterium* spp., and *Chromobacterium* spp.) are present in higher numbers amongst productive, clay sediments of neutral to high pH similar to those present in Lake Pupuke (Wetzel, 2001). Without further bacterial identification we can only demonstrate that hypolimnetic water accumulates TP during stratification whereupon DO injection during Autumnal overturn promptly reduces TP concentrations, probably through oxidation and precipitation of base alkalises as well as productive uptake in Spring algal blooms. Holmes (1994) records a similar profile for REDOX potential in which hypolimnetic water between October 1991 and October 1993 recorded a REDOX potential <0.2 V, a critical value below which nutrient regeneration is accentuated (Wetzel, 2001). Holmes (1994) noted the production of Hydrogen Sulphide (H$_2$S) throughout the hypo- and metalimnion which only occurs under heavily reducing conditions (this point is explored further in Chapter 4 as it presents a significant control upon sedimentary TS signatures within Lake Pupuke).

In summary, essential nutrient cycles (DO, TN, TP) demonstrate marked seasonality in response to the effects of thermal stratification in Lake Pupuke. Under thermal stratification, the oxygen content of the hypolimnion declines, reducing the ability of the sediment surface microzone to retain alkalises (Wetzel, 2001). The release of phosphorus, nitrogen, iron and sulphur increases as reducing potential increases (Wetzel, 2001). Nitrate and nitrite reduction continues in preference to iron or manganese reduction hence Nitrogen is extremely susceptible to changes in the
reducing potential of surface sediment (Wetzel, 2001). Overall nutrient abundance in Lake Pupuke is classified by ARWB (1990) and Holmes (1994) as mesotrophic, a response to the intensive use of water and catchment resources. Lake Pupuke was eutrophic until 1967 but rapid amelioration (e.g., reduced nutrient loading, more luxuriant macroflora, less toxic algal blooms) has resulted from better catchment management and the lake’s residence time (~30 yr) (Holmes, 1994).

2.5.4 pH

![Figure 2.6: Average monthly variation in pH by depth within Lake Pupuke (1976-2009).](image)

Figure 2.6: Average monthly variation in pH by depth within Lake Pupuke (1976-2009).
Thermal stratification also drives changes in pH profiles, albeit indirectly. Although seasonal variation in pH is less distinct than that present in dissolved nutrients there are distinct differences between seasonal values at the surface and to a depth of ~15 m (Figure 2.6). For instance, summer (December to February) and winter months (June to August) record a pH of 8.70 and 7.67 respectively. January observes the highest average monthly surface pH (9.21) and June the lowest (7.40). Highly alkaline conditions likely result from photosynthesis reducing dissolved carbon dioxide concentration (DCO$_2$) and favouring formation of bicarbonate (Holmes, 1994). pH is then able to increase due to the isolation of epilimnetic DCO$_2$ reservoirs by a developed thermocline (Holmes, 1994). Similarly, lower pH recorded in the hypolimnion reflects DO consumption via bacterial decay and respiration of DCO$_2$. pH values beneath the thermocline are variable but average annual values for the hypolimnion are pH ~7.5 favouring preservation of siliceous microfossils (Leng and Barker, 2006). The peaks in pH in October and January likely reflect spring and summer peaks of productivity typical in mid-latitude, monomictic lakes (Wetzel, 2001).

2.6 Modern Ecology of Lake Pupuke

The modern ecology of Lake Pupuke offers an insight into biological responses to thermal stratification and changing seasonal hydrochemistry. The application of biological proxies to reconstruct paleolimnology at the site necessitates an understanding of seasonal responses of biota to changing limnology. Similarly, a paleoclimatic reconstruction would not be complete without reference to the relatively recent impacts of anthropogenic activity on the catchment (see below). Available information on aquatic micro- and macro-flora as well as knowledge of important paleoenvironmental changes associated with Maori and European activity within the region is therefore summarised below.

2.6.1 Aquatic Microflora

A detailed study of the microalgae present in Lake Pupuke between June 1992 and October 1993 can be found in Holmes (1994). Our interpretation of the microalgal community is based upon this work and data collated by the ARC from January 2004 until January 2009. The ARC employs a modified USEPA approach to algal sampling (Neale, pers. comm., 2010) similar to that used by Holmes (1994).

Holmes (1994) noted that four major classes contribute the majority of algal biomass through biovolume; Dinophyceae, Chlorophyceae, Bacillariophyceae and Cyanophyceae (in order of decreasing abundance). These same four orders provide 2.90%, 39.37%, 25.51% and 1.05% respectively of ARC monitoring data and have remained the dominant algal components since Holmes (1994). Figure 2.7 demonstrates seasonal variation by count amongst these orders. The green algae (Chlorophyceae) possess a distinctly bimodal distribution described by a peak in numbers during early spring (September) and late summer (February). Likewise, siliceous diatoms (Bacillariophyceae) dominate throughout much of the year but especially during holomixis (July to August) and late summer/autumn (March to April). A notable decline in all taxa except blue-green algae (Cyanobacteria) occurs during colder winter months (May and July). These patterns mirror those found by Holmes (1994) other
than greater abundance of dinoflagellates (Dinophyceae) and limited diversity of diatom flora in 1992 and 1993. The apparent marked changes in algal community structure over ~11-16 years imply the lake might be subject to marked dynamism and rapid species turnover.

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.

Diatoms (Bacillariophyceae) represent a robust proxy for paleoenvironment and are employed in Chapter 5 to reconstruct the paleolimnology of Lake Pupuke. Whereas Holmes (1994) notes only the presence of *Fragilaria crotonensis* and *Aulacoseira granulata* [previously *Melosira granulata*], ARC data note the presence of at least 17 taxa, of which 4 are annually dominant amongst diatoms (by count); *Asterionella Formosa* (14.91 %), *Fragilaria* spp. (63.22 %), *Frustulia* spp. (13.45 %) and *Aulacoseira granulata* (4.98 %) (refer to Figure 2.8). Of these *Fragilaria* spp. are capable of growth throughout the year although notable peaks occur in January and April, whilst *Frustulia* spp. tend to dominate late summer months (February to March) and *A. formosa* is dominant before, during and following overturn (June to September). *A. granulata* exhibits a similar profile to *A. formosa* but in reduced abundance. Cassie (1989) and Holmes (1994) also note similar patterns enabling a classification of preference for either Spring, Summer, and Autumn conditions. Taxa indicative of spring conditions include those adapted to resuspension during holomixis and are therefore ideal indicators of the onset of thermal stratification within the sedimentary record of Lake Pupuke (Table 2.1). For instance, *A. granulata* is highly adapted in that it produces a resting stage during periods of nutrient scarcity (e.g., summer stratification) and is readily resuspended by strong mixing (e.g., holomixis) (Cochran, 2009).
Chapter Two

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.

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).

<table>
<thead>
<tr>
<th>Season</th>
<th>Dominant Diatom Taxa</th>
<th>Water Quality Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td><em>Aulacoseira granulata</em>, <em>A. varians</em>,</td>
<td>Increasing insolation and temperature, onset of thermal stratification and declining nutrient levels favour rapidly growing, smaller taxa (e.g., <em>F. crotonensis</em>) over larger winter species (e.g., <em>Nitzschia</em> spp.). Peak biomass of <em>A. granulata</em> occurs briefly in July and September during holomixis before declining into summer. Resuspension from benthic resting stages occurs in <em>A. granulata</em> despite the prevalence of extended anoxia and aphytic conditions in the hypolimnion.</td>
</tr>
<tr>
<td></td>
<td><em>Fragilaria crotonensis</em> and <em>Frustulia rhomboids</em> var. <em>saxonia</em></td>
<td></td>
</tr>
<tr>
<td>Summer/Autumn</td>
<td><em>Achnanthes brevipes</em> var. <em>parvula</em>,</td>
<td>Stratification and hypolimnetic anoxia limit diatoms to 0-20 m depth (photic zone), TP limiting and absence of much dissolved nutrients in central pelagic (e.g., absence of centric and abundance of pennate diatoms) increasing water clarity to enable benthic attached taxa to establish themselves on macrophytes, mud and lithic surfaces nearer nutrients.</td>
</tr>
<tr>
<td></td>
<td><em>Amphora perpusilla</em>, <em>Cocconeis placentula</em>, <em>C. placentula</em> var. <em>euglypta</em>, <em>Epithemia sorex</em>, <em>E. zrebra</em>, <em>Gomphonema parvulum</em>, <em>Hantzschia amphioxys</em> and <em>Navicula</em> sp. cf <em>frugalis</em></td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td><em>Aulacoseira granulata</em> (var. <em>angustissima</em>), <em>A. varians</em>, <em>Nitzschia acicularis</em>, <em>N. linearis</em> and <em>N. obtuse</em></td>
<td>Stable thermal conditions, abundance of dissolved nutrients (e.g., Fe, Si and N), high growth rates and resuspension from sediments leading to abundant planktonic diatom abundance during Spring.</td>
</tr>
</tbody>
</table>
2.6.2 Land Use and Anthropogenic History

Contemporary land use within Lake Pupuke’s catchment is primarily suburban with the lake offering recreational pursuits (ARWB, 1990). However, prior uses have included water treatment and extraction until the mid 1940s AD (ARWB, 1979). Late in its history, nuisance algal blooms arose partly as a response to increased nutrient loading, and required copper sulphate (CuSO$_4$) loading to remove their noxious effects (~1933, 1934 and 1939). Whilst nuisance microphytes including *Ceratium* spp. were removed, the earlier loss of native flora meant that much of the photic zone was rapidly colonised by exotic taxa (Cassie, 1989). The modern aquatic macrophyte taxa of Lake Pupuke reflect this palaeolimnology and include *Vallisneria gigantea/americana* (Tape-grass) and *Egeria densa* (Large-flowered waterweed) whose growth is so luxuriant as to pose a nuisance to lake users (ARWB, 1990).

The natural catchment vegetation of Lake Pupuke and the Auckland region has been depleted and heavily modified to the extent that little remains of the indigenous hardwood podocarp forest found further north (Newnham et al., 2007a). Palynological reconstructions of the late Quaternary suggest Auckland would have supported an extensive conifer-angiosperm forest with local volcanic sub-communities (Newnham and Lowe, 1991; Sandiford et al., 2003). Newnham et al. (2007a) lists these distinctive northern taxa to include: *Agathis australis* (Kauri); *Halocarpus kirkii* (Monoao) and *Weinmannia silvicola* (Tawhero). Similarly, several southern taxa indicative of cooler temperate conditions reach their northernmost limit in the Auckland region, including: *Libocedrus bidwillii* (Kaikawaka), *Nothofagus menziesii* (Tāwhai) and *Podocarpus nivalis* (mountain or snow Totara) (Newnham et al., 2007a). As noted, beech communities do not currently thrive north of Auckland but have migrated with the LGCP demonstrating Auckland’s prime location at the boundary of phytogeographic regions (Newnham et al., 2007a). Likewise floral change has been applied to reconstruct the history of anthropogenic change within New Zealand, particularly Northland and Auckland where the earliest known colonisation by Polynesian migrants occurred ~1300 AD prior to a second phase of forest clearance ~1800 AD with the arrival of European migrants (Hayward et al., 2006). AVF maar crater lakes have the potential to accurately date the arrival of Polynesian migrants because the region is thought to have been the one of the first to be colonised (Irwin, 1992). Sediment records from Lake Pupuke have already contributed to the debate surrounding the timings of Polynesian migrants revealing evidence for European clearance ~1840 AD (Augustinus et al., 2006) and Polynesian clearance ~0.6 cal. kyr BP (Striowski et al., 2009) in line with a short prehistory hypothesis of regional arrivals post 1200 AD (e.g., Anderson, 1991). The short prehistory hypothesis (e.g., Irwin, 1992) embraces a later colonisation of New Zealand than that held in the more orthodox and increasingly discredited early hypothesis which sets a date of 800 AD for the earliest colonisation (Wilmshurst and Higham, 2004).
2.7 Summary

Lake Pupuke is a product of late Quaternary basaltic volcanism, one of thirteen other maars but the only to have retained freshwater status to today (Augustinus et al., 2008). Its basin shape (circular, limited fetch ~1025 m) and bathymetry (steeply-shelving sides, max depth ~57 m) aid the preservation of lacustrine sediment by favouring benthic hypoxia (Holmes, 1994; Augustinus et al., 2008). Catchment extent is limited (0.85 km$^2$ compared to lake surface area of 1.10 km$^2$) whilst productivity is augmented by nutrient recycling under reducing benthic conditions, ensuring the accumulation of organic-rich sediments (see Chapter 4). The sediments are subject to lesser wind/wave action due to the onset of laminar, thermal stratification isolating benthic waters from September until June. Lesser wave activity and a ~20-30 m limit to wave mixing reduces the impact on sediment resuspension. Similarly, organic matter (OM) preservation is enhanced by the relatively stable and steep basin edges that enhance the strength and duration of thermal stratification. Stratification results in an average annual temperature difference of 5.15 $^\circ$C between epilimnetic surface (0-20 m) and hypolimnetic water (30-50 m). Seasonal bottom water anoxia also reduces the impact of microbial heterotrophy on detrital OM. Nonetheless, OM reduction by denitrification and methanogenesis is highly likely as benthic hypoxia favours the latter leading to diagenetic alteration of sedimentary properties, particularly stable isotopes of Carbon, Nitrogen and Oxygen. Sedimentary diagenesis is therefore likely to be a significant complicating factor in paleolimnological reconstructions.

Over the ~48 cal. kyr length of the sedimentary record examined in this thesis, substantial changes have likely occurred to the physicochemical regime and ecology of Lake Pupuke as a result of the onset of climate changes associated with glaciation and deglaciation. These changes will be present in environmental proxies of biogenic and non-biogenic origin. The process of thermal stratification – onset, duration and strength - is likely to be the major determinant of proxy variation during the late Holocene in much the same way that contemporary stratification (September to June) affects ecologic and nutrient cycles. This chapter has emphasised the importance of stratification upon nutrient pools and algal ecology, as both have been modelled over the length of the sedimentary record. However, further important attributes of this site include the fact the basin is hydrothermally inactive and therefore will not suffer the impacts of geothermal interactions (e.g., altered radioactive and stable isotope pools) that can complicate proxy inferences and chronological analyses.

The lake is surrounded by felsic lavas, tuffs and basalts characteristic of its volcanic origin and as noted, the Auckland region spans the LGM boundary of wider phytogeographic regions between warmer hardwood forest to the north and cooler alpine forest/scrubland to the south (Lancashire et al., 2002). The Northland region is believed to have offered refugia to hardwood forest taxa throughout the LGCP (Elliott, 1998; Newnham et al., 2004, 2007a; Horrocks et al., 2007). The site is thus ideally situated to observe past climatically induced shifts in vegetation particularly as its tuff crater rim has provided a physical barrier to the Hauraki Gulf, ~200 m away at its closest, effectively maintaining continuous deposition and entrapment of freshwater algae. This point is worth noting as it permits a continuous record of climate to be reconstructed from local floral indicators sensitive to climatic change (see Chapter 5).
Whilst air and water temperature regimes demonstrate marked changes with peaks in summer months (December to February) and lows in winter months (May to July), precipitation is spread evenly throughout much of the year (~1160 mm). The balance of precipitation to evaporation (P/E) records an annual precipitation excess (~39 %) but with marked variation such that evaporation exceeds precipitation during warmer months (November to February). Numerous studies have established the basin is effectively closed (Hoare et al., 1990; Ladd, 1997; Salter et al., 2005) so that evaporation during productive summer months is likely to result in a hydrological deficit. This is significant because during stratification the upper epilimnion of a productive lake will become rapidly enriched in heavier isotopic elements utilised by producers and consumers alike (e.g., δ¹³C, δ¹⁵N and δ¹⁸O) (Leng and Barker, 2006). Thus it is highly likely that the application of microalgal fossil remains to δ¹⁸O analysis will result in a proxy for shifts in P/E balance rather than a direct measure of changes to precipitation δ¹⁸O. A theoretical hydraulic residence time of ~30 yrs further emphasises this point as seasonal patterns of enrichment will occur and be retained by the water column, further distorting the link between lake water δ¹⁸O and precipitation δ¹⁸O (see Chapter 6).

The onset of stratification will be an important marker of climatic amelioration during the Holocene because it presently requires significant summer warmth and water column depth to occur within Lake Pupuke (e.g., >14 ºC; 20-30 m). However, changes to precipitation (e.g., amount, seasonal regime) will in conjunction with changing water table position (e.g., a response to altered sea level) have resulted in further changes to past nutrient cycles and productivity throughout the Quaternary. Superimposed on these changes will be changes to regional climate associated with the shift from glacial to interglacial conditions.
CHAPTER THREE

Sediment Coring, Composite Core Correlation, Age-Depth Modelling and Composite Stratigraphy

3.1 Introduction

This chapter offers a summary of the coring exercise used to collect sediments from Lake Pupuke including construction of a single composite from multiple long (~3 m length, \( n = 16 \)) cores. Construction of the Pupuke composite sequence enables the development an age-depth model from which to infer ages of discrete sediment samples used in proxy analyses (presented in Chapters 4, 5 and 6). Correlation of core lengths to each other was achieved through a standard approach for Auckland maar crater records: analysis and interpretation of macroscopic sedimentary lithology, in addition to tephra geochemical finger-printing and analysis/interpretation of sedimentary low-field magnetic-susceptibility (Sandiford et al., 2002, 2003; Horrocks et al., 2005; Alloway et al., 2007; Molloy et al., 2009). Fortunately, a wealth of Quaternary volcanism has been recorded by tephra layers within the Pupuke sediment record (e.g., Molloy et al., 2009). To meet the objectives of this thesis, a detailed tephra and radiocarbon \(^{14}\text{C}\) based chronology has been constructed from which to infer precise ages for paleolimnological changes in the Pupuke sediment record (Section 1.3. Research Objectives). Such an independent, absolute chronology is necessary to avoid the problems of circular logic or "reinforcement syndrome" (Bennett, 2002), and the use of pre-existing dates from the NZ-INTIMATE climate event stratigraphy to define paleoclimatic changes at Lake Pupuke.

3.2 Sediment Coring

A series of coring locations were chosen in the central pelagic zone of Lake Pupuke \(( n = 9; \text{ approximately } 36^\circ 78.30\text{S}, 174^\circ 76.70\text{E} \text{ [Figure 3.1; Table 3.1]})\). The central location increases the likelihood of continuous sedimentation over the lacustrine series and also enhances contributions from phytoplankton to the organic matter (OM) flux (Talbot, 2001).
Figure 3.1: Coring locations within Lake Pupuke during the 2007 field exercise.

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

<table>
<thead>
<tr>
<th>Core</th>
<th>Core Site</th>
<th>Coordinate</th>
<th>Depth (m beneath mud-water interface)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Latitude (ºS)</td>
<td>Longitude (ºE)</td>
</tr>
<tr>
<td>PUP1A1 (#1)</td>
<td>1</td>
<td>36.78100</td>
<td>174.76500</td>
</tr>
<tr>
<td>PUP1A2 (#2)</td>
<td>1</td>
<td>36.78100</td>
<td>174.76500</td>
</tr>
<tr>
<td>PUP1B3 (#7)</td>
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<td>174.76486</td>
</tr>
<tr>
<td>PUP1B4 (#11)</td>
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</tr>
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<tr>
<td>PUP2C3 (#14)</td>
<td>9</td>
<td>36.78152</td>
<td>174.76494</td>
</tr>
</tbody>
</table>
Figure 3.2: UWITEC percussion fixed-piston coring system and mobile drilling platform (Modified from: UWITEC, 2007a,b).
The Lake Pupuke sediment sequence was cored during a single exercise between 5th and 13th February 2007. Sediment cores were collected using a floating UWITEC mobile coring platform (UWITEC Universal Sampling Platform [UWITEC, 2007a]) with a percussion fixed-piston coring system (40 kg weight and transparent PVC core liners) and core catching system (UWITEC Piston Corer [UWITEC, 2007b]) (Figure 3.2). Sixteen sediment cores (3000 mm by 59.5 mm) were collected, each with ~500-2000 mm overlap, to a total depth of 15.5 m below the sediment surface including an intact sediment-water interface. Cores varied in length from 2500 mm to 3000 mm with an average length of 2738 mm. All cores were extruded into Perspex containers, wrapped and sealed prior to storage at 4 ºC in the School of Environment, University of Auckland. Base depth, total recovery and length were noted in sediment logs (Appendix A).

3.3 Core Description, Sampling and Preliminary Analyses

Prior to the selection of discrete sediment samples for geochemical and physical proxy analysis, the recovered sediment cores were described for evidence of disturbance, reworking and to aid core correlation via overlap between offset cores. Core logs were created to describe sedimentary properties for each core over their entire length. All cores were split and resealed in plastic liners. 38 individual tephra were recorded during this initial phase of sediment description [16 andesitic, 14 rhyolitic and 8 basaltic deposits] [<1 to 330 mm]). The coring process also resulted in numerous transverse fractures across core sections although no evidence suggested core reworking in the vertical plane. The best preserved and least disturbed core half was archived at 4 ºC with working halves subsequently sampled at 1 cm resolution for a range of analyses including sedimentological (bulk density; magnetic-susceptibility; particle-size distribution; water content), geochemical (trace and major elemental composition; bulk stable isotopic composition) and biological paleoenvironmental proxies (diatom taxonomy; diatom silica stable isotopic composition) presented in Chapters 4, 5 and 6.

Prior to sub-sampling, sediment core lithologies were described according to the classification systems of Tröels-Smith (1955) and Kershaw (1997). The cores vary between finely laminated (<1 mm) to massive (non-laminated) lacustrine sequences (Appendix A). Previous research has suggested laminae in Lake Pupuke to be sub-annular responses to changes in algal community structure (Striewski et al., 2009). The sediment is dominated by clayey-silt and distal tephra silty-sand horizons whose colour varies from very dark grey/black (Munsell Colours, 10YR: 3/1, 5Y: 4/1, 4/2) to lighter shades of olive grey/brown (Munsell Colours, 5Y: 3/2, 3/1) (refer to core logs in Appendix A).

The mineral vivianite was recognised in each core at sizes that ranged from mm-size crusts to nodules of 2-3 mm. The presence of vivianite demonstrates reducing conditions implying the presence of deep water, sediment anoxia and an absence of bioturbation over the period of time represented by the sediment series (e.g., Asikainen et al., 2007).
With the exception of tephra and massive deposits including several debris flows used to correlate overlapping sections, cores demonstrate limited lithological variation. All cores are composed of fine-grained (<100 μm), highly organic sediments with little macroscopic organic matter. Limited variation occurs except for the intermittent presence of organic-rich bands (<1-3 mm thick) composed of algal matter (Atkin, pers. comm., 2010) in cores PUP 2C1#4 and PUP 1C2#5, and massive deposits present in cores PUP 1C2#5, PUP 2C1#6 and PUP 1B3#7 (refer to Appendix A). The latter consists of unstructured lacustrine mud with a sharp contact to over- and underlying laminated sediment. Despite the lack of any visible structure these deposits contain relatively large spherical to elongate brown (5Y 3/2) inclusions that range in size from ~1 to 50 mm. Their origin is not clear but sharp contacts likely represent erosive bases to turbidites (e.g., Rothwell et al., 2006). Depths corresponding to these deposits in cores PUP 1C2#5, PUP 2C1#6 and PUP 1B3#7 were excluded from a composite sediment series due to their unknown origin and lack of visible sedimentary structure (Section 3.4. Composite Core Construction).

### 3.3.1 Magnetic Susceptibility

Sediments can be described by their magnetic susceptibility (MS) - the ability for sediments to become magnetised (Nowaczyk, 2001). MS values (κ) report the proportional factor between an applied magnetic field (H) and the magnetization (M) as follows:

\[ M = \kappa \times H \]

MS values vary with the mineralogy of lacustrine sediments, particularly the ferromagnetic content such as magnetite or titanomagnetite (Sandgren and Snowball, 2001). Stratigraphic changes in geochemistry and grain-size alter MS, alongside changes to weathering rates and the influx of iron-bearing minerals (Snowball and Sandgren, 2001). MS can also be used to interpret benthic pore-water pH (e.g., dissolution of ferromagnetic minerals under alkaline or reducing conditions will reduce MS [e.g., Nowaczyk et al., 2007]). To investigate variations in lithostratigraphy, low-field magnetic susceptibility (κ) characteristics were analysed with a *Bartington Instruments MS2E* point-wise MS sensor at a spatial resolution of 4 mm (15 s collection interval) along 10 mm increments of cleaned and levelled composite core sections (warmed to room temperature).

Trends in κ can form recognisable and repeated phenomena in sedimentary deposits (Nowaczyk, 2001). Hence MS is a useful tool for correlating sediment cores, particularly where variable expansion and degassing might have occurred to alter the relative position of absolute depths between cores. In addition, iron-bearing minerals, common in basaltic tephra, permitted the rapid identification of local AVF tephra further aiding sediment core correlation to create a single composite series (see below).
3.3.2 High-resolution imaging

Digital photographic images of each sediment core were taken with a Deutsche Montane Technologie (DMT) CoreScan Colour Unit with a Nikon FM2 digital camera and AF Micro-Nikkor 60 mm/2.8 D lens (in conjunction with a PL circular M62 (IV) polarizer to reduce glare from wet sediment). Images were taken of 40 cm intervals (resolution ~5 pixels per mm/130 dpi) prior to incorporation into a single composite image for each sediment core log within Adobe Photoshop software. These are presented in conjunction with sedimentary parameters for each core in Appendix A.

3.3.3 Chemical Fingerprinting of Tephra

Tephra are valuable paleolimnologic time-parallel age markers, a result of their widespread and geologically instantaneous deposition (e.g., hours to weeks) coupled to distinctive geochemistry enabling individual events to be identified and linked to dated eruptions (Lowe et al., 2008). Fortunately, throughout the late Pleistocene and Holocene, silicic tephra has erupted from several rhyolitic (Taupo Volcanic Zone [TVZ], Mayor Island and Okataina Volcanic Centre [OVC]) and andesitic volcanic centres (Tongariro Volcanic Centre [TgVC] and Taranaki Volcanic Centre [TVC]) in the North Island of New Zealand (Lowe et al., 2008). Shane (2000, 2005) provides a detailed record of these ash fall events which also offer remarkable potential to improve the resolution of lacustrine age-depth models derived from the Auckland maars (e.g., Augustinus et al. 2008, Molloy et al., 2009). Rhyolitic, andesitic and basaltic tephra have been identified and sub-sampled from each of the sixteen sediment cores to facilitate construction of a composite core series. Multiple samples were taken from larger ash fall deposits (>10 mm) to ensure that any multiple, closely-spaced events would be discerned.

A minimum of 10 glass shards within each macroscopic tephra have been analysed for major oxide and trace elemental geochemistry using methods described in Molloy et al. (2009). Samples were wet sieved to remove fine silt (<63 μm) prior to oven drying at 100 C for 24 hrs. Ferromagnesian minerals and glass shards were isolated from sand sized particles (2000 μm > n > 63 μm). Selected shards were mounted in epoxy resin, polished and carbon coated for electron microprobe analysis (as for Froggatt and Gosson, 1982). Electron microprobe analyses were performed with a Jeol JXA-840A electron microprobe and Princeton GammaTech Prism 2000 Si (Li) Energy Dispersive Spectrometer (EDS) X-Ray detector (accelerating voltage 15 kV, beam current 600 pA, 20 μm focus and acquisition time 100 s) at the School of Environment, University of Auckland. Provenance was determined from mineral geochemistry by comparison to a geochemical database held by Dr. Philip Shane (University of Auckland).

38 discrete tephra were identified in the Lake Pupuke composite core series representing a substantial part of the late-Quaternary volcanism in the North Island of New Zealand (Figure 3.3; Table 3.2). Ash sources include the rhyolitic Mayor Island volcano (n = 1), Okataina volcanic centre (n = 8) and Taupo volcanic centres (n = 5);
the andesitic Egmont volcano (Taranaki; \(n = 15\)) and Tongariro volcanic centre (Ruapehu and Tongariro vents; \(n = 1\)); and the local, basaltic Auckland Volcanic Field (AVF; \(n = 8\)). The most recent Rangitoto AVF tephra (\(\sim 504 \pm 5\) cal. yr BP) occurs as two discrete black, coarse ash layers at 57.85 cm and 57.86 cm depth in core PUP 1A1#1 (15 mm total thickness). Glass shard analysis and a recent investigation of Rangitoto volcano (Needham et al., 2010) revealed distinct geochemistry attached to two eruptive vents and formation in a dual event: a main (alkaline olivine) eruptive phase and a second (transitional to tholeiitic) phase.

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).

<table>
<thead>
<tr>
<th>Tephra Name</th>
<th>Source*</th>
<th>Composition</th>
<th>Core (PUP)</th>
<th>Depth (cm)</th>
<th>Thickness (mm)</th>
<th>Age (cal. kyr BP)</th>
<th>Tephra Description (colour, grain size)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rangitoto (AVF 24)</td>
<td>AVF</td>
<td>Basalt</td>
<td>1A1#1</td>
<td>57.88</td>
<td>0.8</td>
<td>0.8</td>
<td>Black, coarse-grain. Separated into 2 lenses</td>
</tr>
<tr>
<td>Taupo (Tp)</td>
<td>TVC</td>
<td>Rhyolite</td>
<td>1A1#1</td>
<td>58.87</td>
<td>1.7</td>
<td>1.7</td>
<td>White, medium/fine</td>
</tr>
<tr>
<td>Tuhua (Tu)</td>
<td>MI</td>
<td>Rhyolite</td>
<td>1C2#5</td>
<td>61.93</td>
<td>7.0</td>
<td>7.0</td>
<td>White, coarse</td>
</tr>
<tr>
<td>Rotoma (Rm)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>1C2#5</td>
<td>62.44</td>
<td>9.5</td>
<td>9.5</td>
<td>Grey/white, medium</td>
</tr>
<tr>
<td>Eg50</td>
<td>Eg</td>
<td>Andesite</td>
<td>2C1#6</td>
<td>63.51</td>
<td>12.3</td>
<td>12.3</td>
<td>Brown, fine</td>
</tr>
<tr>
<td>Eg47</td>
<td>Eg</td>
<td>Andesite</td>
<td>2C1#6</td>
<td>63.88</td>
<td>13.2</td>
<td>13.2</td>
<td>Grey, fine</td>
</tr>
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<td>Waiohau (Wh)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>2C1#6</td>
<td>64.22</td>
<td>2.0</td>
<td>13.6</td>
<td>White, undulated, fine</td>
</tr>
<tr>
<td>Tg4</td>
<td>Tg</td>
<td>Andesite</td>
<td>1B3#7</td>
<td>64.53</td>
<td>1.0</td>
<td>15.3</td>
<td>White, fine</td>
</tr>
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<td>Rotorua(Rr)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>1B3#7</td>
<td>64.62</td>
<td>45.0</td>
<td>15.4</td>
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</tr>
<tr>
<td>Eg43</td>
<td>Eg</td>
<td>Andesite</td>
<td>1D1#9</td>
<td>65.05</td>
<td>2.0</td>
<td>17.6</td>
<td>Pink/purple, medium</td>
</tr>
<tr>
<td>Rerewhakaaitu (Rw)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>1D1#9</td>
<td>65.07</td>
<td>1.5</td>
<td>17.6</td>
<td>Cream, fine</td>
</tr>
<tr>
<td>Okareka(Ok)</td>
<td>PVC</td>
<td>Rhyolite</td>
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<td>66.6</td>
<td>2.0</td>
<td>21.9</td>
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<td>1.0</td>
<td>25.5</td>
<td>Purple/grey, fine</td>
</tr>
<tr>
<td>Oruanui (Kk)</td>
<td>TVC</td>
<td>Rhyolite</td>
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<td>25.0</td>
<td>27.1</td>
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</tr>
<tr>
<td>Polihipi (Po)</td>
<td>TVC</td>
<td>Rhyolite</td>
<td>2C2#10</td>
<td>67.53</td>
<td>1.5</td>
<td>28.6</td>
<td>Cream, fine</td>
</tr>
<tr>
<td>Eg28</td>
<td>Eg</td>
<td>Andesite</td>
<td>1B4#11</td>
<td>67.53</td>
<td>2.0</td>
<td>28.6</td>
<td>Pink/purple, fine</td>
</tr>
<tr>
<td>AVF12</td>
<td>AVF</td>
<td>Basalt</td>
<td>1B4#11</td>
<td>67.59</td>
<td>7.0</td>
<td>28.8</td>
<td>Grey, coarse</td>
</tr>
<tr>
<td>Eg27</td>
<td>Eg</td>
<td>Andesite</td>
<td>1B4#11</td>
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<td>2.0</td>
<td>29.2</td>
<td>Cream/brown, fine</td>
</tr>
<tr>
<td>Okaia (O)</td>
<td>TVC</td>
<td>Rhyolite</td>
<td>1B4#11</td>
<td>67.70</td>
<td>6.0</td>
<td>29.3</td>
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</tr>
<tr>
<td>Eg25</td>
<td>Eg</td>
<td>Andesite</td>
<td>1D2#13</td>
<td>68.07</td>
<td>4.0</td>
<td>30.6</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>AVF10</td>
<td>AVF</td>
<td>Basalt</td>
<td>1D2#13</td>
<td>68.09</td>
<td>3.0</td>
<td>30.6</td>
<td>Grey/black, medium</td>
</tr>
<tr>
<td>AVF9</td>
<td>AVF</td>
<td>Basalt</td>
<td>1D2#13</td>
<td>68.15</td>
<td>6.0</td>
<td>30.8</td>
<td>Grey/black, medium</td>
</tr>
<tr>
<td>AVF8</td>
<td>AVF</td>
<td>Basalt</td>
<td>1D2#13</td>
<td>68.24</td>
<td>20.0</td>
<td>31.1</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>AVF7</td>
<td>AVF</td>
<td>Basalt</td>
<td>1D2#13</td>
<td>68.49</td>
<td>2.0</td>
<td>32.0</td>
<td>Purple, fine</td>
</tr>
<tr>
<td>Eg24</td>
<td>Eg</td>
<td>Andesite</td>
<td>1D2#13</td>
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<td>0.5</td>
<td>32.1</td>
<td>Cream, fine</td>
</tr>
<tr>
<td>Eg21</td>
<td>Eg</td>
<td>Andesite</td>
<td>1D2#13</td>
<td>68.62</td>
<td>1.0</td>
<td>32.4</td>
<td>Black, fine</td>
</tr>
<tr>
<td>Eg19</td>
<td>Eg</td>
<td>Andesite</td>
<td>1D2#13</td>
<td>69.25</td>
<td>1.0</td>
<td>34.4</td>
<td>Purple/grey, fine</td>
</tr>
<tr>
<td>AVF4</td>
<td>AVF</td>
<td>Basalt</td>
<td>1D2#13</td>
<td>69.32</td>
<td>15.0</td>
<td>34.4</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>Hauparu (Hu)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>2B1#15</td>
<td>69.61</td>
<td>13.0</td>
<td>35.6</td>
<td>Grey/white, medium</td>
</tr>
<tr>
<td>Maketu (Mk)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>2B1#15</td>
<td>69.89</td>
<td>60.0</td>
<td>36.3</td>
<td>White, coarse</td>
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<td>Andesite</td>
<td>2B1#15</td>
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<td>37.7</td>
<td>White, fine</td>
</tr>
<tr>
<td>Tahunah (Ta)</td>
<td>TVC</td>
<td>Rhyolite</td>
<td>2B1#15</td>
<td>70.53</td>
<td>8.0</td>
<td>39.3</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>Eg16</td>
<td>Eg</td>
<td>Andesite</td>
<td>2B1#15</td>
<td>70.82</td>
<td>0.5</td>
<td>40.5</td>
<td>White, fine</td>
</tr>
<tr>
<td>Eg14</td>
<td>Eg</td>
<td>Andesite</td>
<td>2B1#15</td>
<td>71.54</td>
<td>1.0</td>
<td>43.8</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>Eg11</td>
<td>Eg</td>
<td>Andesite</td>
<td>2B2#16</td>
<td>71.70</td>
<td>3.0</td>
<td>44.4</td>
<td>Grey, medium</td>
</tr>
<tr>
<td>Rotoehu (Re)</td>
<td>OVC</td>
<td>Rhyolite</td>
<td>2B2#16</td>
<td>72.23</td>
<td>630.0</td>
<td>45.8</td>
<td>White, medium, normally-graded. Separated into 11 bands of ash</td>
</tr>
</tbody>
</table>

Eg10 Eg Andesite 2B2#16 73.04 5.0 48.6 Black, medium

* AVF – Auckland Volcanic Field; OVC – Okataina Volcanic Centre; TVC – Taupo Volcanic Centra; MI = Mayor Island; Eg = Egmont.
Figure 3.3: A summary of the tephrochronological framework for Lake Pupuke and Auckland Crater Maar tephra deposits. Tephra are described in Table 3.2 (Source: Molloy et al., 2009: 1671).
3.3.4 Wet Bulk Density, Water Content and Dry Bulk Density

To facilitate conversion of sediment accumulation rates (SAR) into mass accumulation rates (MAR) with which to later calculate elemental flux (3.6.3. Sediment Accumulation Rate), water content, wet bulk density and dry bulk density have been measured at ~15 cm intervals of the composite series. Samples were selected to exclude tephra which would distort trends in water content and density.

Sediment wet bulk densities (WBD) were recorded by weighing volumetric samples (e.g., weight of fresh, wet bulk sediment per unit volume). A modified graduated pipette was used to extract 1 cm$^3$ of intact sediment prior to weighing to ± 1 mg.

Water content ($W_c$ [wt.%]) was determined from WBD samples by drying 1 cm$^3$ sediment samples in an oven at 108 °C for 48 hrs (e.g., weight of sediment relative to total wet weight at field-moisture [e.g., Gale and Hoare, 1991]). $W_c$ varies in response to changing clay mineralogy (e.g., swelling clays), porosity and compactness, higher values correspond to lesser compacted, more porous sediment (Gale and Hoare, 1991). Organic remains also tend to retain greater moisture than inorganic material thereby enabling inferences on the provenance of sediment, particularly during periods of altered SAR or MAR (Meyers and Teranes, 2001).

Dry bulk density (DBD) was calculated from the difference in weight between volumetric wet and dry samples (e.g., weight of dry bulk sediment per unit volume of wet bulk sediment). DBD is a measure of organic and inorganic content but most importantly offers a means of correcting for variable sedimentation rates that might otherwise distort interpretation of elemental stratigraphy (Meyers and Teranes, 2001).

3.3.3 Sediment Core Logs

Qualitative descriptions of sedimentary properties as for Tröels-Smith (1955) were compiled into core logs for each sediment core extracted from Lake Pupuke over the 2007 field season. MS and high-resolution visual photography were also correlated to sediment cores. Each log is provided in Appendix A with a description of notable features: (1) depth to boundaries based on visual inspection; (2) definition of boundaries (e.g., indistinct, blurred, sharp); (3) colour based on the Munsell (1992) soil colour chart; (4) sediment grain size; (5) physical sedimentary properties (e.g., laminations, mass structures); (6) plant macrofossil, charcoal and vivianite fragments; and (7) tephra descriptions (e.g., thickness, grading, colour, grain size). Based on these sedimentary features and starting depth, each core was ‘tied’ into a composite sequence as detailed below.
Chapter Three

3.4 Composite Core Construction

Sedimentation within lacustrine systems is typically heterogeneous in space and time (Smol et al., 2001). We have already highlighted the capacity to accurately ‘tie’ independent age markers and sedimentary features between cores. This accounts for variable sedimentation in time and across basin space. Of the 16 cores collected, 4 showed evidence for coring artefacts (e.g., realignment of the corer, loss of material) and inclusion of slump deposits. These have been excluded from core correlation. The remaining 12 piston cores have been correlated using MS trends, visible stratigraphy and tephra isochrons (see below).

3.4.1 Tephra Correlation and Removal

Large overlap (~0.5-2.0 m) between individual cores enabled the precise correlation of the 38 visible tephra isochrons between individual sediment cores. Many thicker tephra demonstrate normal grading and several thinner deposits might but are too thin to record gradational change. In some instances there is clear evidence for multiple events (e.g., AVF 24) and possibly density separation into multiple chemically homogenous layers (e.g., Waiohau, 13.6 cal. kyr BP [Molloy et al., 2009] and Rotoehu, 45-61 kyr [Shane, 2005]). Density separation can occur to depths 83 cm beneath lacustrine surface sediment in well-mixed water columns (e.g., Beierle and Bond, 2002). In addition, the possibility of sediment resuspension and mass influx of tephra from the catchment remains a potential source of error. To prevent inclusion of turbidites or reworked material, sediments between multiple single event tephras have been excluded from the composite stratigraphy where they demonstrate clear disturbance but included where laminated. Each corresponding core interval is thus corrected for the depths occupied by tephra. Where tephra have settled (e.g., multiple chemically homogenous horizons), the uppermost and youngest horizon has been selected for age-depth modelling.

3.4.2 Composite Core Correlation

Total composite depth intervals were calculated from the absolute depth intervals of each core situated between known age markers or sedimentary features used to tie each core to the composite stratigraphic series. As noted, depths were corrected for the presence of tephra. Likewise gaps in the sediment attributable to expansion and degassing have been excluded from estimates of the depth occupied by laminated sediment between known isochrons. Thus each core is tied to another in a continuous sequence to a depth of ~1550 cm below the mud-water interface (composite length 1420 cm) with intervening periods of tephra accumulation, turbidites, slumps and gaps removed (~130 cm). Composite depths are read relative to core top. A sediment core used in the composite series thus retains both an observed field and a corresponding composite depth. Note, the term depth hereafter refers to composite depth. The resultant stratigraphy for the Lake Pupuke composite core series is shown in Figure 3.4.
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.
3.5 Chronology

A precise age-depth model was constructed to meet the first objective of this thesis and constrain the timing of environmental proxy change throughout the composite sediment series. The presence of errors in any one chronometric technique (e.g., radiocarbon plateaux, reservoir effects, resuspension and counting error) assigns greater reliability to sediment age estimates derived from a mixed model approach containing discrete radiocarbon (\(^{14}\)C) and tephra isochrons. Lowe et al (2008) recommended the dual application of \(^{14}\)C and tephra isochrons to the development of lacustrine age-depth models in New Zealand because volcanic ash horizons can be readily discerned from the sediment matrix, avoiding the inclusion of erroneous radiocarbon age estimates. The TVZ tephra have been widely described and robustly dated throughout the Late Quaternary across the North Island of New Zealand with the notable exception of the Rotoehu tephra (45-64 cal. kyr BP) (Shane, 2005; Shane et al., 2006; Molloy et al., 2009). Further, until recently (Needham et al., 2010) the Rangitoto tephra lacked an accurate age-estimate and was excluded like the Rotoehu tephra from age-depth models.

Reviews of \(^{14}\)C-dating in Telford et al (2004) and Hua (2009) address a number of questions faced by researchers, notably how to calibrate \(^{14}\)C-ages and the decision on a suitable calibration curve from an array of international radiocarbon datasets. Birks and Heegaard (2003) note the need for a statistical approach to age-depth modelling to better account for the uncertainties in age-depth determinations and estimate associated confidence intervals for inferred ages. The steps taken in the construction of a robust age-depth model for this thesis are listed below in methodological order (modified from Birks and Heegaard [2003]):

1. Selection of reliable tephra and calibrated \(^{14}\)C age-markers;
2. Statistical age-depth modelling of selected age-markers;
3. Age-depth model evaluation and selection.

3.5.1 Tephra

The time parallel nature and accurate identification of tephra by glass chemistry, mineralogy and stratigraphy permitted the accurate correlation of multiple short sediment cores into a 1420 cm sequence. However, to generate an accurate age-depth model for the Pupuke sediment series in line with INTIMATE protocols on the development of chronologies (e.g., Hoek et al., 2008; Lowe et al., 2008), only independently dated tephra have been employed in age modelling (i.e., accurately dated tephra found in deposits throughout the North Island of New Zealand). This thereby ensures the accuracy of comparisons between inferred dates for major climatic events at Lake Pupuke and the NZ-INTIMATE climate event stratigraphy. Of the 38 total tephra deposits identified within the Pupuke composite sediment series only 13 met this criterion (highlighted in **bold** in Table 3.2).
Age constraints on tephra older than the Kawakawa/Oruanui isochron (27.1 cal. kyr BP) are less well defined than those attached to younger tephra (Molloy et al., 2009). Similarly, the rhyolitic Rotoehu tephra (45-64 cal. kyr BP [Shane et al., 2002; Wilson et al., 2007]) is very poorly constrained due to its position at the present upper limit of 14C age estimation. The rhyolitic Hauparu tephra (35.9 ± 1.3 cal. kyr BP) is also poorly constrained due to variable 14C age estimates on organic inclusions (Shane, 2005). As noted, until recently the Rangitoto tephra retained a poor age estimate, since dated to ~504 ± 5 cal. yr BP (Needham et al., 2010). Consequently these tephra have been excluded from incorporation into the composite age-depth relationship, meaning 11 independently and well-dated tephra isochrons have been applied in conjunction with 14C-age estimates to a composite age-depth model for Pupuke (underscored and highlighted in bold in Table 3.2).

### 3.5.2 Radiocarbon Dating and Calibration

Accelerator mass spectrometry (AMS) radiocarbon ages have been obtained on 32 plant macrofossil and bulk sediment samples (reported with metadata including laboratory reference codes in Table 3.3). Of these, 13 reported highly erroneous age estimates (e.g., markedly deviated from a linear trend between age markers) permitting use of 19 in the composite sediment series: 5 analyses performed at the Australian Nuclear Science and Technology Organisation (ANSTO); 6 analyses at the Quaternary Sciences Radiocarbon Dating Laboratory (University of Lund, Sweden); and 8 at the Rafter Radiocarbon Laboratory (GNS, New Zealand). Each radiocarbon sample was treated with an identical acid-alkali-acid (AAA) washing sequence prior to AMS analysis, to remove carbonate, bacterial CO2 and humic/fulvic acids. Graphite targets were produced according to protocols used in each laboratory. Erroneous ages have been attributed to the influx of old-Carbon via catchment reworking and a hard-water effect which affected charcoal and bulk sediment extractions (e.g., Newnham et al., 1998; McGlone and Wilmshurst, 1999; Sandiford et al., 2001).

Radiocarbon ages have been calibrated to calendrical age, relative to Before Present (1950 AD) in OxCal v.4.1 (Ramsey, 2009) using a range of calibration datasets. NZ33095 was calibrated with ShCal04 (McCormac et al., 2004) as this lay within its temporal limits whilst the other 18 radiocarbon age estimates were calibrated with the IntCal 09 dataset (Reimer et al., 2009).

Comparison of 14C calibrated isochrons with more reliable tephra isochrons enabled outliers to be identified from the total age distribution. To ensure the Law of Superposition was met by all isochrons (e.g., chronological order of isochrons by depth) 6 further 14C dates have been excluded from age-depth models (Figure 3.5; Table 3.3). Previous studies by Horrocks et al (2005) and Augustinus et al (2006) reported similar problems due to an older Carbon effect present in bulk sedimentary age estimates. In total, 11 independent tephra and 13 calibrated radiocarbon dates were employed in the composite age-depth model (Table 3.3).
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.

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

<table>
<thead>
<tr>
<th>Age Marker</th>
<th>Composite Depth (cm)</th>
<th>(^{14}C) Age</th>
<th>± 1σ</th>
<th>Calibrated Age (yr BP)</th>
<th>± 2σ</th>
<th>Reference*</th>
<th>Calibration Dataset**</th>
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<td>11700</td>
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<tr>
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<td>12542</td>
<td>116</td>
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</tr>
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</tr>
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<td>60</td>
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<td>165</td>
<td>Lowe et al (2008)</td>
<td></td>
</tr>
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<td>14700</td>
<td>95</td>
<td>17625</td>
<td>425</td>
<td>Lowe et al (2008)</td>
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</tr>
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<td>21875</td>
<td>418</td>
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</tr>
<tr>
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<td>18323</td>
<td>56</td>
<td>21992</td>
<td>634</td>
<td>Molloy et al (2009)</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
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<td>110</td>
<td>24494</td>
<td>432</td>
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<td></td>
</tr>
<tr>
<td>Okaia</td>
<td>959</td>
<td>24600</td>
<td>160</td>
<td>29252</td>
<td>868</td>
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</tr>
<tr>
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<td></td>
</tr>
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<td>906</td>
<td>NZA33100(^{B})</td>
<td></td>
</tr>
<tr>
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<td>LuS8443(^{B})</td>
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</tr>
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<td>350</td>
<td>35576</td>
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<td>1150</td>
<td>Molloy et al (2009)</td>
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</tr>
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<td>349</td>
<td>39268</td>
<td>2386</td>
<td>Molloy et al (2009)</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>1235</td>
<td>35100</td>
<td>1000</td>
<td>40110</td>
<td>2078</td>
<td>LuS7482(^{B})</td>
<td></td>
</tr>
</tbody>
</table>

* Refers to source of calibrated age estimate for tephra and laboratory reference code for radiocarbon age marker.
** ShCal04 (McCormac et al., 2004); IntCal09 (Reimer et al., 2009). \(^{A}\) Macrofossil charcoal; \(^{B}\) Bulk sediment.
3.5.3 Age-Depth Model Construction

To evaluate the effect of the age-depth model on sedimentation rates, and consequently, sediment accumulation, we tested several interpolation procedures: linear segments, exponential functions, power functions, best-fit polynomials, cubic splines and mixed effect regression models. All age models were calculated using Microsoft Excel, DepthAge software (developed by Louis Maher Jr., and available for free download at the INQUA file boutique @ http://www.geology.wisc.edu/~maher/inqua.html [last accessed November 18, 2009]) and the Agedepth function (described by Heegard et al [2005] and available for download into the statistical package R @ http://cran.r-project.org/ [last accessed November 19, 2009]).

*DepthAge* and *Agedepth* are designed to facilitate the conversion of sediment core depths (cm) into estimates of their age in calibrated years (Maher, 1992; Heegaard et al., 2005). Both offer the benefit of constraining isochrons by an upper and lower composite depth. Depth is plotted as the average of the upper and lower limits of sample depth. Curves are fitted using a least-squares method, minimising the variance between observed and predicted ages (Maher, 1992; Birks and Heegaard, 2003). Measures of curve fit (e.g., $R^2$, standard error) were used to estimate graphical performance for those models in which values for isochrons could be predicted (e.g., exponential functions, power functions and smoothed polynomials).

![Figure 3.6](image-url)

*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.*
Figure 3.7: Linear-segment, power ($y = 1.9235 \cdot x^{0.6048}$), exponential ($y = 319.8 \cdot e^{0.0005x}$), 3rd order polynomial age-depth models ($y = -1\cdot10^{-5} \cdot x^3 + 0.0342 \cdot x^2 + 7.0856 \cdot x - 57$) 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.
The most widely applied depth-age function in paleolimnology employs linear segment regression between paired age markers (Enters et al., 2006). The key benefit of this approach is its simplicity. However, the inherent simplicity of this approach results in sediment accumulation rates (SAR) that vary suddenly in time and markedly in magnitude between isochrons, whereby all trends must fit through a series of ‘knots’ (e.g., isochrons) (Birks and Heegaard, 2003). Similarly, such models take no account of the uncertainty attached to each age marker and weight them equally for the purpose of fitting a trend. Consequently, where the latter deviate from a generalised trend due to some error (inherent in probabilistic $^{14}$C inferences) there is a greater likelihood of significant change to SAR coincident with new age marker information (Birks and Heegaard, 2003). When applied to dry bulk density (DBD) to infer proxy flux deposition rates (e.g., g/cm$^{-2}$/yr - $^{1}$TOC) variations in the latter are driven not by changing DBD or %TOC but rather ‘plateaux’ in SAR, each defined in x or y by two isochrons (Figure 3.6). Hence, a smoothed trend which varies by some function of y or x can better capture natural variability and is therefore more robust than a rigid linear interpolation (Heegaard et al., 2005). For these reasons linear segment interpolation was not selected for age-depth modelling of the Pupuke composite series.

Exponential, power function and polynomial trends were calculated and applied to calibrated $^{14}$C and tephra ages (Figure 3.7). Maher (1992) notes that exponential rates are a common feature of natural distributions but are rare in lacustrine deposits. Likewise power functions are suited to log-log variability in x and y. Examination of variation in depth (x) by calibrated age (y) reveals a log-log relationship between the two. This is reflected in a coefficient of determination ($R^2$) of 0.979 attached to a power function ($y = 1.9235 \cdot x^{0.6048}$). The calculated power function curve exceeded an exponential goodness of fit ($R^2 = 0.904$) ($y = 319.8 \cdot e^{0.0005x}$). The latter describe early changes in sedimentation very well but older changes are modelled less well. Thus an nth order function was employed to model age and depth. Nth order functions enable a smoothed trend to be fitted to data that do not conform to simpler linear trends and which might possess a combination of both logistic and linear relationships between x and y over a range in either or both variables (Maher, pers. comm., 2010). A 1st order function is a straight line, a 2nd order is a convex or concave function, and an nth order polynomial has in general n-1 bends. Thus a preliminary examination of the data will aid development of a suitable regression model. In our age model there are two distinct regions of variable sedimentation, an initial highly logistic variation in age by depth (presumably a result of early diagenetic compaction) followed by a more linear relationship (once compaction has attained equilibrium). Unsurprisingly a 3rd order polynomial function ($y = -1*10^{-11} \cdot x^3 + -1*10^{-6} \cdot x^2 + 0.0511 \cdot x – 57.592$) described the variation in age by depth very well ($R^2 = 0.993$).

Cubic splines are a particularly robust approach to SAR estimation because the ‘spline’ fits through all specified control points or ‘knots’ with a series of cubic polynomial trends that often better represent natural changes to SAR (Birks and Heegaard, 2003; Telford et al., 2004). *DepthAge* fitted a 2nd order or cubic spline to the isochron dataset (e.g., smoothing function is a piecewise polynomial of degree equal to 2 * order - 1) (Maher, 1992). By smoothing the trend between data points into a polynomial, natural splines result in variable SAR by depth, preventing SAR plateaux present in other segment approaches. However, where isochrons are very closely distributed in x or y, the spline curve will result in ‘ruffle-like bends’ (Maher, 1992:4) that contain sections of...
negative accretion and infinite SAR (Figure 3.7). To prevent impossible negative accretion, an alternative approach is to exclude those isochrons which are causing splines to curve back on their prior knot. Whilst this results in a smooth cubic spline that captures most of the SAR variability, the decision made on which isochrons to exclude is highly subjective and furthermore might exclude short, sharp deviations in SAR. Moreover like the earlier linear segment approach, spline fits assume age markers are devoid of error preventing derivation of a goodness of fit estimate.

An error-weighted mixed effect regression (MER) procedure was applied to the composite sediment series from Lake Pupuke to account for uncertainty in derived age markers and to employ a more realistic or natural smoothing function (e.g., Telford et al., 2004). This approach lies within the framework of generalised additive models (GAMs) which can be implemented by Heegaard’s (2003) R function Agedepth. GAMs offer the benefit over prior generalised linear models (GLMs) of being driven primarily by the data rather than prespecified relationships inherent in polynomial, \( n \)th power or exponential relationships (Birks and Heegaard, 2003). The model uses the central points of lower and upper calibrated age (e.g., upper and lower depth of dated sediment sample) in conjunction with the calibrated \(^{14}\text{C} \) standard deviation (2\( \sigma \)) of age estimates as weights in a linear regression of age on depth. Calibrated ages with lower standard deviation about their mean possess greater weighting and vice versa. The procedure is classified as a mixed-effect model that comprises a fixed effect (depth on age) and two random effects (within-object variance [i.e., variability attached to the calibrated age estimate] and between-object variance [i.e., variability attached to the representivity of a particular date within that section of the composite sequence]) (Heegaard et al., 2005). The benefit of this approach is that ages below a fitted age marker are more heavily influenced by the directly preceding date than in a polynomial approach (Heegaard et al., 2005).

Within the statistical program \( R \) (R Development Core Team, 2008), Agedepth uses a 2\textsuperscript{nd} order (e.g., cubic) smooth spline function with a knot at each isochron prior to beginning the shrinkage process (Heegaard et al., 2005). Thereafter a Generalised Additive Model (GAM; Wood, 2000) will model a regression relationship between a linear predictor and expected response combined with different variance functions (Heegaard et al., 2005). Pointwise standard errors for mean regression responses were added to standard errors of individual age estimates to calculate 95% confidence intervals over the composite series. Input data for the Lake Pupuke composite sediment series is presented in Table 3.4. Diagnostic plots revealed a simpler, constant-variance model performed better than a \( \mu \)-variance model at predicting dated layer depths (i.e., lesser mean and max residuals attached to observed age markers; inclusion of all age markers in the 95% confidence interval overlap) (Figure 3.8).
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.

<table>
<thead>
<tr>
<th>Age Marker</th>
<th>Composite Depth (cm)</th>
<th>Depthup (Upper composite depth)</th>
<th>Depthdo (Lower composite depth)</th>
<th>Calibrated Age (yr BP) ± 2σ</th>
<th>Cageup (Upper composite age)</th>
<th>Cagedo (Lower composite age)</th>
</tr>
</thead>
<tbody>
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<td>-57</td>
<td>0</td>
<td>-58</td>
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Depthup = upper composite depth of sampled layer (cm); Depthdo = lower composite depth of sampled layer (cm); Cageup = younger border of 95% central calibrated age distribution (calibrated years BP); Cagedo = older border of 95% central calibrated age distribution (calibrated years BP).

A benefit of the mixed effect approach is the ability to weight isochrons measured through different procedures by the uncertainty in their age estimation. The model will best approximate ages by applying weights equal to the inverse of within-object variance (e.g., standard deviation) (Heegaard et al., 2005). Estimates of the sedimentation rate and age will be weighted to more precisely dated age markers. As noted in Figure 3.8, the 95% confidence interval increases in width with uncertainty about calibrated age. Residuals of predicted and observed ages for all 24 age markers vary widely with no trend by age (i.e., no increase or decrease of prediction accuracy by time). Residual age estimates are >5% of the observed age in only 3 age markers (e.g., residual age/observed age * 100%): two 14C (NZA33095 [9.3 cal. kyr BP] and NZA 33683 [11.7 cal. kyr BP]) were over-predicted by 6.5% (+0.6 kyr) and 9.2% (+1.1 kyr) respectively; and one tephra isochron (Okareka [22.0 cal. kyr BP]) was under-predicted by 6.2% [-1.4 yr]. These isochrons are particularly poorly constrained compared to precedent and antecedent markers, and thus it is to be expected that the constant variance mixed effect model will discriminate against these in favour of those isochrons with greater age certainty. On average all isochrons are predicted to an age value within ± 440 yrs of their observed value (± 350 yr excluding NZA 33095, NZA 33683 and the Okareka isochron). Hence, the MER predicts age markers to within 2σ of their published age estimates confirming the model accuracy ($R^2 = 0.9996$).
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 q-q-normplot. Note the greater residuals attached to μ-variance making the constant-variance model more robust at predicting age from depth for age-markers.
3.5.4 Age-Depth Model Evaluation and Selection

In adopting an age model it is essential that the researcher acknowledge the effects of different mathematical forms on subsequent age distributions (Telford et al., 2004). The Pupuke composite series demonstrates an initial exponential change in age by depth prior to a cessation of either a compaction process and/or near recent rapid increase of SAR. Subsequently there are marked deviations in sedimentation at ~6.0-10.0 cal. kyr BP, ~13.0-14.5 cal. kyr BP and ~20.0-22.0 cal. kyr BP. Despite their widespread application, simple linear models would not faithfully capture the former changes. Polynomial relationships, whilst suited to initial changes, do not faithfully capture later linearity. A mixed effect regression (MER) generalised additive model can however, capture these older deviations in sedimentation in addition to rapid early changes, as well as, offering a smoothed cubic spline model without the limitations of negative SAR attributable to a more rigid cubic spline model (Heegaard et al., 2005). The MER approach offers an estimate of the uncertainty attached to inferred ages through inclusion of the uncertainty in age markers (Heegaard et al., 2005).

Pearson’s correlation coefficient of determination ($R^2$) can be employed to denote goodness-of-fit in age-depth models. However, paleolimnological series suffer from several drawbacks to its application: (1) a high-goodness-of fit arbitrarily characterises longer series as a result of a long gradient in depth and/or age; and (2) calculation of squared error in linear trends assumes that age markers lack any error. Nonetheless, the constant variance MER age-depth model possesses a higher $R^2$ than the next best, 3rd order polynomial model ($R^2$ of 0.9996 to 0.9939 respectively). This thesis employs a constant variance MER model of calibrated age on composite depth based on a greater goodness-of-fit, the ability to fit splines to ‘knots’ composed of isochrons weighted by their uncertainty, estimation of the probable uncertainty attached to inferred age, and the recognition that cubic splines can better model natural sedimentation relationships (e.g., Telford et al., 2004). MER age-depth models have been successfully employed to reconstruct past environment in several other recent paleolimnological investigations (e.g., Bjune, 2005; Colman et al., 2006; Panizzo et al., 2008a; Cooke et al., 2009; De Vleeschouwer et al., 2009).

Inspection of MER modelled ages reveals 3 broad zones of variable age uncertainty: (1) initial sediments (< 10 cal. kyr BP) less subject to uncertainty due to lesser absolute uncertainty in younger age markers (± 405 yr, 2σ, n = 472); (2) intermediate sediments (10. -33.6 cal. kyr BP) of moderate uncertainty (± 1407 yr, 2σ, n = 608); and (3) older sediments (33.6-48.2 cal. kyr BP) in which uncertainty reaches a maximum (± 3993 yr, 2σ, n = 340). Although the MER model weights inferred ages by the uncertainty in nearest age markers, it does not account for the distribution of age markers. For instance, earlier trends suggest the most precise inferred ages are those attached to the last ~10 cal. kyr BP, but inspection of Figure 3.8 demonstrates that age markers are sparsely distributed in this interval (n = 4; isochron spacing 2500 yr). The interval 10-33.5 cal. kyr BP possesses the greatest frequency of age markers (n = 16; isochron spacing 1475 yr). Accordingly the later interval (33.6-48.2 cal. kyr BP) is poorly confined by age markers of greatest uncertainty (n = 4; isochron spacing 3650 yr). Furthermore, the presence of only a single age marker between the core top (~57 cal. yr BP) and the Tuhua
tephra (7.0 cal. kyr BP), namely the Taupo tephra (1.7 cal. kyr BP), suggests that unless sedimentation has remained relatively constant, ages attached to proxy inferences during the early Holocene are likely to suffer from error. Nonetheless, the MER age-depth model is best suited to the Pupuke composite series as in any case the latter error would be present in all age models. This is clearly shown in Table 3.5 through the close approximation of ‘inferred’ and ‘applied’ age-marker ages (i.e., those ages taken from the literature [Lowe et al., 2008 and Molloy et al., 2009] and corresponding modelled ages). Basal sediment at 1420 cm (composite depth) is dated to ~48.2 cal. kyr BP such that proxy samples (~1 cm) correspond to 34 ± 15 yr intervals (µ ± σ, n = 1420; maximum and minimum, ~61 and ~5 yr respectively).

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

<table>
<thead>
<tr>
<th>Age Marker</th>
<th>Composite Depth (cm)</th>
<th>(^{14}C) Age</th>
<th>±1σ</th>
<th>Applied age (cal. yr BP)</th>
<th>±2σ</th>
<th>MER age (cal. yr BP)</th>
<th>±95% (2σ)*</th>
<th>Reference**</th>
</tr>
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<tr>
<td>Taupo</td>
<td>207</td>
<td>1845</td>
<td>38</td>
<td>1717</td>
<td>13</td>
<td>1709</td>
<td>266</td>
<td>Lowe et al (2008)</td>
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<tr>
<td>(^{14}C)</td>
<td>442</td>
<td>8346</td>
<td>35</td>
<td>9283</td>
<td>147</td>
<td>8677</td>
<td>615 NZA33095</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>483</td>
<td>10124</td>
<td>45</td>
<td>11700</td>
<td>290</td>
<td>10628</td>
<td>713 NZA33683</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>512</td>
<td>10604</td>
<td>45</td>
<td>12542</td>
<td>116</td>
<td>12195</td>
<td>690 NZA33096</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>585</td>
<td>11673</td>
<td>45</td>
<td>13536</td>
<td>160</td>
<td>13494</td>
<td>808 NZA33097</td>
<td></td>
</tr>
<tr>
<td>Waiohau</td>
<td>620</td>
<td>11850</td>
<td>60</td>
<td>13635</td>
<td>165</td>
<td>13976</td>
<td>776 Lowe et al (2008)</td>
<td></td>
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<tr>
<td>Rerewhakaitu</td>
<td>703</td>
<td>14700</td>
<td>95</td>
<td>17625</td>
<td>425</td>
<td>17614</td>
<td>1360 Lowe et al (2008)</td>
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<tr>
<td>(^{14}C)</td>
<td>757</td>
<td>17296</td>
<td>70</td>
<td>20663</td>
<td>412</td>
<td>20068</td>
<td>1413 NZA33099</td>
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</tr>
<tr>
<td>(^{14}C)</td>
<td>827</td>
<td>18310</td>
<td>160</td>
<td>21875</td>
<td>418</td>
<td>22249</td>
<td>1291 OZK261</td>
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</tr>
<tr>
<td>Okareka</td>
<td>851</td>
<td>18323</td>
<td>56</td>
<td>21992</td>
<td>634</td>
<td>23364</td>
<td>1531 Molloy et al (2009)</td>
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</tr>
<tr>
<td>(^{14}C)</td>
<td>860</td>
<td>20490</td>
<td>110</td>
<td>24944</td>
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<td>23868</td>
<td>1276 NZA33684</td>
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<td>160</td>
<td>29252</td>
<td>868</td>
<td>29103</td>
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<td>250</td>
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<td>524</td>
<td>31919</td>
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<tr>
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<td>1038</td>
<td>27470</td>
<td>350</td>
<td>31920</td>
<td>748</td>
<td>32029</td>
<td>1747 OZK270</td>
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</tr>
<tr>
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<td>28820</td>
<td>240</td>
<td>33576</td>
<td>906</td>
<td>32960</td>
<td>2068 NZA33100</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>1103</td>
<td>28900</td>
<td>300</td>
<td>33604</td>
<td>939</td>
<td>34410</td>
<td>2187 LuS8443</td>
<td></td>
</tr>
<tr>
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<td>350</td>
<td>35576</td>
<td>770</td>
<td>34892</td>
<td>1963 LuS8444</td>
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<td>32078</td>
<td>306</td>
<td>36320</td>
<td>1150</td>
<td>36734</td>
<td>2748 Molloy et al (2009)</td>
<td></td>
</tr>
<tr>
<td>Tahuna</td>
<td>1224</td>
<td>33737</td>
<td>349</td>
<td>39268</td>
<td>2366</td>
<td>39283</td>
<td>5115 Molloy et al (2009)</td>
<td></td>
</tr>
<tr>
<td>(^{14}C)</td>
<td>1235</td>
<td>35100</td>
<td>1000</td>
<td>40110</td>
<td>2078</td>
<td>39783</td>
<td>4766 LuS7482</td>
<td></td>
</tr>
</tbody>
</table>

* Refers to 95% uncertainty in MER-inferred age (cal. yr BP).
** Refers to source of calibrated age estimate for tephra and laboratory reference code for radiocarbon age marker. All radiocarbon age markers calibrated in IntCal09 (Reimer et al., 2009) except for NZA33095 that was calibrated in ShCal04 (McCormac et al., 2004).

3.6 Lithology and Stratigraphy

Construction of a precise and accurate MER age-depth model permits stratigraphic changes in sedimentary properties to be described (e.g., sediment accumulation rate [SAR], wet bulk density [WBD], water content [Wc], dry bulk density [DBD] and mass accumulation rate [MAR]). Although capable of recording paleoclimatic events, they do not offer as detailed a record as subsequent limnologic proxies (discussed in Chapters 4, 5 and 6). Instead, to define key boundaries in sediment lithology, stratigraphic changes to sedimentation and broad physical properties are included here.
3.6.1 Lithology

The composite sediment record covers 1420 cm of biogenic siliceous/carbonaceous gyttja (>20% amorphous organic matter [OM] content). Throughout, the sediments demonstrate limited variation in sediment character (e.g., colour, induration, plasticity, degree of lamination) consisting of fine-grained, dark, highly organic lake mud interspersed with coarser tephra. Similarly, there is no evidence of marine breaching; in other AVF maars that have been marine breached this is denoted by a colour change from light olive brown (2.5Y 5/3) carbonaceous gyttja to dark grey (5Y 4/1) calcareous clay (e.g., Hayward et al., 2002). The composite sediment record is continuous with no evidence of reworking or lake desiccation (e.g., laminae and bands are horizontal throughout with no transverse or slump derived intervals). The presence of vivianite flecks throughout the sequence suggests a reducing sedimentary environment and deep water column (Asikainen et al., 2007). The presence of laminations throughout the composite sequence requires sufficient depth to favour benthic anoxia and preclude sediment disturbance (e.g., wave, current, bioturbation) during sediment deposition (Wetzel, 2001).

Despite the absence of marked lithological change, the composite sequence can be divided into 3 distinctive subfacies summarised below. The most distinctive feature is a subtle change to lighter colour in Subfacies 2 and variation in the degree of lamination enabling Subfacies 1 and 3 to be further subdivided. Sediment compaction is evident in the near recent sediments which are only faintly laminated, reflecting very loose consolidation.

SUBFACIES 1a: (0-224 cm; Present to 2.0 cal. kyr BP) Loose silt, poorly-laminated, black (5Y 2.5/1);

SUBFACIES 1b: (224-401 cm; 2.0-7.1 cal. kyr BP) More consolidated silt, moderately-laminated (0.5-1.0 mm), dark olive grey (5Y 3/2)

SUBFACIES 1c: (401-715 cm; 7.1-18.2 cal. kyr BP) Firm consistent, finely laminated silt (<0.5 mm), very dark grey/dark olive grey (10YR 3/1; 5Y 3/1) including notable organic-rich oily laminae (20-320 mm thickness) beneath the Tahua (~7.0 cal. kyr BP) and above the Rotoma (~9.5 cal. kyr BP) tephra;

SUBFACIES 2: (715-954 cm; 18.2-28.9 cal. kyr BP) Firm, finely laminated silt (<0.5 mm), dark grey (5Y 4/2);

SUBFACIES 3a: (954-1333 cm; 28.9-44.2 cal. kyr BP) Firm, finely laminated silt (<0.5 mm), dark olive grey (5Y 3/2);

SUBFACIES 3b: (1333-1420 cm; 44.2-48.2 cal. kyr BP) Firm, finely laminated silt (<0.5 mm), very dark grey/black (10YR 3/1; 5Y 2.5/1).
3.6.2 Sediment Accumulation Rate

Variation in the rate of sediment accumulation can suggest changes in paleoenvironment. Sediment accumulation rate (SAR) is dependent upon input of inorganic matter via clastic influx and organic matter via productivity (autochthonous and allochthonous) (Zolitschka, 1998). As such, changes in SAR can record changes in paleoproductivity and erosion within a sediment sequence (Magny et al., 2006; Page et al., 2010). Here SAR has been calculated for the composite sequence as the reciprocal of the difference in estimated age at the top and base of a 1 cm interval centred on a specified depth:

\[
\text{SAR (cm yr}^{-1} \text{)} = \frac{\text{composite depth interval (cm)}}{\text{corresponding time interval (yr)}}
\]

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.

SAR estimates over the 1420 cm of the composite sequence are presented in Figure 3.9. These vary from 0.09 to 5.77 mm/yr with an average (\(\mu\)) of 0.51 mm/yr. A notable feature of SAR is a significant change prior to and after ~7.2 cal. kyr BP (SAR \(\mu\) before and after = 0.29 and 0.91 mm/yr respectively), including a likely early diagenetic compaction process. However, the most notable features of SAR are distinct maxima occurring from ~37.5 cal. kyr BP until ~29.2 cal. kyr BP (SAR 0.28 mm/yr), ~22.8-19.8 cal. kyr BP (SAR 0.36 mm/yr), ~15.1-12.4
cal. kyr BP (SAR 1.43 mm/yr) and ~10.2-8.4 cal. kyr BP (SAR 0.27 mm/yr). These events range in duration from ~1.4 kyr to ~8.3 kyr (~8.3 kyr, ~3.0 kyr, ~2.7 kyr and ~1.8 kyr respectively) and record distinct periods of enhanced sedimentation. With the exception of the initial compaction driven SAR trend, the increase in SAR over the period ~12.5-14.5 cal. kyr BP represents the greatest observed SAR in the composite series.

Brief excursions in SAR are broadly coincident with age markers meaning they could represent artefacts of the spline smoothing age function (Figure 3.9). Errors attached to the latter will undoubtedly have contributed to the magnitude of SAR variance and to their timing (e.g., ± 440 yr average MER residual error). However, this is an unavoidable uncertainty and because of the high frequency of age markers (n = 24), changes to SAR likely offer a reliable picture of millennial scale excursions in the accumulation of organic and/or inorganic matter within Lake Pupuke.

### 3.6.3 Wet and Dry Bulk Density

The composite series is characterised overall by moderate to low densities coupled with high water content (WBD, WC and DBD \( \mu = 1.12 \text{ g cm}^{-3}, 75\% \) and 0.29 g cm\(^{-3} \) respectively) (Figure 3.10). There is a significant inverse correlation between DBD and sedimentary water content \( r = -0.98, \ P < 0.0001, \ n = 1420 \). Although there is only limited variability in WBD \( (1\sigma = 0.09 \text{ g cm}^{-3}) \), there is marked variability in WC and DBD \( (1\sigma = 8.5\% \) and 0.11 g cm\(^{-3} \) respectively). Further inspection of Figure 3.10 reveals DBD and WC to vary within defined temporal zones:

**ZONE 1** (Today to 18.2 cal. kyr BP, \( n = 714 \)) – higher WC \( (81.3 \pm 4.9 \% \ [\mu \pm 1\sigma]) \) and lower DBD \( (0.20 \pm 0.06 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \) combined with lower WBD values \( (1.06 \pm 0.06 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \). Zone 1 exhibits a trend to higher WC and lower DBD to Present though changes in compaction noted above at 224 cm (Section 3.6.1. Lithology) are not readily apparent.

**ZONE 2** (18.2-22.8 cal. kyr BP, \( n = 126 \)) – lower WC \( (59.3 \pm 5.1 \% \ [\mu \pm 1\sigma]) \) and higher DBD \( (0.47 \pm 0.06 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \) combined with moderate WBD values \( (1.16 \pm 0.08 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \).

**ZONE 3** (22.8-48.2 cal. kyr BP, \( n = 580 \)) – higher WC \( (69.3 \pm 3.0 \% \ [\mu \pm 1\sigma]) \) and lower DBD \( (0.36 \pm 0.04 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \) combined with near higher WBD values \( (1.18 \pm 0.09 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \). Zone 3 can be subdivided into 2 minor subzones:

**SUBZONE 3a** (22.8-31.0 cal. kyr BP, \( n = 169 \)) – relatively lower WC \( (66.6 \pm 3.7 \% \ [\mu \pm 1\sigma]) \) and higher DBD \( (0.39 \pm 0.05 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \);

**SUBZONE 3b** (31.0-48.2 cal. kyr BP, \( n = 411 \)) – relatively higher WC \( (70.5 \pm 1.5 \% \ [\mu \pm 1\sigma]) \) and lower DBD \( (0.35 \pm 0.04 \text{ g cm}^{-3} \ [\mu \pm 1\sigma]) \).
The striking changes in $W_c$ and DBD present in Zone 2 imply the accumulation of denser, more compact lacustrine sediment between ~18.2 and 22.8 cal. kyr BP. This might be a response to the influx of dense minerogenic sediment or post-depositional density settling of cryptotephra. In Figure 3.10 there is little evidence of increased tephra deposition compared to Zones 1 or 3. Thus changes to $W_c$ and DBD likely reflect a compaction effect and/or a response to the influx of denser sedimentary matter. It should also be noted that early diagenetic compaction is evident in Zone 1 by a declining trend in DBD and increasing $W_c$ from 18.2 cal. kyr BP to today. However, the increase to DBD from Zone 1 to 2 ($\mu_{\text{Zone1}} = 0.20 \text{ g cm}^{-3}$; $\mu_{\text{Zone2}} = 0.47 \text{ g cm}^{-3}$) is far greater than that attributed to recent compaction (e.g., up to 224 cm [2.0 cal. kyr BP] $\mu_{\text{Zone3}} = 0.14 \text{ g cm}^{-3}$) suggesting the influx of denser sediment rather than compaction has driven changes to DBD and $W_c$ over the interval 18.2 to 22.8 cal. kyr BP.
3.6.4 Mass Accumulation Rate

SAR is a useful means of characterising changes to sediment loads and compaction over sedimentary records (Street-Perrott et al., 2007). However, application of SAR to paleolimnology is complicated as observed changes might not necessarily reflect changing sedimentation rate but rather, changes in degree of compaction. Conversion of SAR to MAR is essential to remove dilution or concentration effects in subsequent environmental proxy analysis (Street-Perrott et al., 2007). A change in the relative (%) abundance can result from increased or decreased sedimentation rather than an absolute change in abundance (e.g., % abundance of Carbon, Nitrogen and Sulphur) (Meyers and Teranes, 2001). Mass accumulation rates (MAR) are generated as the product of SAR and DBD ($\rho_{\text{dry}}$) for a sample as follows:

$$\text{MAR} \ (g \ cm^{-2} \ yr^{-1}) = \rho_{\text{dry}} \ (g \ cm^{-3}) \times \text{SAR} \ (cm \ yr^{-1})$$

MAR is included here as it can be generated independently of proxy environmental data and is dependent upon the choice of age-depth model. Nonetheless, MAR like SAR can provide paleoclimatic information. Changes to MAR reflect a variety of processes, namely a change to productivity and/or catchment erosion. An increase to either would result in an increased MAR and vice versa. For instance, increased catchment vegetation can be indicative of an amelioration of climate which would reduce erosion and result in enhanced productivity (e.g., Rodbell et al., 2008). Thus it is essential to distinguish between the two mechanisms for enhanced MAR. This is made possible through interpretation of the DBD data. Lacustrine minerogenic matter is characterised by greater density than biogenic matter so that greater erosion would be coincident with higher sediment DBD (Gale and Hoare, 1991).

Trends in DBD, $W_c$ and MAR are shown together in Figure 3.11. Average MAR is $0.011 \pm 0.006 \ g \ cm^{-2} \ yr^{-1}$ ($\mu \pm \sigma, n = 1419$). Whereas changes to SAR revealed 5 events of increased sedimentation at Lake Pupuke during the last ~48 cal. kyr BP, conversion to MAR helps to elicit only those events likely to drive changes in the flux of proxy indicators. Inspection of Figure 3.11 reveals the presence of 3 broad peaks of sediment mass delivery: near-recent (Today to 2.0 cal. kyr BP, MAR $\mu = 0.019 \ g \ cm^{-2} \ yr^{-1}$), late Glacial (12.7-14.8 cal. kyr BP, MAR $\mu = 0.018 \ g \ cm^{-2} \ yr^{-1}$) and Late Glacial Maximum (18.4-23.5 cal. kyr BP, MAR $\mu = 0.013 \ g \ cm^{-2} \ yr^{-1}$). The most recent increase in MAR corresponds to a decline in DBD indicative of increased organic matter content and hence higher autochthonous and/or allochthonous productivity. However, increased MAR from 12.7-14.8 cal. kyr BP and 18.4-23.5 cal. kyr BP are notable as whilst both represent increases in sediment delivery rate, the two events are largely composed of less dense and more dense sediment respectively. Increased MAR and DBD during the latter event indicates influx of eroded minerogenic matter to the lacustrine sedimentary record, whereas increased MAR and decreased DBD during the former indicates an increase in the productivity of the system and associated organic matter input to the lake. The MAR excursion from 12.7-14.8 cal. kyr BP could also include a brief initial erosive phase as prior trends to reduced DBD and increased $W_c$ content halted prior to and for ~400 yrs of increased MAR (from ~16.0 until ~14.4 cal. kyr BP).
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 largely inorganic, later highly organic sedimentation 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 $W_c$).

3.7 Summary of Stratigraphic Framework

A composite sediment series of 1420 cm length has been generated from twelve 3 m piston cores recovered from the centre of Lake Pupuke at a depth of ~57 m during February 2007. The composite series extends continuously from today (~57 cal. yr BP) to just beyond the Rotoehu tephra (~45-61 kyr [Shane, 2005]). Sediment cores were described for characteristic index properties (e.g., visual appearance as per Tröels-Smith [1955] and Kershaw [1997], magnetic-susceptibility, wet bulk density [WBD], water content [$W_c$], and dry bulk density [DBD]). Composite interval sediments are very finely laminated throughout (<1 mm), with no evidence of desiccation or reworking suggesting the presence of overlying water to sufficient depth to prevent bioturbation and wave or current activity. Laminations do not conform to the standard varved couplets typical of Northern European maar crater sediments but instead represent seasonal diatom blooms of variable taxa (Striewski et al., 2009), permitting the reconstruction of diatom paleolimnology (see Chapter 5).
The presence of 38 tephra ash-fall events within the composite series is also notable as reworking of cryptotephra could substantially contaminate diatom silica stable isotope analyses (see Chapter 6). Of these, 11 offer robust independent \(^{14}\)C-age estimates which in addition to 13 AMS \(^{14}\)C-age estimates have enabled a suite of age-depth relationships to be modelled and compared statistically over the composite series (e.g., linear segments, power, polynomial, spline, mixed effect regression [MER]). An age-depth model that is statistically based offers the benefits of comparison through estimated model fit parameters. However, statistical age-depth models also necessitate several assumptions: (1) tephra ages are reliable; (2) \(^{14}\)C calibrations are reliable (e.g., weighting functions are also reliable); (3) sample age is known with a larger error than sample depth (e.g., to permit regression of age on depth); (4) balancing model accuracy against population representivity; (5) composite depth sequences are intact and undisturbed; and (6) \(^{14}\)C-dating means are independent of their variances (Birks and Heegaard, 2003). These have been met by the composite series allowing selection of an MER age-depth model (e.g., Heegaard et al., 2005) which provides an exceptional fit to modelled age markers (\(R^2 = 0.9979\)). Notably however, age-depth models are just that, models, and have inherent uncertainties attached to all age estimates (Telford et al., 2004), meaning that uncertainty will remain in MER-inferred ages despite modelling for variable error between and in each age marker.

Trends in SAR have been generated from MER-inferred age estimates, revealing the presence of 4 marked excursions (increases) from a simple linear accumulation rate in addition to recent compaction (from ~7.2 cal. kyr BP): (1) ~10.2-8.4 cal. kyr BP; (2) ~15.1-12.4 cal. kyr BP; (3) ~22.8-19.8 cal. kyr BP; (4) ~37.5-29.2 cal. kyr BP. Estimates of DBD have been combined with SAR to yield changes to mass accumulation rate (MAR) devoid of changes due to variable density or compaction. MAR averages \(0.011 \pm 0.006 \text{ g cm}^{-2} \text{ yr}^{-1} (\mu \pm \sigma, n = 1420)\) for the composite series. Trends in DBD demonstrate enhanced delivery of organic matter from today to 2.0 cal. kyr BP and 12.7-14.8 cal. kyr BP accompanied by increased erosion throughout the period 18.4-23.5 cal. kyr BP.

Earlier we noted that variation in SAR might have arisen from unequal distribution of age markers over the composite series. The coincidence of marked changes to SAR with changing \(W_c\) and DBD confirm the likelihood that changes were actually system-based and not an artefact of poor core extraction, spatial-heterogeneity in SAR, and/or age-depth modelling. Furthermore, elimination of slump deposits from the composite series as well as continuation of trends in SAR and MAR over several cal. kyr BP (Figures 3.9 and 3.11), reduces the likelihood that they are sourced from discontinuities (e.g., turbidite slumps, paleosols, and flood events). Instead it is highly likely that increased erosion occurred from ~18.4-23.5 cal. kyr BP and increased productivity from ~12.7-14.8 cal. kyr BP. These dates lay notably close to the Last Glacial Maximum (LGM; ~23-19 cal. kyr BP [Hoek et al., 2008]) and Antarctic Cold Reversal respectively (ACR; ~14.5-12.7 cal. kyr BP [EPICA, 2006]). Shifts in MAR alone are important indicators of paleoenvironmental change in Lake Pupuke but the remit of this chapter is age-modelling and lithology, hence their implications are discussed further in Chapters 4, 5 and 6.
CHAPTER FOUR
Paleolimnology of Lake Pupuke inferred from Bulk Geochemical and Physical Environmental Proxies

4.1 Introduction to Geochemical and Physical Paleolimnology

Hydrological, ecological and hydrochemical information can be recorded by lacustrine sedimentary organic and inorganic matter (Birks and Birks, 2006). Recovering this information requires specific methodologies, each aimed at isolating a specific fraction of the sediment matrix (Last and Smol, 2001). Some of these proxies are more aligned to atmospheric and others to aquatic drivers of change, notably changing erosion, productivity or benthic REDOX state. For instance, elemental and isotopic analysis of sedimentary organic matter (OM) provides important paleolimnological information about past productivity in the lake environment and surrounding catchment (Talbot, 2001). Productivity refers to the rate of production of biomass (Talbot, 2001). Productivity is dependent upon the availability of nutrients, which depends on rates of delivery of by-products of catchment soil decomposition, erosion and in-lake water column mixing, meaning changes to productivity are often aligned to changing hydrology and climate through changes in benthic REDOX state (Meyers and Teranes, 2001). Consequently, the interpretation of proxies more aligned to hydrological change (e.g., elemental profiles of Fe and Mn that respond to changing REDOX potential within benthic pore waters [e.g., Shanahan et al., 2008]) and those aligned to ecological change (e.g., atomic ratios of C/N record the balance of terrestrial to aquatic vegetation [e.g., Meyers and Teranes, 2001]), as well as those of catchment processes (e.g., grain-size distributions reflect changes to catchment erosion [e.g., Gale and Hoare, 1991]), can offer a complimentary image of paleolimnology at a site (e.g., Birks and Wright, 2000). This holistic approach is termed the multi-proxy approach and has been adopted in this study of the Pupuke composite sediment series (Birks and Birks, 2006).

In this chapter, those techniques capable of eliciting a clear ecologic and environmental response to climatic variability from the bulk sediment, that is the combined sedimentary organic or inorganic component, are discerned and applied to the continuous composite sequence (from ~48 cal. kyr BP to today). Each is assessed from the critical perspective of changing source and preservation. The robust nature of these physical and geochemical proxies confers greater reliability in the inferred direction of change whilst the MER age-depth model affords the necessary accuracy essential to reliably assign timing, duration and rate of identified changes. Coupled to the great number of analyses undertaken (from 1 to 15 cm intervals) this ensures we can meet our initial aim outlined in Chapter 1, that is the production of a highly-resolute, continuous climate event stratigraphy (CES) for Lake Pupuke. However, deciphering seasonal variability in certain environmental proxies from longer-term paleoenvironmental trends requires an understanding of their modern-day systematics. We have therefore
undertaken a seasonal monitoring study of contemporary total organic Carbon (TOC), total Nitrogen (TN), total Sulphur (TS) and Carbon stable isotopes ($\delta^{13}$C) amongst sedimenting matter within Lake Pupuke (2008-2009). Accordingly we begin this chapter by examining the seasonal variability present in proxies for productivity, before examining the physical and geochemical proxy indicators throughout the composite sequence.

4.2 The Modern Geochemical Framework of Lake Pupuke (TOC, TN, TS and $\delta^{13}$C)

Information on the total organic Carbon (TOC), total Nitrogen (TN), total Sulphur (TS) and stable Carbon isotope ($\delta^{13}$C) cycles is a valuable corollary to ecological surveys in identifying the seasonal cycle of productivity within Lake Pupuke (see Chapter 2). Furthermore, there is a paucity of limnologic information on the Sulphur cycle of freshwater lacustrine systems (Holmer and Storholm, 2001). Thus, information on seasonal TS variations can better determine whether paleolimnological changes exceed modern variability and demonstrate whether TS abundance is linked to productivity. For the purpose of examining change in contemporary productivity only seasonal drivers of variation in TOC, TN and TS are discussed below (refer to 4.4.3.1. Bulk TOC, TN and TS Analyses for detailed discussion of longer-term causes).

Sedimentary lacustrine matter (inorganic and organic) is characterised by changing concentrations of elemental Carbon, Nitrogen and Sulphur directly in line with changing productivity whereby increases in productivity result in greater concentrations of TOC, TN and TS (Talbot, 2001; Russell and Werne, 2009). Thus from inspection of sediment trap TOC, TN and TS sample concentrations the seasonal pattern of peaks and troughs in productivity can be discerned. Likewise, the fact that Lake Pupuke undergoes thermal stratification for much of the year (September to June [Holmes, 1994]) effectively isolates hypolimnetic sources of Carbon from primary producers in the epilimnion. As rates of Carbon diffusion are slower than physical mixing within lakes, the uptake of dissolved inorganic Carbon (DIC) by primary producers through photosynthesis results in depletion of the DIC pool within a stratified epilimnion (Meyers and Teranes, 2001). A characteristic pattern of $\delta^{13}$C enrichment can therefore indicate seasonal changes to DIC-availability and productivity (Meyers and Teranes, 2001). Thus by inspection of TOC, TN, TS and $\delta^{13}$C variation amongst seasonally sampled sedimentary matter it is possible to investigate the present seasonal pattern of stratification and productivity within Lake Pupuke, whilst simultaneously identifying a value for intra-annual variation by which to confine our longer-term estimates of change.

The Total Organic Carbon (TOC) and Total Nitrogen (TN) content of sedimentary matter can also be used to identify source (e.g., autochthonous lake organic matter [algae, submerged, floating or emergent macrophyte tissue] can be discriminated from allochthonous terrestrial input [organic and inorganic]). C/N ratios can be calculated for mass or atomic weights (e.g., Meyers and Teranes, 2001). As per the recommendation of Meyers and Teranes (2001) we have employed C/N atomic ratios in all subsequent discussions and analyses to better reflect biochemical stoichiometry. C/N values will be lowest amongst phytoplankton (between 4 and 10), due to their lower relative abundance of carbohydrate relative to protein (e.g., cellulose, lignin and xylan) (Meyers and
Lallier-Vergès, 1999). Vascular land plants possess C/N ratios of 20 and higher due to the greater presence of structural polysaccharides (Meyers and Lallier-Vergès, 1999). Aquatic macrophytes produce organic tissue of a C/N ratio between phytoplankton and terrestrial macrophytes (between 10 and 20) (Meyers and Lallier-Vergès, 1999). There are however, notable exceptions including the phytoplankton *Botryococcus braunii* which has been recorded within sediments of Lake Pupuke and whose C/N ratio of 36 is more typical of terrestrial flora (Street-Perrott et al., 1997). Nonetheless, unless present in massive quantities the characteristic trends of each class of primary producer will be retained by sedimentary organic matter (OM). Information on OM-provenance can thus be compared by season to identify present seasonal changes in the supply of OM to sediments within Lake Pupuke.

4.2.1 Modern Sampling Methods and Analyses

4.2.1.1 Sediment Sampling

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]).
Two sediment traps were constructed at the School of Engineering, University of Auckland and placed at a depth of 40 m in Lake Pupuke to ensure sufficient depth beneath oxycline and wave base over the majority of the annual cycle (Figure 4.1). Each was fitted with a ca. 20 cm funnel to increase collection aperture size. However, owing to the loss of the latter during immersion, calculation of present-day sedimentation rate would be inaccurate and thus collected sediment weights must not be used in estimates of the latter. Refer to 3.5.6. Mass Accumulation Rate for more information on modern rates of mass accumulation.

Sufficient material was collected during the periods March to June (2008), June to October (2008), October to February (2009) and February to July (2009) to enable analysis of total organic Carbon (TOC), total Nitrogen (TN), total Sulphur (TS), and bulk sedimentary δ13C at the School of Environment, University of Auckland (TOC, TN, TS) and University of Waikato Stable Isotope Laboratory (δ13C).

4.2.1.2 Total Organic Carbon (TOC), Total Nitrogen (TN) and Total Sulphur (TS) Analyses

Sediment trap and core TOC, TN and TS analyses were determined with a direct-determination procedure. Collected sediment samples were first acidified with 2N HCl (10 ml per 1 dry wt. g.) overnight, followed by Vortex mixing and x3 rinses with deionised H2O (x4000 rpm 5 min) – supernatant being discarded. Sediment was dried under vacuum and homogenised in an agate pestle and mortar. TOC and TN analyses were performed by dry combustion simultaneously on 0.1 dry wt. g. mixed sediment using a LECO TruSpec C and N determinator (LECO Corporation, St. Joseph, MI, USA). Combustion was achieved at 900 ºC and 850 ºC for furnace and afterburner respectively within an Oxygen-rich atmosphere. TS analyses were performed by dry combustion on a further 0.1 dry wt. g. sediment using a LECO TruSpec Add-on S analyser (Leco Corporation, St. Joseph, MI, USA) interfaced with the TruSpec C and N determinator. Samples were combusted in an Oxygen-rich atmosphere at 1350 ºC.

The limit of determination (6σ) for elemental Carbon is ± 0.0031%, Nitrogen is ± 0.2528% and Sulphur is ± 0.0192%. Sample analyses failing to exceed their respective detectable limit have been excluded. TOC/TN mass ratios were computed in Excel from elemental weight percentages of sediment samples. C/N mass ratios were multiplied by 1.167 (the ratio of atomic weights of Nitrogen and Carbon) to yield C/N atomic or Redfield ratios (e.g., Meyers and Teranes, 2001).

Both TruSpec and Add-on module were calibrated to laboratory standards (EDTA [40.99% C; 9.57% N] and coal [1.14% S]) and all subsequent analyses were corrected for analytical drift (1 in 20 samples). Temporal drift was found to be -0.01% in C and N and − 0.0002% in S (30/08/2008 – 19/10/2008 and 3/11/2008 – 23/12/2008 respectively). A linear unfixed calibrated model was chosen for all elements to account for any low-level background noise.
4.2.1.3 Bulk Stable Carbon Isotope Analyses

Bulk sediment trap OM δ\textsuperscript{13}C analyses were conducted at the University of Waikato, New Zealand (Waikato Stable Isotope Unit). Sample preparation methods are standard involving acidification by 1 N HCl followed by centrifugation (x2500 rpm 5 min) and rinsing with deionised H\textsubscript{2}O three times before oven-drying (~105 °C) (e.g., Boutton, 1991; Talbot, 2001). Dried OM was homogenised and ~0.01 g was combusted at 800 °C to ensure complete oxidation and analysis using an online Elemental Analyser (EA) coupled to a Continuous Flow-Isotope Ratio Mass Spectrometer (CF-IRMS) (Europa Scientific 20-20 Stable Isotope Analyser). Values are reported as per mille (‰) variation from a standard ratio format (Pee Dee Belemnite):

$$\delta \text{ (‰)} = ((R_{\text{sample}} / R_{\text{std}}) - 1) \times 10^3$$

where R is the isotope ratio and is equal to \textsuperscript{13}C/\textsuperscript{12}C, referring to the sample or standard. Analytical uncertainty for the Waikato Laboratory's measurement of δ\textsuperscript{13}C is ± 0.5 ‰. All δ\textsuperscript{13}C ratios are referenced to a precalibrated C4 sucrose standard that is cross-referenced to PDB.

4.2.2 Modern Sediment Results

4.2.2.1 Correction for Inorganic Nitrogen

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).

$$y = 0.0905x + 0.425$$

$$R^2 = 0.9532$$
The presence of inorganic Nitrogen can alter the results of provenance (e.g., C/N atomic ratio) and productivity (e.g., TN) indicators which assume all Carbon and Nitrogen is organic in origin. Talbot (2001) describes a relatively simple procedure to remove inorganic Nitrogen fractions by regressing TOC onto TN, generate an intercept value (c) of the form \( y = m \times x + c \), and if positive, subtracting this value from all estimates of TN. Figure 4.2 presents TOC by TN for sediment trap collected samples \( (TN = 0.0905 \times TOC + 0.425) \). Accordingly a correction of 0.425 wt.% was subtracted from TN estimates to yield total organic Nitrogen (TON) and C/N atomic ratios calculated from corrected TON.

### 4.2.2.2 TOC, TN and TS

Sediment has been collected over the interval 15th March 2008 and 22nd July 2009 representing a complete annual cycle of sedimentation. Seasonal estimates of TOC, corrected TN and TS are presented in Figure 4.3 and Table 4.1. Corrected TOC/TN atomic ratios are also shown. A variable seasonal profile is apparent in TOC, TN and to a lesser extent TS. The relative proportion of organic Carbon and Nitrogen peaks between the months of June and October (Winter/Spring; 27.80 wt.% and 2.49 wt.% respectively) and troughs between the months of October and February (Spring/Summer; 14.70 wt.% and 1.29 wt.% respectively). TS varies much less markedly from 1.07 wt.% to 1.28 wt.% and also observes a similar seasonal profile to TOC or TN in that high sedimentary TS occurs during Winter/Spring. However, a trough in TS occurs from February to July (Autumn/Winter), falling by 0.21 wt.% on a Spring maximum. Corrected TOC/TN ratios also display very limited intra-annual variation \( (\mu = 14.81 \pm 0.80 \ [1\sigma]) \) and reveal little change to seasonal OM provenance in Lake Pupuke.

### 4.2.2.1 Bulk OM δ\(^{13}\)C

Seasonal profiles in sedimentary TOC δ\(^{13}\)C are presented in Figure 4.3 and Table 4.1. Marked seasonal variation occurs in δ\(^{13}\)C including a shift of -2 ‰ over the annual cycle of productivity \( (\mu \pm 1\sigma = -23.17 \pm 1.87 \%) \). Relatively enriched values are attached to TOC collected between October and February (Summer; -20.54 ‰) preceded by depleted values during the interval June to October (Spring; -24.91 ‰). Autumn/Winter δ\(^{13}\)C values resemble those recorded for Spring (-24.91 ‰ and -23.62 ‰ respectively).

<table>
<thead>
<tr>
<th>Deployment</th>
<th>Collection</th>
<th>TOC (wt. %)</th>
<th>TN (wt. %)</th>
<th>C/N (corrected)</th>
<th>TS (wt. %)</th>
<th>δ(^{13})C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/03/2008</td>
<td>19/06/2008</td>
<td>18.25</td>
<td>2.04</td>
<td>10.43 (11.28)</td>
<td>1.15</td>
<td>-23.40</td>
</tr>
<tr>
<td>20/06/2008</td>
<td>08/10/2008</td>
<td>27.80</td>
<td>2.92</td>
<td>11.11 (11.15)</td>
<td>1.28</td>
<td>-24.91</td>
</tr>
<tr>
<td>09/10/2008</td>
<td>21/02/2009</td>
<td>14.70</td>
<td>1.71</td>
<td>10.02 (11.43)</td>
<td>1.23</td>
<td>-20.54</td>
</tr>
<tr>
<td>22/02/2009</td>
<td>22/07/2009</td>
<td>18.60</td>
<td>2.20</td>
<td>9.85 (10.45)</td>
<td>0.99</td>
<td>-23.83</td>
</tr>
</tbody>
</table>
Figure 4.3: Seasonal variation in TOC, TN, TS and δ¹³C 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.
4.2.3 Implications for Sedimentary Proxy Indicators

As noted earlier, sedimentary OM is comprised of both within column (autochthonous) and catchment produced (allochthonous) constituents (Wetzel, 2001). Peaks and troughs in prolonged productivity can be inferred from the relative abundance of organic Carbon and Nitrogen (Meyers and Teranes, 2001). Likewise, increased weathering and erosion increase flux of allochthonous inorganic matter to lacustrine settling matter. This dilution of bulk OM will reduce TOC and TN values as the relative proportion of inorganic matter rises (in the absence of inorganic carbonates). Interpretation of seasonal profiles in TOC/TN atomic ratios and the corresponding TOC, TN and TS cycles can thereby highlight the periods of greatest sedimentary OM contribution. These then will best correlate with the paleo-record and enable a narrower window of seasonality to be recorded by bulk sedimentary stable isotope proxies for productivity.

The TOC, TN and TS patterns evident in Lake Pupuke between 2008 and 2009 are typical of a mesotrophic, monomictic freshwater lake in which spring highs in productivity result in greater TOC and TN content of sedimenting matter (Wetzel, 2001). Summer lows reflect both the position of the sediment trap beneath a strong thermocline (40 m depth) that would restrict sedimentation, and lesser productivity due to consumption of essential nutrients in the epilimnion (Wetzel, 2001). The seasonal pattern of TS also appears dependent upon OM production and sedimentation with peaks in spring (June to October) coincident with enhanced productivity following overturn (nutrient resupply to the water column from benthic water) and amelioration of local climate. Thereafter, summer TS values (1.23 wt.%) do not follow a reduced pattern evident in TOC and TN. This records a complex response to stratification-induced hypolimnetic hypoxia. Sulphate reducing bacteria (SRB) are capable of reducing dissolved sulphate, often generating iron monosulphides and/or iron pyrite in the process. SRB are incapable of fixing sulphate in even modest levels of oxygenation (Holmer and Stockholm, 2001). Hence, the seasonal drop in TS during Autumn/Winter likely reflects the breakdown of stratification, overturn and oxygenation of deeper waters preventing the formation of iron pyrite. As Lake Pupuke is surrounded by an iron-rich tuff crater ring and exhibits a fairly evenly distributed annual precipitation pattern, SRB are likely not limited by availability of dissolved iron but rather by the degree of hypoxia. Thus, whilst sediment trap data suggest a seasonal profile to TOC, TN and TS with peaks in all three elemental indicators coincident with Spring, there is evidence for a breakdown in coherence between TOC and TS cycles during overturn.

Distinct seasonal changes are also displayed in bulk OM δ^{13}C. Greatest enrichment occurs throughout summer months during the period of strongest thermal stratification and a drop in the OM content of sedimenting matter, recording resource limitation and greater competition for depleted Carbon amongst the epilimnion. Likewise, methanogenic bacteria present within the hypolimnion will likely generate lighter isotopic carbon in methane leaving the remnant OM with an enriched signature. Depleted δ^{13}C values throughout Autumn to Spring likely reflect greater available DIC (e.g., via weaker stratification), reduced competition for inorganic carbon and lesser rates of methanogenesis (e.g., less enriched DIC pool).
Whilst sedimenting OM expresses seasonality in TOC, TN, TS and $\delta^{13}$C, it is worth noting that such variation offers a window in which to bracket long-term proxy variability, assuming the same boundary conditions operate today as they did over the paleolimnologic record. Paleolimnologic TOC, TN, TS and $\delta^{13}$C analyses have therefore been referenced to total seasonal changes of 9.38 wt.%, 0.80 wt.%, 0.21 wt.% and -1.29 ‰. Changes in these proxies must exceed the latter to reliably exclude changing seasonal patterns of productivity influencing long-term changes to biological productivity.

An average C/N value of ~15 in contemporary sediment indicates a mixed algal/aquatic macrophyte source of OM, representative of recent ecological change (e.g., luxuriant growths of *V.gigantea* and *E.densa* and abundant microflora). Relatively high average TOC and TN values (19.84 wt.% and 1.79 wt.%), coupled to an algal provenance, confirm Lake Pupuke’s meso/eutrophic status. Limited variability therein (C/N $1\sigma$ = 0.80) also demonstrates limited seasonal changes in basin vegetation (i.e., proportion terrestrial vs. aquatic).

### 4.3 Paleolimnologic Methods

The following section refers to the paleolimnological methods applied to the Lake Pupuke sediment cores. These have been obtained from sediment core material within the earlier defined composite sequence (see Chapter 3). Depths for sample analyses are recorded in Appendix A.

#### 4.3.1 Magnetic Susceptibility

As noted in 3.3.1.1. *Magnetic Susceptibility*, sediments can be described by their magnetic susceptibility (MS). Low field MS ($\kappa_{LF}$) has been analysed at 1 cm intervals (~35 yr) using a *Bartington Instruments MS2E* point-wise MS sensor. Stratigraphic changes in geochemistry and grain-size alter MS, alongside changes to weathering rate and influx of iron-bearing minerals (i.e., derived from tuff crater walls). MS can also be used to interpret benthic pore-water pH (i.e., dissolution of ferromagnetic minerals under alkaline or reducing conditions will reduce susceptibility [e.g., Nowaczyk et al., 2007]).

#### 4.3.2 Grain Size Analyses

Grain size analyses were conducted on composite sequence sediment samples to define changes in the lake and catchment environment and offer comparison to other proxies for paleoenvironment and erosion (i.e., composite sediment accumulation rate, ITRAX elemental geochemistry). Grain size distributions can offer an insight into changing wave energy regime, weathering and erosion rate, and source of inorganic material to lacustrine sediment (Beierle et al., 2002).

Sample preparation of involved oxidation of dry sediment samples (~1.0 g dry wt.) with 27% (v/v) H$_2$O$_2$ in 50 ml plastic sterile centrifuge tubes immersed in a water bath at 50 °C. Inorganic carbonate was removed by reaction
with 5 ml of 32% (v/v) HCL overnight. Reagents were removed by dilution with ultra pure water (UPW) and repeated centrifugation (x4000 rpm, 5 min). Digested samples did not require sieving to exclude macroscopic (>1 mm) minerogenic components. No attempt was made to remove biogenic silica owing to the presence of erosional/volcanic silicates within the basin (e.g., removal of biogenic silica in a NaOH alkaline solution would necessitate the removal of weathered inorganic silicates). Diluted grain size samples were treated with 10% (v/v) Calgon (Sodium hexametaphosphate) to dissociate clays bound by electrostatic forces (e.g., Van Der Waals forces) and prevent flocculation during measurement of particle size distribution.

Analysis was performed with a Malvern Mastersizer 2000 automated laser particle size detector in combination with a Malvern Hydro-G accessory sonification unit. Samples can be analysed for particle sizes between 0.02 and 2000 μm with a precision of ± 1.0 %. A laser-target obscuration (sample concentration) of 10-20% was achieved in all analyses. Values of particle refractive index and absorption were set for glass (density of 2.615 g cm\(^{-3}\)) as for other AVF studies (Augustinus, pers. comm., 2009). Each sample was measured 5 times over a 10s cycle to determine an averaged distribution of grain size. Sediment samples were analysed at 5-10 cm composite depth intervals throughout the composite sequence offering a corresponding temporal resolution of ~16-560 yrs.

4.3.3 Elemental Analyses

Paleolimnology has a long history of interpreting organic and inorganic elemental concentrations (e.g., Mackereth, 1969). Given its biological origin, organic matter is often of greatest use to past reconstructions (Meyers and Teranes, 2001). Nevertheless, inorganic elemental and isotopic ratios offer proxies of environmental processes including erosion and REDOX state. Together these can reveal changes to ecosystem structure and function mediated through environmental change (Meyers, 1997).

4.3.3.1 Bulk TOC, TN and TS Analyses

Lake sediments are a complex of catchment and within-lake productivity, preserving organic compounds synthesised by higher and lower plants (terrestrial, emergent and aquatic micro- and macro-flora, and bacteria) (Meyers and Ishiwatari, 1993). Allochthonous detritus will be sourced from fibrous tissues such as grasses, shrubs and trees, whereas autochthonous organic matter (OM) is very often dominated by single-celled phytoplankton (Meyers, 1994; Meyers and Teranes, 2001). Autochthonous OM can also be produced by aquatic macrophytes although the latter require suitable lake sediments to colonise, which are limited by water clarity, nutrient availability and oxygenation (Wetzel, 2001). The contribution of allochthonous and autochthonous producers to a sedimentary matrix will vary as lake, catchment and climatic conditions change (Meyers and Horie, 1993). These changes are recorded by the elemental and structural properties of detrital OM although significant within-column and early diagenetic changes can alter the sedimentary record (Meyers and Eadie, 1993; Meyers et al.,1984a,b; Bernasconi et al., 1997). However, a number of bulk OM parameters suffer from
very little alteration following sedimentation. Most notably, the concentration of TOC is an increasingly fundamental parameter with which to reconstruct past lacustrine environments (Meyers and Terane, 2001). TOC is contributed by all living organisms within the lake and catchment such that increased TOC concentration records greater productivity (e.g., improved paleoclimate) (Meyers and Teranes, 2001). Importantly, settling and early diagenesis alter the amounts and composition of TOC present in lake sediments, particularly in oxic sediments (Hodell and Schelske, 1998). TOC concentration can also be diluted or enriched by a number of factors extraneous to bioproduction (Meyers and Teranes, 2001). The influx of clastic material such as clays and volcanic glass can reduce TOC whether or not any change to productivity has occurred. It is therefore essential to convert TOC concentrations or percentages to an elemental mass accumulation rate (MAR) to take account of changes in sedimentation rate. MAR’s are expressed relative to unit area lake bottom and unit time (g cm⁻² yr⁻¹) meaning a reliable age-model is essential for their determination (Meyers and Teranes, 2001). The construction of a suitably resolute and robust age-depth model and MARs for the last ~45 cal. kyr BP have already been examined in Section 3.5. Chronology.

Many freshwater bodies receive limited nutrient supply from the terrestrial environment, since terrestrial systems are highly efficient at trapping essential macro- and micronutrients, and dissolved nutrients are lost by burial of detrital OM. Lakes are thus highly sensitive to levels of limiting and key dissolved nutrients including nitrogen and phosphorus (Meyers, 1994). Nitrogen has a fundamental role to play in OM cycling, so that in addition to offering an indicator of competition and productivity, TN and TOC provide diagnostic information on the composition and trophic state of freshwater lakes (Talbot, 2001). Within aquatic systems, the major sources of the dissolved inorganic Nitrogen (DIN) pool to primary producers are ammonia (primarily as NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂⁻) (Figure 4.4) (Talbot, 2001). Dissolved ammonium and nitrate are the principal pathways for nitrogen to be obtained in photosynthesis whilst nitrogen fixation represents the main mechanism by which N₂ is assimilated into biota, particularly by blue-green algae (cyanobacteria) whose source of atmospheric N₂ can generate marked variations in sedimentary OM δ¹⁵N (see below). Bacterial reduction of organic NOₓ to NH₃ and NH₄⁺ (ammonification) is a fundamental process of OM decomposition dependent upon sediment anoxia and that can also alter sedimentary OM δ¹⁵N ratios (Wetzel, 2001). The inverse process (nitrification) occurs under aerobic conditions (Wetzel, 2001). Finally, denitrification is another process by which bacteria can reduce NO₃⁻ to gaseous N₂. Denitrification occurs in anoxic and dysoxic conditions, particularly strongly stratifying lakes whose oxycline lies within the water column (Talbot, 2001). Denitrification is a significant efflux of N from OM leading to lower sedimentary TN in meso/eutrophic lacustrine systems (Talbot, 2001).
Figure 4.4: Sources of dissolved Nitrogen and stable isotopic signatures within lacustrine systems (Modified from: Talbot, 2001).

Total Sulphur (TS) can also enable reconstruction of changes in lake productivity, nutrient cycles and hydrochemistry (Håkanson and Jansson, 1983; Berner, 1970; Rudd et al., 1986). Natural Sulphur concentrations within terrestrial OM are low in line with atmospheric concentrations, resulting from limited weathering of sulphur-containing catchment rock (Brimblecombe et al., 1989). However, lakes accumulate greater concentrations of TS from terrestrial diffusion and via OM cycling (Holmer and Storkholm, 2001). Very little is known of the lacustrine S-cycle although increasing amounts of sedimentary OM tend to result in greater sedimentary TS (Holmer and Storkholm, 2001). Nevertheless as the concentration of TS within lake sediments is often very low, diagenetic processes affecting S-cycling are particularly important. Hence, S-cycling is very heterogenous in space and time with shifts in OM-availability, trophic status, pH, oxygenation and temperature favouring greater and lesser amounts of sulphate reducing bacteria (SRB) (Holmer and Storkholm, 2001). Whilst it is still unclear which form of Sulphur contributes greatest to sedimentary TS, Holmer and Storkholm (2001) suggest that the largest control on sedimentary TS appears to be the amount and degree of sulphate reduction. Anaerobic decomposition of OM is a complex series of steps between physiologically different organisms, beginning with fermenting bacteria whose by-products fuel SRB and methane producing bacteria (MPB) before reaching acteogenic bacteria that can cleave humic acids and alcohols into H₂ and CO₂ that are utilised by SRB and MPB again (Holmer and Storkholm, 2001). Under conditions of anoxia or hypoxia, SRB will actively reduce dissolved sulphate and sulphate containing OM to H₂S which in turn will readily bind with iron to form insoluble pyrite, thereby favouring greater preservation in the sediment record (Figure 4.5) (Holmer and Storkholm, 2001).
Reoxidation of sulphate is another significant pathway for TS under anoxic and oxic conditions. Benthic fauna, macrophytes and sulphide oxidizing bacteria (SOB) are important agents of reoxidation (Wetzel, 2001). However, deep eutrophic basins like Lake Pupuke favour lower loss of sedimentary TS to reoxidation because of limited benthic oxygenation (e.g., during overturn in July and August). Periods of higher productivity will supply greater TS via OM, result in higher concentrations of sulphate and generate hypoxia or anoxia via OM decay (and thermal stratification) that favour the preservation of TS as iron pyrite (FeS$_2$). Whilst TS concentration thereby offers a proxy for productivity in the composite sequence, it must be interpreted with care to exclude changes to benthic REDOX state.

As noted in section 4.3. The Modern Geochemical Framework of Lake Pupuke, C/N ratios enable past changes to lacustrine community structure and OM pathway to be modelled (Meyers and Lallier-Vergès, 1999). However, several limitations apply to its interpretation. Allochthonous OM suffers from the selective degradation of carbon-rich sugars and lipids during early diagenesis causing lower observed C/N ratios (Meyers et al., 1995). In contrast, autochthonous algal OM suffers the selective degradation of nitrogen-rich proteins leading to higher C/N ratios within the water column. Several studies have demonstrated this pre-taphonomic effect (Müller, 1977;
Meyers, 1997; Meyers and Takemura, 1997). Meyers and Takemura (1997) report a gradual decline in C/N ratios attributed to oxidation and reduction of TOC to CO$_2$ and CH$_4$ that escape whilst TN is reduced to NH$_4^+$ that binds to clay minerals and remains in situ. Meyers and Ishiwatari (1993) stress that decay associated changes in C/N ratios are typically minor and largely halted by burial. Thus an interpretation of C/N ratios can be highly informative about catchment and lake contributions to sedimentary OM (e.g., Lehmann et al., 2002).

### 4.3.3.2 Analytical Methods

TOC, TN and TS were determined as percentage estimates with a direct-determination procedure applied to 1 cm sample intervals (~2-3 dry wt. g) as for sediment trap material (Section 4.3.2.1 Total Organic Carbon, Total Nitrogen and Total Sulphur Analyses). The TruSpec C, N and S elemental analysers have been calibrated to laboratory standards (EDTA [40.99% C; 9.57% N] and coal [1.14% S]) to ensure accuracy. All samples were corrected for analytical drift (1 in 20 samples) to ensure sample precision (-0.01% in C and N, and -0.0002% in S). The limit of determination (6 SD) for elemental Carbon is ± 0.0031%, Nitrogen is ± 0.2528% and Sulphur is ± 0.0192%. Those analyses failing to exceed their respective detectable limit have been excluded.

#### 4.3.3.2.1 Flux Calculation (CAR, NAR and SAR)

To account for the effects of variable minerogenic and/or biogenic flux, all percentage estimates of TOC, TN and TS were converted to element fluxes (e.g., flux TOC g cm$^{-2}$ yr$^{-1}$). Fluxes were calculated as follows (as per Grant and Dickens, 2002):

$$\text{Flux TOC} = \frac{\%\text{TOC}}{100} \times \text{MAR}$$

where %TOC is the relative element abundance (%) and MAR is the mass accumulation rate (g cm$^{-2}$ yr$^{-1}$) obtained from the age model described in 3.6.4. Mass Accumulation Rate.

#### 4.3.3.3 Bulk XRF (ITRAX) Analyses

Micro-XRF techniques are a novel proxy for reconstructing paleoenvironment through changes to inorganic geochemistry (Thomson et al., 2006). Whilst traditional XRF geochemical methods are time consuming and invariably destroy the sediment sample, micro-XRF provides a rapid non-destructive means of characterising down core geochemical properties (Rothwell et al., 2006). However, the approach suffers from the reduced sensitivity and semi-quantitative nature of collected data. Nonetheless the continual stratigraphy developed from intact sediment cores enables equipment including the ITRAX Energy Dispersive (EDS) micro-X-ray Fluorescence (XRF) core scanner to provide detailed information on a suite of sedimentary characteristics (e.g., textural bedding, distinctive marker bed geochemistry, bioturbation activity) (Croudace et al., 2006).
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).

<table>
<thead>
<tr>
<th>Property, element</th>
<th>Sensitivity to ITRAX detection</th>
<th>Indicator properties</th>
</tr>
</thead>
</table>
| Compton scattering | High | • Relates inversely to mean atomic number, commonly decreases in silt and sand layers due to size/density-related mineral fractionation  
• May show grading due to mineralogical variation  
• Inflections in profile commonly correlate with bed boundaries  
• Mean atomic number falls with looser sediment packing, so winnowing of sediment may be seen as decreased Compton scattering |
| Ca/Fe | High | • Indicative of biogenic carbonate:detrital clay ratio  
• May show strong correlation with sedimentary units  
• Turbidites sourced from shallow water tend to be richer in Fe and poorer in Ca than pelagic interbeds  
• Ca/Fe profile is a good proxy for sediment grading, for identifying textural subdivisions within turbidites and for assessing source distality–proximity relationships  
• Ca/Fe profile within pelagites typically more variable than in turbidites, reflecting more heterogeneous sediment fabric  
• Ca peaks or their absence (commonly associated with increased Si) within turbidite bases distinguish foraminifer- or shell-rich and more terrigenous quartz-rich bases |
| Sr/Ca | High | • Enhanced Sr may indicate presence of high-Sr aragonite which requires a shallow-water source  
• Affected by sediment packing/porosity and grain-size/shape variations |
| Fe, Mn, Ti | High | • Delivered from catchment/terrestrial soils enabling their use as indicators of erosion and sediment delivery  
• Interpretation complicated by REDOX effects which can enhance the dissolution or precipitation of ferric compounds under reducing and oxidizing conditions respectively (Mn and Ti less susceptible to REDOX diagenesis) |
| Fe/Rb | Good | • Commonly shows grain-size related fractionation effects within turbidites  
• Fe mobilized during redox-related diagenesis and elevated Fe commonly seen in oxic, or formerly oxic, parts of turbidites  
• Rb is an element commonly associated with detrital clay and may be enhanced in turbidite muds |
| Mn/Fe | Moderate | • Fe is more sensitive to changing REDOX compared to Mn  
• If Fe and Mn are supplied in constant proportion as would occur in a limited catchment (e.g., limited catchment lithology, changes to proportions over time), than changes in Mn/Fe record benthic REDOX change  
• Greater and lower ratios are indicative of more reducing and oxidizing conditions respectively |
| K/Rb | Moderate | • K is commonly associated with detrital clay and may be enhanced in turbidite muds  
• Unreliable parameter as sea-water Cl absorbs potassium X-rays, so apparent high K may reflect increased porosity |
| Zr/Rb | Moderate | • Zr and Ti high in heavy resistate minerals and may be enhanced in turbidite bases  
• Sediment source/provenance indicators |
| Ti/Rb | Moderate | • Behaviour of Cu poorly understood but Cu peaks largely of diagenetic origin |
| Cu/Rb | Moderate | • Commonly an indicator of pyrite which may be detrital or authigenic in origin |
| Br/Cl | Moderate | • Indicator of organic-rich layers as Br high in organic-rich sediments. For marine sediments a constant ratio implies sea-water ratio |
| Si | Moderate | • Important terrigenous or productivity indicator  
• Normalization using detrital divisor can distinguish terrigenous or productivity origin  
• When terrigenous, useful as a sediment source and perhaps provenance indicator |
Application of continuous XRF core scanning has until recently been applied solely to marine oceanographic studies of sediment cores (e.g., Haug et al., 2001; Jahn et al., 2003; Rothwell et al., 2006). However several recent studies have applied the automated multi-function core scanners to lacustrine sediments revealing the potential to investigate changes to productivity, erosion and REDOX potential (Kristin et al., 2007; Moreno et al., 2007; Unkel et al., 2008; Jackel, 2009). Table 4.2 presents a detailed summary of key element indicators provided by recent reviews of ITRAX applications in Rothwell et al. (2006) and Shanahan et al. (2008).

Pupuke composite core sections were run through the University of Aberystwyth ITRAX micro-XRF core scanner by Dr. S. Davies along their split longitudinal axes in 2007 and 2008. A continuous high-resolution (200 μm step size) optical and XRF profile for each core section was generated over each composite core interval. A 3 kW Mo target was focussed through a flat-glass capillary waveguide over a 30 s step count time. Elements were deconvoluted from XRF spectra through the range of Al to Ba. Data have been filtered for erroneous results (e.g., core fractures, tephra inclusions, equipment failure) by comparison to the incoherent peak number and validity value (e.g., 1 = valid, 2 = invalid [distance to core]). Data with an invalid score were excluded except where their total counts per second (cps) were in excess of 10000 (their invalid scores were a function of a software update at the University of Aberystwyth [Davies, pers. comm., 2009]).

24 elemental XRF spectra were collected over the ~1420 cm composite sequence. An arbitrary decision to present only those counts and peak areas obtained on or nearest a cm interval of the composite sediment core series was made because averaged trends over 200 μm intervals resulted in excessive data for graphical analysis in Excel. Thus XRF spectra are presented at 1 cm resolution for the 1420 cm composite sequence.

### 4.3.4 Bulk Stable Isotopic Analyses

Stable isotopes are atomic forms of an element with variable neutron but identical electron or proton number to their elemental standard. Although OM can constitute a minor component of lake sediment, changes in the isotopic composition of OM provide a sensitive record of changes to lacustrine paleohydrology. In particular the ratios of lighter to heavier isotopic forms of Carbon and Nitrogen (δ¹³C and δ¹⁵N respectively) offer a wealth of information on photosynthetic pathway, atmospheric composition and diagenesis which can offer valuable insight to paleoenvironment (Meyers and Lallier-Vergès, 1999).

#### 4.3.4.1 Bulk δ¹³C

Carbon exists as one of two naturally occurring stable isotopes, ¹²C (98.89%) and ¹³C (1.11%) (Meyers and Teranes, 2001). The Carbon isotope (δ¹³C [¹³C/¹²C]) signature of bulk OM can vary through a change to several factors, notably: (1) catchment vegetation; (2) aquatic productivity; (3) and paleo-atmospheric pCO₂ (including effects amongst each attributable to sediment diagenesis). Changes to the above are discussed below to frame
the subsequent discussion of the sedimentary OM δ¹³C results. Whilst diagenetic change can alter TOC estimates, there is little evidence to date of changes induced in sedimentary OM δ¹³C values (Meyers and Eadie, 1993; Hodell and Schelske, 1998). The presence of a deep lake throughout the composite sequence will also have reduced the action of detritivores by restricting sediment oxygenation.

Primary producers can incorporate atmospheric or dissolved Carbon via the C3 Calvin, C4 Hatch-Slack and CAM (Crassulacean Acid Metabolism) pathways (Meyers and Lallier-Vergès, 1999). Each has an associated isotopic discrimination or fractionation that averages -20‰, -4 to -6‰ and -4 to -20‰ respectively (¹³C/¹²C) (Meyer and Teranes, 2001; Wolfe et al., 2001). Consequently OM derived from each pathway can be discriminated from each other, with terrestrial C3 OM produced from atmospheric CO₂ (δ¹³C = -7‰) providing an average δ¹³C of ~28‰ (O’Leary, 1981, 1988). Consequently ¹³C/¹²C ratios have been widely used to reconstruct shifts in primary producing class (Hollander et al., 1992; Hodell and Schelske, 1998; Brenner et al., 1999). However, this ability to distinguish OM by photosynthetic pathways cannot be applied to different primary producers within each pathway. For instance C3 phytoplankton fixes dissolved CO₂ in isotopic equilibrium with the atmosphere making it indistinguishable by δ¹³C from terrestrial C3 flora. Only if algae suffer from competition (e.g., limited dissolved CO₂) and/or changes to pH (e.g., favouring uptake of HCO₃⁻ [δ¹³C = +1‰]), will their signatures vary markedly from terrestrial C3 producers (Meyers and Lallier-Vergès, 1999).

With the exception of two halophytic plants (Atriplex buchananii and Theleophyton billardierei), the majority of native flora within New Zealand are C3 (Carter, 2007). The lack of many C4 plants and their restriction to coastal locales ensures that little or no change has occurred to the proportion of C3 vegetation within or around Lake Pupuke throughout the composite sequence. Without the complicating factor of shifting photosynthetic pathway, changes to δ¹³C within OM can thus more easily be used to infer changes to aquatic productivity. For instance, increased productivity amongst phytoplankton will result in greater uptake of dissolved inorganic ¹²C, which following senescence and settling will be removed from the total dissolved pool, thereby leading to greater incorporation of ¹³C and enrichment of OM δ¹³C (Meyers and Lallier-Vergès, 1999). Increases and decreases in OM δ¹³C values can thereby record past increases and decreases in demand for dissolved inorganic Carbon (DIC).

An idealised stable Carbon isotope cycle is demonstrated in Figure 4.6 to better describe how changes in the atmospheric pCO₂ can alter and effect lacustrine primary producers, ultimately leading to a notable change in ¹³C/¹²C ratios amongst sedimentary OM. A series of recent publications on East African alpine lakes (e.g., Ficken et al., 1998; Street-Perrott et al., 2004) demonstrate characteristic enrichment of δ¹³C in sedimentary OM coincident with colder glacial conditions during which atmospheric pCO₂ was significantly reduced (-80 to -100 p.p.m.v. [Leuenberger et al., 1992]). Similar responses have been noted in lacustrine systems around the globe (Lake Baikal [Morley, 2005]; Lake Biwa [Meyers and Horie, 1993]). Global change in paleo-pCO₂ levels were initially described in Leuenberger et al (1992) who described an LGM ice core bubble pCO₂ of 180-200 p.p.m.v compared to a pre-industrial Holocene pCO₂ value of 280 p.p.m.v. A more efficient 'biological pump' is thought to
have decreased surface water DCO₂, transporting and locking Carbon in deeper waters during a period of reduced ventilation (Broecker and Henderson, 1998). Simultaneous changes to oceanic pH are thought to have amplified ocean productivity driven declines in pCO₂ (Archer et al., 2000). The net result of a shift to alkaline pH and higher productivity coupled to greater export of oceanic OM, led to lower atmospheric pCO₂ and Carbon starvation amongst terrestrial vegetation, particularly aquatic vegetation that could more readily exhaust DCO₂ in surface waters. Hence, a clear indication of the LGCP in New Zealand might very well be a shift to enriched δ¹³C signatures of terrestrial and aquatic OM (Alloway et al., 2007).

The importance of adopting a multi-proxy paleolimnological approach is underscored by further complicated responses of δ¹³C to changes in pH, nutrient cycling, temperature and growth rate (Takahashi et al., 1990; Wolfe et al., 2001; Talbot and Laerdal, 2000). Studies of East African lakes demonstrate glacially-mediated enrichment of OM δ¹³C through reductions in DIC availability and a greater contribution of enriched detrital terrestrial Carbon, enhanced floral competition and increased utilisation of HCO₃⁻ by aquatic plants (Ficken et al., 1998; Street-Perrott et al., 2004). To discriminate changes in δ¹³C attributable to enhanced productivity alone one must examine other proxies such as C/N ratios or TOC influx rates, the former being reflected by enhanced TOC influx and higher δ¹³C rather than a reduction in TOC and enriched δ¹³C associated with colder conditions.

**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 CO₃²⁻) 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)
Nitrogen exists as one of two naturally occurring stable isotopes, $^{14}\text{N}$ ($\sim 0.37\%$) and $^{15}\text{N}$ ($\sim 99.63\%$) (Talbot, 2001). Nitrogen isotope ($\delta^{15}\text{N}$ [$^{15}\text{N}/^{14}\text{N}$]) values of lacustrine sediment are valuable proxies for past changes in catchment-lake ecosystem productivity in much the same way as Carbon (Talbot, 2001). Differences in sources of inorganic Nitrogen reservoirs can be quite marked within lakes. Atmospheric molecular Nitrogen has a $\delta^{15}\text{N}$ value of $\sim 0\‰$ whilst dissolved $\text{NO}_3^-$ possesses a $\delta^{15}\text{N}$ value of $+7$ to $+10\‰$ (Peters et al., 1978). Source $\delta^{15}\text{N}$ values are apparently preserved in lake sediment to much the same extent as $\delta^{13}\text{C}$. There are marked diagenetic changes to TN, but Meyers and Lallier-Vergès (1999:350) report the absence of ‘potential isotopic biasing’ to nitrogenous matter from a study of 0.5 m cores taken in Lakes Superior and Ontario (Pang and Nriagu, 1977). Peterson and Howarth (1987) also noted the preservation of nitrogen provenance in the isotopic contents of detrital marine plankton ($\delta^{15}\text{N}$ of $+8\‰$ [dissolved nitrate $= +7$ to $+10\‰$]) and C3 terrestrial flora ($\delta^{15}\text{N}$ of $+1.0\‰$ [atmospheric $\text{N}_2 = 0\‰$]). Although Meyers and Eadie (1993) have noted a characteristic -1 to $-2\‰$ depletion in particulate OM between near-surface and near-bottom sediments, it is likely isotope shifts occur systematically and prior to sedimentation (Meyers and Ishiwatari, 1993). Nevertheless, changes to lacustrine $\delta^{15}\text{N}$ can arise from a number of biogeochemical processes: atmospheric $\text{N}_2$ fixation and depletion of $\delta^{15}\text{N}$ by cyanobacteria ($[-4$ to $+2\‰]$ Fogel and Cifuentes, 1993); enrichment of $\delta^{15}\text{N}$ by $\text{NH}_3$ volatilisation and denitrification in anoxic basins ($[+34\‰]$ Meyers and Teranes, 2001); enrichment through nitrification ($+20\‰$) and denitrification ($+20\‰$) of detrital OM by nitrifying and denitrifying bacteria (Yoshioka et al., 1988); competition amongst primary producers (Jones et al., 2004); enrichment through greater heterotrophy ($[+10\‰$ per trophic level] Deniro and Epstein, 1981); and changes to relative autochthonous and allochthonous inputs of Nitrogen (Table 4.3) (Figure 4.7). Changing pore-water pH can also alter sedimentary $\delta^{15}\text{N}$ - alkaline lakes heavily fractionate sedimentary N through ammonia volatilisation and degassing ($+34\‰$ enrichment of sedimentary N) (Talbot and Johannessen, 1992; Talbot, 2001). Furthermore, in certain lakes there might be a natural seasonal transition of N-containing OM from different functional groups (e.g., a shift from spring DIN to summer atmospheric Nitrogen use) (e.g., Gu et al., 1996). Changes in sedimentary $\delta^{15}\text{N}$ might therefore reflect changes in the Nitrogen reservoir rather than environmental change (Talbot, 2001). However, in these circumstances $\delta^{15}\text{N}$ provides a ready proxy to identify changes in the dominance of different N-utilising functional groups which in the instance of “Nitrogen fixers” (e.g., cyanobacteria) flourish under only certain conditions (e.g., exhaustion of DIN reservoir, sufficient P or Fe). Due to the inherent complexity and range of processes affecting lacustrine sedimentary $\delta^{15}\text{N}$ and TN values, Talbot (2001) has recommended that their use in paleolimnology accompany the application of multiple proxies in which other organic and inorganic proxies are used to generate hypotheses. Combined with other OM provenance indicators, $\delta^{15}\text{N}$ offers a robust proxy with which to reveal information on past productivity.
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 δ$^{15}$N of ca. 20‰ between the reactant and product. In the case of N$_2$ gas dissolution therefore, δ$^{15}$N 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).

<table>
<thead>
<tr>
<th>Process</th>
<th>Fractionation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Inorganic</td>
<td></td>
</tr>
<tr>
<td>Nitrogen dissolution: N$_2$(gas) → N$_2$(aq)</td>
<td>1.00085</td>
</tr>
<tr>
<td>Ammonia volatilisation: NH$_4^+$ (aq) → NH$_3$(gas)</td>
<td>1.034</td>
</tr>
<tr>
<td>(b) Biochemical</td>
<td></td>
</tr>
<tr>
<td>Nitrogen fixation: N$_2$(gas) → Cell-N</td>
<td>0.996-1.0024</td>
</tr>
<tr>
<td>Nitrate assimilation: NO$_3^-$ → Cell-N</td>
<td>1.011-1.023</td>
</tr>
<tr>
<td>Ammonium assimilation: NH$_4^+$ → Cell-N</td>
<td>0.993-1.013</td>
</tr>
<tr>
<td>Remineralisation: Cell-N →NH$_4^+$</td>
<td>1.001</td>
</tr>
<tr>
<td>Nitrification: NH$_4^+$ → NO$_2^-$</td>
<td>1.020</td>
</tr>
<tr>
<td>Denitrification: NO$_3^-$ → N$_2$(gas)</td>
<td>1.020</td>
</tr>
</tbody>
</table>

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 N$_2$ and that the importance of Nitrogen fixation can vary greatly from lake to lake (Modified from: Meyers and Teranes, 2001: 249).
4.3.4.3 Analytical Methods

Bulk OM $\delta^{13}$C and total $\delta^{15}$N analyses were conducted at the University of Waikato, New Zealand (Waikato Stable Isotope Unit) as per standard (Section 4.2.1.3. Bulk Stable Carbon Isotope Analyses). Analysis was conducted using an online Elemental Analyser (EA) coupled to a Continuous Flow-Isotope Ratio Mass Spectrometer (CF-IRMS) (Europa Scientific 20-20 Stable Isotope Analyser). Values are reported as per mille (‰) variation from a standard ratio format ($\delta^{13}$C = Pee Dee Belemnite and $\delta^{15}$N = AIR):

$$\delta (\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 10^3$$

where $R$ is the isotope ratio and is equal to $^{13}$C/$^{12}$C or $^{15}$N/$^{14}$N, referring to the sample or standard. Analytical uncertainty for the Waikato Laboratory’s measurement of $\delta^{13}$C is ± 0.5 ‰ and for $\delta^{15}$N is ± 1.0 ‰. All $\delta^{13}$C ratios are referenced to a precalibrated C4 sucrose standard that is cross-referenced to PDB. All $\delta^{15}$N ratios are referenced to a urea standard that is traceable to atmospheric Nitrogen.

4.3.5 Data Analysis and Presentation

4.3.5.1 Zonation

Several bulk sediment environmental proxies are regularly examined in paleolimnological exercises, notably TOC, TN, $\delta^{13}$C and $\delta^{15}$N. Talbot (2001) sets out an approach for presenting these proxies as a series of biplots, including a technique for the removal of trace inorganic Nitrogen from TN estimates. Notably proxy biplots enable clusters of similar samples (by geochemistry) to be identified. Samples ages can then be employed to identify those periods (e.g., samples) that represent transitions from one cluster to another. Ordination or factor analyses could similarly be employed to identify change in the geochemistry of sediment samples, though because many of the above proxies are destructive no single sample could yield values for all proxies. Hence we would need to interpolate between samples to ensure all proxy data was available at a single unit of composite depth. Likewise a factor analysis would weight each proxy equally in the definition of a composite principal or secondary axis. The Talbot (2001) approach overcomes the difficulties of deciding on weightings for each proxy although establishing zones in this way is an artificial process, one in which sampling resolution dictates the boundaries of zonal change. Nonetheless the magnitudes of change described below are sufficient to permit zonal changes visually negating the use of further statistical methods (e.g., cluster analysis).
4.4 Paleolimnologic Results

4.4.1 Magnetic Susceptibility (MS)

The composite low-field magnetic susceptibility ($\kappa_{LF}$) record has been filtered to exclude samples containing tephra and/or cryptotephra (e.g., >1.0% coarser than 64 μm) and is presented in Figure 4.8. $\kappa_{LF}$ values are dominated by low positive $\kappa_{LF}$ values ($\mu = 36 \times 10^{-6}$ SI, $n = 1378$). These values are in line with previous studies and confirm the paramagnetic nature of sediment in Lake Pupuke during the late Holocene (Striewski et al., 2009). Values rise most sharply at ~0.7 cal. kyr BP but also records several maxima from ~38.7-38.1 cal. kyr BP, ~32.1-30.3 cal. kyr BP, ~20.0-18.2 cal. kyr BP and ~8.0-5.6 cal. kyr BP, the latter of which is comprised of two separate peaks in $\kappa_{LF}$ at ~6.4 cal. kyr BP and ~5.7 cal. kyr BP. There are also MS minima occurring at ~26.0 cal. kyr BP and ~14.9 cal. kyr BP. A period of relative stability occurs between ~47.9 cal. kyr BP and ~38.7 cal. kyr BP ($1\sigma = 8.1 \times 10^{-6}$ SI, $n = 202$) but followed by another relatively stable interval between ~38.1 cal. kyr BP and ~32.1 cal. kyr BP ($1\sigma = 6.6 \times 10^{-6}$ SI, $n = 95$) (refer to Figure 4.8). Thereafter the $\kappa_{LF}$ record is particularly noisy with marked variations to today ($1\sigma = 46.8 \times 10^{-6}$ SI, $n = 1059$).

Notably, $\kappa_{LF}$ values demonstrate weak but significant correlations with wet bulk density ($r_{LF,WBD} = -0.26$, $P < 0.001$, $n = 1374$), water content ($r_{LF,Wc} = 0.29$, $P < 0.001$, $n = 1374$) and dry bulk density ($r_{LF,DBD} = -0.30$, $P < 0.001$, $n = 1374$). Insignificant correlations exist between $\kappa_{LF}$ and mean grain size (volumetric weighted mean [$r_{LF,MGS} = -0.01$, $P > 0.01$, $n = 219$]), the proportion of sand ($r_{LF,sand} = 0.01$, $P > 0.01$, $n = 219$) and silt ($r_{LF,silt} = -0.16$, $P > 0.001$, $n = 219$) (note: clay observes a significant correlation to $\kappa_{LF}$ [$r_{LF,clay} = 0.33$, $P < 0.001$, $n = 219$]). Stronger correlations are present with influx estimates SAR ($r_{LF,SAR} = 0.67$, $P < 0.001$, $n = 1373$) and MAR ($r_{LF,MAR} = 0.60$, $P < 0.001$, $n = 1373$) although this is to be expected from the exponential increases in SAR and MAR over the last ~800 yr (Figure 4.8). For instance, correlation analyses of >800 yr $\kappa_{LF}$ and SAR ($r_{LF,SAR} = -0.01$, $P > 0.001$, $n = 1240$) and MAR ($r_{LF,SAR} = -0.03$, $P > 0.001$, $n = 1240$) are very weak. Thus variation in $\kappa_{LF}$ and sediment influx is very well correlated throughout the last ~800 yrs ($r_{LF,SAR} = 0.81$, $P < 0.001$, $n = 133$; $r_{LF,MAR} = 0.75$, $P < 0.001$, $n = 133$).

4.4.2 Grain Size Analyses

A total of 225 grain size analyses were performed on composite sediment which is composed largely of fine grains (<32 μm) ($\mu = 79.8 \pm 7.61\%$ [1σ]) (Figure 4.8). Throughout the composite sequence, the median size interval occurs in the range 7.80-15.60 μm (26.31 ± 4.85% [$\mu \pm 1\sigma$]) whilst the volume-weighted mean grain size is 23.43 ± 5.21 μm ($\mu \pm 1\sigma$). The clay (<2 μm) and silt size fraction (2-63 μm) contribute on average 15.31 ± 2.49% and 75.90 ± 5.34% respectively ($\mu \pm 1\sigma$) to sediment grain size distributions. The remaining 10.66% of average sample grains are classified as sand (62.5-2000 μm) (Figure 4.8). Examining changes to percentage contributions between clay, silt and sand down core reveals marked variations largely amongst clay and sand content. Clay content varies between 10.13% and 26.68% with two features evident: (1) a marked dip in content
between 12.7 and 7.7 cal. kyr BP (15.09 ± 3.98% [μ ± 1σ, n = 10]); and (2) a marked rise in clay content beginning ~0.8 cal. kyr BP (16.02 ± 3.58% [μ ± 1σ, n = 20]).

Silts dominate composite grain size distributions but exhibit limited variability. However, a marked decline occurs from 14.8 cal. kyr BP until 13.2 cal. kyr BP (67.3 ± 3.44% [μ ± 1σ, n = 14]) followed by a trend to higher silt content until today (78.0 ± 4.83% [μ ± 1σ, n = 82]). Relative sand content demonstrates far more variability than clay and silt despite a markedly lower average abundance (1σ, Silt = 5.34%). However, little variation exists prior to ~30.0 cal. kyr BP (8.03 ± 2.56% [μ ± 1σ, n = 68]). Sediments thereafter contain relatively more sand-sized grains between ~30.0 cal. kyr BP and ~18.3 cal. kyr BP (14.88 ± 5.38% [μ ± 1σ, n = 51]). The period between 15.7 cal. kyr BP and 12.7 cal. kyr BP is also marked by elevated sand content (19.63 ± 5.80% [μ ± 1σ, n = 19]) prior to a declining trend throughout the interval ~12.7 cal. kyr BP until today (8.01 ± 4.07% [μ ± 1σ, n = 79]). Imposed upon this trend is a distinct recent rise beginning ~0.2 cal. kyr BP to today (maximum 18.74%).

To better elicit which size intervals are driving total grain size variation down core, grain size distributions are plotted in Figure 4.9. Each is displayed by cumulative volume percent for size fractions of 0.01-3.90 μm, 3.90-7.80 μm, 7.80-15.60 μm, 15.60-31.00 μm, 31.00-44.00 μm, 44.00-62.50 μm, 62.50-88.00 μm, 88.00-125.00 μm, and 125.00-1000 μm (Figure 4.9). There are marked similarities in abundance between two broad classes of particle size: grains less than and greater than 32 μm. The latter discriminates between fine silts/clays and coarse silts/sands, and has been demonstrated to reflect the influx of terrigeneous detritus to other maar lakes (e.g., Onepoto Maar [Augustinus et al., 2010]). Accordingly, abundance of grains >32 μm have also been presented in Figure 4.9. Little variation occurs therein prior to ~30.0 cal. kyr BP whose lesser proportions of particles >32 μm (15.11 ± 3.75% [μ ± 1σ, n = 68]) contrast with greater abundance during the interval ~30.0 cal. kyr BP to today (22.47 ± 7.79% [μ ± 1σ, n = 157]). The latter period of larger particle size contains 2 periods of greatest abundance of particles >32 μm: (1) between ~31.5 and 18.5 cal. kyr BP (24.31 ± 6.37% [μ ± 1σ, n = 56]); and (2) between ~15.6 and 13.2 cal. kyr BP (35.18 ± 4.07% [μ ± 1σ, n = 15]). Post ~13.2 cal. kyr BP, grain sizes continue to fine until an abrupt reversal from ~0.8 cal. kyr BP until today (16.42 ± 5.10% [μ ± 1σ, n = 20]).
Figure 4.8: Magnetic susceptibility ($\kappa_{LF}$), volume-weighted mean particle size ($\mu$m), the proportions of clay, silt and sand-sized particles ($\%$), sediment accumulation rate (SAR) and mass accumulation rate (MAR) of Lake Pupuke composite sediments. Note $\kappa_{LF}$ have been filtered to exclude tephra contamination, please refer to core log files in Appendix A for $\kappa_{LF}$ including tephra. Further note that the series mean of $\sim23.43\,\mu$m is highlighted on volume-weighted mean particle size (dashed line).

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

Elemental data have been acquired at a sampling resolution of 1 to 15 cm (~10 to 730 yr) over the entire composite sequence (1420 cm, ~48.2 cal. kyr BP to today). Geochemical changes in the lacustrine sediments reflect changes in productivity and vegetation structure, as well as erosional, depositional and diagenetic processes. Organic matter geochemistry (TOC, TN and TS) offers the greatest insight into the former, whilst inorganic geochemistry (ITRAX) offers a greater insight to the latter processes. Thus the following considers each separately within the framework of elemental analyses, beginning with OM elemental geochemistry.

4.4.3.1 Correction for Inorganic Nitrogen

![Graph showing relationship between TOC and TN](image)

\[ y = 0.066x - 0.1623 \]
\[ R^2 = 0.6722 \]

*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.*

Interpretation of TOC and TN can yield important information on the likely source of lacustrine OM through generation of C/N atomic ratios (Talbot, 2001). However, interpretation C/N ratios can be complicated by inclusion of an inorganic Nitrogen component. For instance, altered C/N ratios can arise through variable inorganic input rather than shifts in the dominant primary producer. However, this is largely a problem with low OM sediments (TOC < 0.3 wt.%) in which a relatively low abundance of organic Nitrogen can suffer relatively
large changes in abundance by contribution of inorganic Nitrogen. Pupuke composite sediments possess an average TOC concentration of 13.21 wt.% (μ) and at least 5.95 wt.% such that it is unlikely to be a problem. Indeed as per Talbot (2001), the effect of inorganic Nitrogen on TOC/TN ratio can be removed. A simple regression of TOC on TN will highlight non-organic N-contributions by an intercept on the TN axis of a positive value. This can thereafter be systematically removed from TN values for all samples to model only organic-N contributions. Sedimentary TOC and TN data from Lake Pupuke are plotted in Figure 4.10.

Little if any inorganic Nitrogen contributes to TN estimates (e.g., TN= 0.066*TOC - 0.1623 [R² = 0.6722]; the intercept on TN in Figure 4.10 is negative). Acid-leaching of sediment has prevented the inclusion of inorganic Carbon, thus it is likely the negative intercept reflects either a loss of organic Nitrogen (e.g., via diagenesis) or a minimum organic Carbon offset (e.g., minimum amount of Carbon prior to inclusion of Nitrogen). As we cannot distinguish between the two we have applied no correction to sample TN data.

4.4.3.2 Total Organic Carbon, Nitrogen and Sulphur

Bulk sediment TOC and TN analyses were conducted on 270 composite sediment samples. Both demonstrate high concentration throughout the composite sequence, but particularly from ~13.8 cal. kyr BP to today (17.73 ± 3.30 wt.% and 1.10 ± 0.29% respectively [μ ± 1σ, n = 100]) (Figure 4.11). Prior to this TOC and TN values are markedly lower (10.56 ± 2.85 wt.% and 0.48 ± 0.15 wt.% respectively [μ ± 1σ, n = 170]). Between 17.9 cal. kyr BP and ~14.4 cal. kyr BP TOC and TN values continue to rise (11.89 ± 4.33 wt.% and 0.37 ± 0.18 wt.% respectively [μ ± 1σ, n = 15]) though reductions occur from ~14.4 cal. kyr BP until ~13.8 cal. kyr BP. Further less pronounced reductions occur from ~12.8 cal. kyr BP until 12.0 cal. kyr BP (15.02 ± 2.51 wt.% and 0.80 ± 0.11 wt.% [μ ± 1σ, n = 5]), ~7.6 to 5.7 cal. kyr BP (13.99 ± 1.47 wt.% and 0.89 ± 0.11 wt.% [μ ± 1σ, n = 11]), ~5.0 cal. kyr BP to 4.7 cal. kyr BP (17.37 ± 0.28 wt.% [μ ± 1σ, n = 3]) and ~3.9 cal. kyr BP to 3.2 cal. kyr BP (18.62 ± 1.01 wt.% [μ ± 1σ, n = 5]).

Sedimentary TOC and TN are also strongly positively correlated, thus confirming the lack of significant inorganic N within the lacustrine TN series (r_TOC,TN = 0.82, P <0.001, n = 272). At closer inspection, the two proxies lose symmetry from 6.2 cal. kyr BP to today (r_TOC,TN = 0.55, P <0.001, n = 70). Whereas TOC and TN increase synchronously from 13.5 cal. kyr BP to 7.8 cal. kyr BP, relative TN rises are far greater than relative TOC increase from ~6.2 cal. kyr BP to today. Similarly during the interval 30.0 cal. kyr BP to 18.2 cal. kyr BP, TN reductions exceed those to TOC causing a corresponding rise in C/N ratios (Figure 4.11).

C/N ratios have been calculated for 270 sediment samples, averaging 24.41 but demonstrate marked variability (1σ = 8.33), ranging from 75.02 to 9.57 (Figure 4.11). Changes in C/N ratios record the marked expansion and recession of terrestrial flora within Lake Pupuke’s catchment over the sedimentary archive. In particular, older samples (>33.5 cal. kyr BP) are predominantly aquatic in origin (21.54 ± 3.01 [μ ± 1σ, n = 65]) whilst youngest (<14.0 cal. kyr BP) also display an aquatic signature (20.08 ± 4.35 [μ ± 1σ, n = 115]). The intervening samples
(33.5 cal. kyr BP to 14.0 cal. kyr BP) are derived from largely terrestrial sources (32.03 ± 9.49 [μ ± 1σ, n = 90]). Within this period however, distinction can be made between 2 periods of mixed lesser and greater terrestrial contributions to sedimentary OM: 33.5 cal. kyr BP to 17.5 cal. kyr BP (29.37 ± 6.35 [μ ± 1σ, n = 74]) and 17.5 cal. kyr BP to 14.0 cal. kyr BP (44.35 ± 11.90 [μ ± 1σ, n = 16]). Within the last 10 kyrs, subtle variability is present in the C/N ratio data, notably a decline in values between ~7.6 cal. kyr BP and ~5.7 cal. kyr BP (minimum = 15.95; 18.51 ± 1.77 [μ ± 1σ, n = 11]) followed by a return to early Holocene values (18.33 ± 4.03 [μ ± 1σ, n = 76]).

Stratigraphic changes in the abundance of sedimentary TS record paleoproductivity and pore-water conditions (Holmer and Storkholm, 2001). Within the Lake Pupuke composite sequence estimates of maximum (2.82 wt.%), minimum (0.24 wt.%) and average TS abundance (0.80 wt.%) are nearer values for TN than TOC (Figure 4.11). Variation in TS is however, relatively greater than TOC or TN (1σTS = 0.44 wt.%; 1σTOC = 4.60 wt.%; 1σTN = 0.37 wt.%). Nonetheless there are several notable periods of similarity, particularly the interval ~31.5 cal. kyr BP to ~16.0 cal. kyr BP when TS drops to a low of 0.40 ± 0.08 wt.% (μ ± 1σ, n = 70). Prior to and after this interval, TS values are relatively high (0.80 ± 0.21 wt.%, 1.05 ± 0.50 wt.% respectively [μ ± 1σ, n = 76, 124]). There is a notable drop in TS to 0.58 ± 0.08 wt.% (μ ± 1σ, n = 9) between ~13.8 cal. kyr BP and ~13.4 cal. kyr BP followed by a rise to 1.56 ± 0.69 wt.% (μ ± 1σ, n = 29) over the period ~13.4 cal. kyr BP to ~7.6 cal. kyr BP. The middle Holocene (~7.6 cal. kyr BP) to today is also characterised by variability in TS but values are consistently lower than early Holocene equivalents (0.90 ± 0.26 wt.% [μ ± 1σ, n = 76]).

### 4.4.3.3 Elemental Fluxes

As noted earlier, interpretation of relative abundance (e.g., wt.%) is subject to dilution and concentration uncertainty via changes to erosional influx rather than productivity per se. The product of TOC, TN or TS by mass accumulation rate (MAR) yields accumulation rates (AR’s) for each (e.g., CAR, NAR and SAR) which represent the absolute variation in elemental geochemistry of OM. Each is presented in Figure 4.11.

The TOC, TN and TS fluxes over the composite sequence are relatively high (1.394 ± 0.989 mg cm⁻² yr CAR; 0.078 ± 0.073 mg cm⁻² yr NAR; 0.075 ± 0.043 mg cm⁻² yr SAR [μ ± 1σ]). TOC flux is greatest and varies from 5.249 to 0.423 mg cm⁻² yr (n = 270). TON and TS fluxes are a magnitude lower, varying from 0.486 to 0.007 mg cm⁻² yr (n = 270) and 0.344 to 0.020 mg cm⁻² yr respectively (n = 263). The three elemental fluxes display coeval responses, demonstrating a high correlation with MAR; CAR by MAR (rCAR,MAR = 0.88, P <0.001, n = 270); NAR by MAR (rNAR,MAR = 0.80, P <0.001, n = 270); and SAR by MAR (rSAR,MAR = 0.59, P <0.001, n = 263). There are 4 periods of coeval peak flux across the three proxies: (1) ~23.3 cal. kyr BP to ~18.3 cal. kyr BP (1.334 ± 0.503 mg cm⁻² yr CAR; 0.050 ± 0.016 mg cm⁻² yr NAR; 0.048 ± 0.020 mg cm⁻² yr SAR [μ ± 1σ, nCAR,NAR,SAR = 30, 30, 29]); (2) ~15.8 cal. kyr BP to ~12.5 cal. kyr BP (2.458 ± 1.420 mg cm⁻² yr CAR; 0.112 ± 0.073 mg cm⁻² yr NAR; 0.121 ± 0.064 mg cm⁻² yr SAR [μ ± 1σ, nCAR,NAR,SAR = 29, 29, 28]); (3) ~10.1 cal. kyr BP to ~7.8 cal. kyr BP (1.232 ± 0.276 mg cm⁻² yr CAR; 0.059 ± 0.009 mg cm⁻² yr NAR; 0.115 ± 0.034 mg cm⁻² yr SAR [μ ± 1σ, nCAR,NAR,SAR = 12,
12, 12)); and most recently (4) an exponential increase to today, beginning ~5.0 cal. kyr BP (2.363 ± 0.976 mg cm⁻² yr CAR; 0.171 ± 0.093 mg cm⁻² yr NAR; 0.103 ± 0.036 mg cm⁻² yr SAR [μ ± 1σ, n_CAR,NAR,SAR = 59, 59, 54]). Prior to the onset of (1) CAR and NAR were relatively stable to ~48.0 cal. kyr BP (0.807 ± 0.171 mg cm⁻² yr CAR; 0.040 ± 0.012 mg cm⁻² yr NAR [μ ± 1σ, n_CAR,NAR = 108, 108]) whilst SAR reflects earlier noted drops in TS at ~31.5 cal. kyr BP, SAR being low and stable between ~31.5 cal. kyr BP and ~23.3 cal. kyr BP (0.033 ± 0.011 mg cm⁻² yr SAR [μ ± 1σ, n_SAR = 31]) and greater and more variable prior to ~31.5 cal. kyr BP (0.068 ± 0.023 mg cm⁻² yr SAR [μ ± 1σ, n_SAR = 77]).
Figure 4.1: 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.
4.4.3.4 Bulk XRF (ITRAX) Analyses

ITRAX micro-XRF core profiles were analysed for each core and then linked to create a composite elemental series as for Chapter 3.3.5.2 Composite Core Construction. ITRAX data are essentially semi-quantitative and enable discrimination of trends in mineral geochemistry (Rothwell et al., 2006). Interpretation of micro-XRF downcore profiles however, necessitates caution because of the propensity for coring artefacts (e.g., variable water or OM content, compaction and surface irregularities) to introduce variations to closely spaced element XRF peaks. Indeed spectra need to be precisely separated from crack-related effects, low count rates and grain size effects (Rothwell et al., 2006). Thus elemental abundances are presented below as normalised integers relative to incoherent peak area or Compton scattering (i.e., the relative amount of noise introduced by moisture and air) (Figure 4.12). The latter relates inversely to sediment packing, decreasing in more dense sediment (Rothwell et al., 2006).

The response of the ITRAX core scanner to individual elements was highly variable with several elements demonstrating notable similarity in both magnitude and timing of change so as to suggest covariation and poor isolation of XRF spectra (Table 4.4). Unfortunately, cores were analysed with 2 technical settings at the University of Aberystwyth that resulted in marked variation in sediment geochemistry between changes in settings (Figure 4.12). As we cannot exclude the possibility of error attributed to changing ITRAX sensitivity under different methodologies, and likewise, as automated XRF core scanning is also a novel paleolimnologic technique, to reliably employ elemental series in this paleolimnological study we have limited analysis to cover the period ~17.0 cal. kyr BP to today (e.g., period analysed prior to a change of settings).

Anomalous samples containing disproportionately greater rare earth elements (e.g., Ti, Y) have been excluded owing to their proximity to and likelihood of tephra reworking ($n = 7$ [6902, 6941, 9654, 15156, 15200, 15852 and 15900 cal. yr BP] coincident with Tuhua [7.0 cal. kyr BP], Rotoma [9.5 cal. kyr BP] and Rotorua tephras [15.4 cal. kyr BP]). Resultant elemental spectra are dominated by Fe ($0.855 \pm 0.703$ cps/inc [$\mu \pm 1\sigma$, $n = 671$]) with markedly less abundant Ti ($0.008 \pm 0.003$ cps/inc [$\mu \pm 1\sigma$, $n = 671$]) and Co ($0.006 \pm 0.006$ cps/inc [$\mu \pm 1\sigma$, $n = 671$]) forming subdominant species. The latter are associated with allochthonous components, in this case local basaltic volcanism.

From Figure 4.13 it is evident that the older (~17.0-15.2 cal. kyr BP) sediments are particularly Fe-rich ($2.466 \pm 1.790$ cps/inc [$\mu \pm 1\sigma$, $n = 27$]). Later sediments contain less Fe except for the periods, ~6.9 to 5.4 cal. kyr BP ($1.181 \pm 0.527$ cps/inc [$\mu \pm 1\sigma$, $n = 22$]) and ~0.6 to 0.3 cal. kyr BP ($1.273 \pm 0.739$ cps/inc [$\mu \pm 1\sigma$, $n = 45$]). The basaltic Rangitoto tephra might explain increased Fe after 0.6 cal. kyr BP through Fe-dissolution and mobility under reducing conditions. However, increased Fe from 6.9-5.4 cal. kyr BP occurs in the absence of basalt input and records a period of enhanced Fe-delivery and/or precipitation in line with greater erosion and/or benthic oxygenation.
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.
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.
Table 4.4: Correlation coefficients among ITRAX elemental profiles (bold are significant at $P < 0.001$) (Pearson’s $r$, $n = 671$).

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Chapter Four
4.4.4 Comparison of EA-TS and XRF-TS

The novel nature of ITRAX data presents an opportunity to compare trends between XRF- and EA-recorded Sulphur. EA and XRF trends within the Pupuke composite sequence demonstrate limited similarity ($r_{EA,XRF} = 0.187, n = 122$) (Figure 4.14). Covariation with other lighter atomic elements (e.g., Al, Si, P and Cl) has likely contributed to between-technique variance. For instance, there are clear similarities between XRF and EA Sulphur profiles including increased abundance between ~12.1 and ~7.6 cal. kyr BP. These similarities suggest a proportion of XRF-inferred TS abundance is accurately derived from spectral absorbance by S-bearing compounds. Nonetheless, noticeable differences in the XRF-inferred TS profile relative to the EA-inferred TS profile suggest some proportion of the XRF-TS peak is incorrectly modelled (e.g., through interference of other lighter elements such as Al and Si). Peaks in XRF-TS at ~0.7 cal. kyr BP, ~1.6 cal. kyr BP, ~2.5 cal. kyr BP and ~3.8 cal. kyr BP are not demonstrated by EA-TS. The likelihood of interference by Al-bearing compounds with their clastic source, limit application of XRF-derived lighter elements (e.g., Si, P and S) and effectively prevent their application to infer paleoproductivity.

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]).
4.4.5 Paleoerosion Profile (Ti)

Climate affects erosional fluxes in lacustrine sediment by impacting upon vegetation cover and weathering. Hence changes in the abundance of allochthonous elements offer a record of past erosion. Paleolimnologic approaches typically employ Al and K as clastic indicators particularly in developed soils with a high proportion of clays (Rollinson, 1993; Van Der Weijden, 2002). However, Al spectra were poorly discerned from other light elements (e.g., Al highly correlated with Si, P, S and Cl). Instead the Lake Pupuke catchment offers an abundance of mafic rock supporting a choice of Ti or Fe as a detrital indicator. The latter is heavily influenced by changing REDOX potential (Rothwell et al., 2006; Unkel et al., 2008). In order to avoid poorly defined Al spectra and greater diagenetic changes inherent in Fe, Ti is therefore employed as a paleoerosion indicator (Figure 4.15).

![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).](image-url)

Titanium is the second most abundant element within the ITRAX composite sequence with an average of 0.008 ± 0.003 cps/inc ($\mu \pm 1\sigma, n = 671$) and marked by a declining trend beginning ~16.9 cal. kyr BP until ~0.8 cal. kyr BP. Subsequently Ti-concentration increases markedly to values characteristic of the Last Glacial Interglacial Transition (LGIT). An inverse relationship to TOC (%) is evident in Figure 4.15 supporting the use of Ti as a proxy for erosion as the influx of clastic material represents the principle Ti-source and dilutes autochthonous OM to yield lesser TOC values. Several of the Ti peaks likely represent periods of greater erosion and
allochthonous input to Lake Pupuke: (1) between ~13.6 and 11.3 cal. kyr BP (0.012 ± 0.001 cps/inc [$\mu$ ± $\sigma$, $n$ = 102]); and (2) between ~7.8 and 5.7 cal. kyr BP (0.008 ± 0.001 cps/inc [$\mu$ ± $\sigma$, $n$ = 56]). Lower Ti-values throughout the late Holocene beginning ~5.6 cal. kyr BP are interspersed with increases from ~4.7 to 4.1 cal. kyr BP, ~3.6 to 3.0 cal. kyr BP and ~2.6 to 2.3 cal. kyr BP (Figure 4.15). Increased Ti abundance from ~0.8 cal. kyr BP to today (0.008 ± 0.003 cps/inc [$\mu$ ± $\sigma$, $n$ = 135]) records increased rates of erosion probably driven by agriculture and clearing associated with occupation of the catchment.

4.4.6 Paleo-REDOX Profile (Mn/Fe)

Mn and Fe are REDOX sensitive metals whose presence in lacustrine sediments depends on supply via erosion and benthic pore-water conditions (Shanahan et al., 2008). Differences in preservation enable the reconstruction of past REDOX potential whereby ferric hydroxides are more stable under reducing conditions than Mn-oxides resulting in a relative depletion and enrichment of Mn under less and more oxic conditions respectively (Shanahan et al., 2008).

![Figure 4.16](image-url)

*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.*

To avoid variations in Mn and Fe concentration due to varying sediment accumulation rate, element abundance is expressed relative to a detrital phase element (Ti). The corrected Mn/Fe ratios demonstrate the effects of changing REDOX at the sediment-water interface on the composite sediment series (Figure 4.16). The Mn/Fe profile reveals average ratios of 0.0073 ± 0.0071 ($\mu$ ± $\sigma$, $n$ = 671) with three periods of relative Mn-depletion
indicative of lower benthic oxygenation: (1) ~14.0 to 13.2 cal. kyr BP (0.0032 ± 0.0021 [μ ± 1σ, n = 71]); (2) ~11.2 to 9.6 cal. kyr BP (0.0028 ± 0.0033 [μ ± 1σ, n = 29]); and (3) ~7.1 to 5.8 cal. kyr BP (0.0016 ± 0.0019 [μ ± 1σ, n = 33]). Periods of lower oxygenation might reflect lesser mixing and/or greater BOD driving a reduction in available DO and favouring the preservation of more readily oxidised Fe (3+) compounds over Mn (3+) oxides (Rothwell et al., 2006). Comparison of TOC and Mn/Fe trends supports a response to mixing because periods of depleted Mn record lesser TOC (e.g., lower productivity, lesser detrital TOC and lower BOD) (Figure 4.16). Thus greater reducing potential during intervals (1) to (3) likely resulted from weaker mixing of the water column.

4.4.7 Bulk Stable Isotopic Analyses

Stable isotopes of Carbon (δ13C) and Nitrogen (δ15N) provide a window on past changes to nutrient cycles, productivity, ecosystem structure and atmospheric abundance. A total of 266 and 45 analyses were conducted respectively, at varying resolution: δ13C at intervals of ~5 cm composite depth (~180 yr); and δ15N at intervals of ~31 cm composite depth (~1090 yr).

4.4.7.1 Bulk δ13C

The bulk organic Carbon (δ13C) series for the entire composite sequence (~48.2 cal. kyr BP to today) is presented in Figure 4.17. δ13C values range from -27.92‰ to -15.27‰ with an average signature of -23.12 ± 2.74‰ (μ ± 1σ, n = 266). Patterns in δ13C differ markedly from those present in TOC or C/N ratios, particularly during the Last Glacial (δ13CTOC = -0.14, P >0.001, n = 266; δ13CN = 0.50, P <0.001, n = 262). Enrichment patterns are particularly informative and reveal two periods of Carbon scarcity between ~44.5 cal. kyr BP and ~37.0 cal. kyr BP (~23.46 ± 1.45‰ [μ ± 1σ, n = 30]), and ~28.8 cal. kyr BP and ~18.3 cal. kyr BP (~18.41 ± 1.72‰ [μ ± 1σ, n = 44]). At ~18.3 cal. kyr BP δ13C values are depleted and continue to remain relatively low until ~10.1 cal. kyr BP (~22.85 ± 1.82‰ [μ ± 1σ, n = 46]) whereupon several brief periods of enrichment occur: (1) ~9.3 cal. kyr BP to ~8.0 cal. kyr BP (~21.32 ± 0.65‰ [μ ± 1σ, n = 8]); (2) ~6.5 cal. kyr BP to ~5.7 cal. kyr BP (~21.78 ± 0.77‰ [μ ± 1σ, n = 5]); (3) ~4.2 cal. kyr BP to ~2.9 cal. kyr BP (~22.52 ± 0.59‰ [μ ± 1σ, n = 10]); and (4) ~1.8 cal. kyr BP to ~1.5 cal. kyr BP (~22.64 ± 0.43‰ [μ ± 1σ, n = 6]). Intervening periods experience a corresponding depletion of δ13C. From ~0.7 cal. kyr BP δ13C values increase to today (Figure 4.17).

During the transition from enriched to depleted δ13C signatures from ~18.3 cal. kyr BP to ~9.3 cal. kyr BP, there is a marked reversal to enriched δ13C occupied by 2 samples in close stratigraphic order (~13.7 cal. kyr BP, ~13.7 cal. kyr BP) whose enriched signatures (~21.35‰, ~21.37‰ respectively) indicate greater demand for Carbon. The close proximity of these samples, their similarity in δ13C and marked enrichment over prior samples (~2.02‰) are particularly notable as they reduce the likelihood of analytical or sampling error and increase the reliability of the inferred enrichment event.
Figure 4.17: Carbon and Nitrogen stable isotope signatures ($\delta^{13}$C, $\delta^{15}$N [%]), 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‰ [$\mu \pm 1\sigma$, n = 87]); (2) enrichment between ~30.0 cal. kyr BP and ~18.2 cal. kyr BP (-18.54 ± 1.86‰ [$\mu \pm 1\sigma$, n = 46]); and (3) depletion beginning ~18.2 cal. kyr BP to today (-23.67 ±1.79‰ [$\mu \pm 1\sigma$, 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‰ [$\mu \pm 1\sigma$, n = 32]); and (2) enrichment after ~6.0 cal. kyr BP (5.04 ± 0.55‰ [$\mu \pm 1\sigma$, n = 13]).
4.4.7.2 Bulk $\delta^{15}N$  

The bulk organic Nitrogen ($\delta^{15}N$) series has been analysed for the Pupuke composite sequence (Figure 4.17). $\delta^{15}N$ values range from 2.17‰ to 6.10‰ with an average of 3.56 ± 1.07‰ ($\mu \pm 1\sigma$, $n = 45$). $\delta^{15}N$ vary from trends of $\delta^{13}C$ ($r_{51SN, 31SN} = -0.14$, $P > 0.001$, $n = 45$), TN ($r_{51SN, TN} = 0.49$, $P > 0.001$, $n = 44$) and C/N atomic ratios ($r_{51SN, C/N} = -0.33$, $P > 0.001$, $n = 44$). There is no clear change to $^{15}N$-availability prior to ~6.0 cal. kyr BP (2.96 ± 0.46‰ [$\mu \pm 1\sigma$, $n = 32$]) whereupon enrichment of $\delta^{15}N$ values occurs until today (5.04 ± 0.55‰ [$\mu \pm 1\sigma$, $n = 13$]). The range of values in the interval ~6.0 cal. kyr BP to today is nearly equal that for the preceding ~42. kyrs (1.70‰ compared to 1.75‰ respectively).

4.4.8 Geochemical Zonation Analyses

The process of zoning geochemical data can be complex, particularly where multivariate responses are exhibited, requiring factor analysis to simplify inherent variability (see Chapter 5). Likewise, often simple data exploration can result in the identification of periods of greatest change between sedimentary samples. Talbot (2001) has established the potential to zone geochemical multi-proxy stratigraphic data by a series of sample biplots. This approach has been highly successful in numerous paleolimnologic investigations (e.g., Talbot, 2001 for examples) and involves generating a series of biplots (TOC by TN, TOC by C/N and $\delta^{13}C$ by $\delta^{15}N$). These are presented in Figure 4.18 below.

From Figure 4.18 one can isolate 2 broad clusters of sediment samples by provenance (C/N) and $\delta^{15}N$: (1) relatively depleted $\delta^{15}N$ samples (2.92 ± 0.44 ‰ [$\mu \pm 1\sigma$, $n = 30$]) with a highly variable but mixed terrestrial C/N signature (25.37 ± 4.81 [$\mu \pm 1\sigma$, $n = 30$]) between 47.8 cal. kyr BP and 6.5 cal. kyr BP; and (2) relatively enriched $\delta^{15}N$ samples (5.08 ± 0.58 ‰ [$\mu \pm 1\sigma$, $n = 10$]) with a stable, aquatic C/N signature (16.79 ± 2.65 [$\mu \pm 1\sigma$, $n = 10$]) between 3.8 cal. kyr BP and today. There are two notable outliers, comprising terrestrial OM (C/N > 35; 25.8 cal. kyr BP and 17.0 cal. kyr BP). A marked change favouring the enrichment of sedimentary Nitrogen occurred between 6.5 cal. kyr BP and 3.8 cal. kyr BP with several intervening samples (e.g., 5.5 cal. kyr BP and 4.9 cal. kyr BP).

Interpretation of $\delta^{13}C$ by $\delta^{15}N$ reveals 4 clusters of geochemically similar sediment samples: (1) relatively depleted $\delta^{15}N$ and $\delta^{13}C$ samples (2.91 ± 0.37 ‰ and -24.47 ± 1.45 ‰ respectively [$\mu \pm 1\sigma$, $n = 12$]) between 47.8 cal. kyr BP and 28.8 cal. kyr BP; (2) relatively depleted $\delta^{15}N$ but enriched $\delta^{13}C$ (3.39 ± 0.33 ‰ and -18.40 ± 1.30 ‰ respectively [$\mu \pm 1\sigma$, $n = 9$]) between 27.3 cal. kyr BP and 17.0 cal. kyr BP; (3) relatively depleted $\delta^{15}N$ and $\delta^{13}C$ (2.67 ± 0.39 ‰ and -23.26 ± 0.94 ‰ respectively [$\mu \pm 1\sigma$, $n = 11$]) between 15.5 cal. kyr BP and 6.5 cal. kyr BP; and (4) relatively enriched $\delta^{15}N$ and depleted $\delta^{13}C$ (5.04 ± 0.55 ‰ and -24.35 ± 1.55 ‰ respectively [$\mu \pm 1\sigma$, $n = 13$]) between 5.5 cal. kyr BP and today. Whereas transitional samples exist between clusters 1 and 2 (27.3 cal. kyr BP) and 2 and 3 (17.0 cal. kyr BP), the change in sediment geochemistry is very marked between clusters 3 and 4 with a boundary therefore between 6.5 cal. kyr BP and 5.5 cal. kyr BP.
Figure 4.18: Biplots of paired elemental (total organic Carbon [TOC] and Nitrogen [TN]) and stable isotopic data ($\delta^{13}$C and $\delta^{15}$N) from the Lake Pupuke composite sequence. Note that C/N ratios did not require correction for inorganic Nitrogen. Four clusters of geochemically similar sediment samples (e.g., deposited under similar limnological and diagenetic conditions) are apparent in a biplot of $\delta^{15}$N by $\delta^{13}$C (~47.8-28.8 cal. kyr BP, ~27.3-17.0 cal. kyr BP, ~15.5-6.5 cal. kyr BP and from ~5.5 cal. kyr BP until today). Two clusters are apparent in a biplot of $\delta^{15}$N by C/N atomic ratios (~47.8 cal. kyr BP and ~3.8 cal. kyr BP until today). Anomalous samples are highlighted in red. A single sample (~6.5 cal. kyr BP) belongs to separate geochemical clusters depending on which biplot is selected and is highlighted in green.
4.5 Discussion

The allochthonous supply of clastic and organic matter (OM) via erosion, in addition to the autochthonous production of OM, controls the rate of lacustrine sedimentation (Dearing, 1991). Thus changes in environment can alter the balance of sediment production between catchment and lake, altering corresponding sediment geochemistry (Meyers and Teranes, 2001). Changes in pore-water conditions can also result in diagenetic changes to sediment geochemistry (Holmer and Storkholm, 2001). Changes in erosion, productivity and REDOX can drive variation in physical and geochemical paleolimnologic proxies (Last and Smol, 2001). Examining changes to each process across a suite of proxies confers greater reliability to discussion of the composite record for paleoerosion, paleoproductivity and paleo-REDOX (Birks and Birks, 2006).

Physical, biological and chemical processes within lakes are intimately linked via feedback mechanisms (Wetzel, 2001). Whilst the paleolimnological records of erosion, productivity and REDOX are treated separately below, synchronous changes reflect the presence of these feedback mechanisms within the composite sequence. For instance, changes in sediment geochemistry likely reflect interactions between erosional supply of minerogenic matter, productive supply of biogenic matter and post-depositional conditions. Coupled to a precise and accurate MER model of age-depth this permits a high-resolution event history for the composite sequence to be constructed (Table 4.5). Owing to the greater temporal resolution and reliability attached to bulk physical and geochemical proxy analyses, subsequent proxy discussions in Chapters 5 and 6 will build upon the inferences discussed below. A synthesis of all physical, geochemical and biological proxies is provided and compared to the NZ-INTIMATE Climate Event Stratigraphy (CES) in Chapter 7.
<table>
<thead>
<tr>
<th>Zones</th>
<th>Paleoerosion</th>
<th>Paleoproductivity</th>
<th>Paleo-mixing and REDOX state</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4 (~6.4 to today)</strong></td>
<td>• Greater coarse (&gt;32 μm) sediment, magnetic susceptibility (MS) and Ti-</td>
<td>• This zone is one of greatest productivity and biomass recorded by heightened total</td>
<td>• Increased seasonal variability in REDOX state occurs from ~5.6 cal. kyr BP recorded by increased denitrification of sedimetary δ¹⁵N and the increased oxygenation of deeper water resulting in greater Mn relative to Fe</td>
</tr>
<tr>
<td><strong>Deep, productive lake</strong></td>
<td>concentration from ~7.6 to 5.7 cal. kyr BP records a brief interval of greater</td>
<td>concentration and flux mark the termination of the LGCP at ~18.5 cal. kyr BP.</td>
<td>• Seasonal variability in REDOX state is driven by changes to the intensity of thermal stratification</td>
</tr>
<tr>
<td></td>
<td>catchment disturbance</td>
<td>Increased TOC, TN and TS concentration and flux recorded by declining productivity</td>
<td>• More intense thermal stratification occurred from ~3.2 cal. kyr BP recorded by greater inorganic Nitrogen content of TN through greater denitrification under intensely reducing conditions</td>
</tr>
<tr>
<td></td>
<td>• Little change to erosion occurs from ~5.7 cal. kyr BP until ~0.6 cal. kyr BP</td>
<td>• Several brief reversals in climatic improvement are recorded by ~15.5 to 13.8 cal. kyr BP and ~12.8 to 12.0 cal. kyr BP</td>
<td>• A lack of changes in δ¹⁵N until ~5.6 cal. kyr BP suggests limited changes to benthic REDOX prior to the coeval onset of thermal stratification</td>
</tr>
<tr>
<td></td>
<td>whereupon greater influx of coarse (&gt;32 μm) sediment of greater Ti-concentration</td>
<td>• Brief reductions in biomass and productivity during the Last Glacial Interglacial</td>
<td>• A lack of changes in δ¹⁵N until ~5.6 cal. kyr BP due to the difficulties of interpreting ITRAX geochemistry</td>
</tr>
<tr>
<td></td>
<td>and MS corresponds to the likely arrival of Polynesian migrants through</td>
<td>Period (LGIT) correspond to enhanced erosion.</td>
<td>• A lack of changes in δ¹⁵N until ~5.6 cal. kyr BP due to the difficulties of interpreting ITRAX geochemistry</td>
</tr>
<tr>
<td></td>
<td>catchment clearance</td>
<td>• An LGIT peak in productivity occurs from ~13.8 to 13.0 cal. kyr BP. A coeval rise in MAR is driven by heightened biomass and productivity between ~14.8 and 12.7 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td><strong>3 (~17.0 to 6.4)</strong></td>
<td>• Reduced erosion occurs from ~18.5 cal. kyr BP with several brief reversals to</td>
<td>• Increasing TOC, TN and TS concentration and flux mark the termination of the LGCP at ~18.5 cal. kyr BP</td>
<td>• No change to mixing or benthic REDOX can be inferred beyond ~17.0 cal. kyr BP due to the difficulties of interpreting ITRAX geochemistry</td>
</tr>
<tr>
<td>**Deep (deepening),</td>
<td>increased influx of clastic sediment</td>
<td>• Several brief reversals in climatic improvement are recorded by ~15.5 to 13.8 cal. kyr BP and ~12.8 to 12.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td>transitional lake**</td>
<td>• A reversal to greater erosion occurs between ~15.5 and 13.8 cal. kyr BP</td>
<td>• Brief reductions in biomass and productivity during the Last Glacial Interglacial</td>
<td>• A lack of changes in δ¹⁵N until ~5.6 cal. kyr BP suggests limited changes to benthic REDOX prior to the coeval onset of thermal stratification</td>
</tr>
<tr>
<td></td>
<td>recorded by increased Ti-concentration, coarse (&gt;32 μm) sediment and magnetic</td>
<td>Period (LGIT) correspond to enhanced erosion.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>susceptibility (MS). This reversal contributes little to increased mass</td>
<td>• An LGIT peak in productivity occurs from ~13.8 to 13.0 cal. kyr BP. A coeval rise in MAR is driven by heightened biomass and productivity between ~14.8 and 12.7 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>accumulation rate (MAR) between ~14.8 and 12.7 cal. kyr BP</td>
<td>• An LGIT peak in productivity occurs from ~13.8 to 13.0 cal. kyr BP. A coeval rise in MAR is driven by heightened biomass and productivity between ~14.8 and 12.7 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• The zone terminates in heightened erosion from ~7.6 to 5.7 cal. kyr BP</td>
<td>• Lower productivity and biomass is recorded by reduced TOC, TN and TS concentration and flux recorded by ~18.5 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td><strong>2 (~28.8 to 17.0)</strong></td>
<td>• Heightened erosion between ~31.5 and 18.5 cal. kyr BP is indicated by greater</td>
<td>• The LGCP is recorded by a rise in C/N ratios and coeval enhancement of erosion indicating a lake level decline and reduction in aquatic biomass between ~28.5 and ~18.5 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td>**Shallow, unproductive</td>
<td>delivery of coarse (&gt;32 μm) clastic sediment, increased dry bulk density</td>
<td>• Two brief periods of enhanced glacial conditions are noted by further decline in already low biomass between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td><strong>lake</strong></td>
<td>(DBD) and reduced water content (Wc)</td>
<td>• Two brief periods of enhanced glacial conditions are noted by further decline in already low biomass between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Increased MAR between ~23.5 and 18.4 cal. kyr BP corresponds to greatest</td>
<td>• Two brief periods of enhanced glacial conditions are noted by further decline in already low biomass between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DBD and least Wc and peak erosion during the Last Glacial Coldest Period</td>
<td>• Two brief periods of enhanced glacial conditions are noted by further decline in already low biomass between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(LGCP)</td>
<td>• Two brief periods of enhanced glacial conditions are noted by further decline in already low biomass between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP</td>
<td></td>
</tr>
<tr>
<td><strong>1 (~47.8 to 28.8)</strong></td>
<td>• Little change occurs to erosional proxies and lake level prior to ~31.5 cal. kyr BP</td>
<td>• Low overall biomass and productivity is recorded by low TOC and TN concentrations and fluxes throughout zone</td>
<td></td>
</tr>
<tr>
<td>**Deep (shallowing),</td>
<td>• Increased delivery of coarse (&gt;32 μm) clastic sediment occurs between ~31.5</td>
<td>• TS concentration and flux declines from ~31.7 cal. kyr BP recording a decline in aquatic productivity until ~16.5 cal. kyr BP through reduced lake level</td>
<td></td>
</tr>
<tr>
<td><strong>unproductive lake</strong></td>
<td>and ~18.5 cal. kyr BP)</td>
<td>• Low overall biomass and productivity is recorded by low TOC and TN concentrations and fluxes throughout zone</td>
<td></td>
</tr>
</tbody>
</table>
4.5.1 Paleoerosion

Hydrologically closed lakes often record simpler responses to changing erosion or sediment delivery than open basins as they lack the filtering effects of fluvial systems, as well as the complicated delivery pathways arising from more numerous sediment sources (Zolitschka, 1998). The small, circular, steep-sided catchments typical of maar lakes offer greater potential to reconstruct paleoerosion. Firstly, because sediment delivery is typically confined to runoff and secondly, because a larger proportion of the catchment is occupied by lake water meaning that even minor changes to vegetation or exposed catchment area may markedly impact upon erosion (Dearing, 1991). The hydrologically-closed status and relatively large proportion of its small catchment occupied by water makes Lake Pupuke particularly sensitive to natural and anthropogenic changes in erosion and sediment delivery (catchment area ~1.85 km\(^2\); ~62 % lake surface).

Erosion and sediment delivery rates are primarily controlled by four factors: (1) precipitation; (2) catchment vegetation; (3) catchment surface area; and (4) anthropogenic activity (Engstrom and Wright, 1984; Berglund et al., 1986). Climate directly controls (1), and also indirectly limits (2) and (3) by determining phytogeographic boundaries, and by altering lake level through changes to the balance of effective precipitation (e.g., precipitative gains minus evaporative losses) (Berglund et al., 1986). Greater precipitation is often accompanied by increased weathering and erosion through increased surface and subsurface discharge (Dearing, 1991). Changes to catchment vegetation are superimposed, increased catchment biomass effectively reducing surface and subsurface flow by interception and evapotranspiration, and vice-versa if biomass is reduced (Engstrom and Wright, 1984). Reduced lake level effectively increases the catchment surface area exposed to aerial weathering and erosion. Shallowing also enables a greater proportion of catchment-derived sediment to be focussed on central, deeper regions increasing both the amount and sizes of clastic particles (Engstrom and Wright, 1984). In addition, rapid changes in lake level can enhance erosion by periodically inundating and drying catchment soil, disturbing vegetation and wave/current scour in an alternating littoral zone (Boyle, 2001). Anthropogenic activity can result in changes to catchment vegetation (e.g., deforestation, disturbance) and hydrology (e.g., irrigation, damming, draining) which typically enhance sediment delivery to lacustrine systems in New Zealand (e.g., Page et al., 2010; Orpin et al., 2010).

Pupuke composite sediment geochemistry is dominated by iron (Fe), titanium (Ti) and cobalt (Co) (in order of decreasing abundance). Aluminium (Al) is much less abundant and poorly separated by micro-XRF from other lighter elements (e.g., Si, P, S, Cl), precluding its use as a paleoerosion indicator. Neolimnological studies have also demonstrated abundant precipitation of iron pyrite (FeS\(_2\)) within the anoxic bottom-waters of Lake Pupuke (Holmes, 1994; see Chapter 2). Formation of iron pyrite is partly dependent on productivity for release of dissolved sulphate in mineralisation of organic sediment (Holmer and Storkholm, 2001). As the abundance of ferromagnetic minerals governs sediment susceptibility to magnetisation, increased biological productivity rather than erosion can therefore alter corresponding MS and Fe-abundance in sediment. Furthermore, dissolution and reprecipitation of ferromagnetic minerals can occur through changing reducing potential in sediment pore-waters.
leading to further post-depositional artefacts in Fe-abundance and MS through ion mobility (Rothwell et al., 2006). Accordingly, Ti-abundance has been selected to monitor downcore changes in erosion as the latter is less susceptible to changing REDOX. Basaltic tephra are however rich in Ti and present throughout the composite sequence with the potential to alter sedimentary TS-abundance through post-depositional reworking (e.g., density-induced settling [see Chapter 3]). Greater emphasis must therefore be attached to changes in particle-size distribution as composite sediments have been sampled to exclude tephra and are finely laminated suggesting little physical reworking.

Although dominated by silt (75.90 ± 5.34 % [μ ± 1σ]) Pupuke composite sediments exhibited marked variation in the proportion of particles >32 μm in size (18.04 ± 7.61 % [μ ± 1σ]). Limited variation prior to ~31.5 cal. kyr BP suggests a relatively stable erosional regime from ~48.2 to 31.5 cal. kyr BP. Increased delivery of coarser particles between ~31.5 and 18.5 cal. kyr BP indicates heightened erosion and sediment delivery during an enhancement of cold, glacial conditions. A similar rise between ~15.6 and 13.2 cal. kyr BP also indicates a return to heightened erosion following an intervening period of climatic amelioration and reduction in erosion. Thereafter declining abundance of coarse particles until ~0.6 cal. kyr BP implies reducing erosion and sediment delivery until a near-recent reversal and increase in erosion. Inspection of MS also underscores heightened erosion between ~31.5 and 18.5 cal. kyr BP with increased MS occurring both at the start and finish of this latter interval: (1) between ~32.1 and 30.3 cal. kyr BP; and (2) between ~20.0 and 18.2 cal. kyr BP. A return to lower MS values in the intervening years suggests that MS profiles are subject to a complicating diagenetic effect (e.g., post-depositional changes in the abundance of ferromagnetic minerals in response to altered REDOX state).

The abundance of particles >32 μm in size records the influx of allochthonous sediment as can be seen by comparing trends in the latter to C/N atomic ratios (Figure 4.19). Increases to the proportion of sediment >32 μm in size between ~18.5 and 31.5 cal. kyr BP are mirrored by increases in C/N values of OM. With the exception of two brief intervals (~15.5-17.8 cal. kyr BP and ~31.3-33.8 cal. kyr BP) trends in C/N throughout the composite sequence correlate significantly with changes to the proportion of particles >32 μm ($r_{32μm,C/N} = 0.52$, $P < 0.01$, $n = 195$). During these intervals an increasing proportion of OM is terrestrial whilst little change in clastic influx occurs (e.g., no change to >32 μm proportion) suggesting a reduction in aquatic productivity. A reduction in aquatic productivity despite increased erosion and delivery of terrestrial nutrients would necessitate a reduction in lake volume. Reduced lake level would simultaneously enable greater catchment area to be eroded by runoff and sub-surface flow, whilst simultaneously enabling coarser material to be focussed on central, shallower regions, thereby offering an explanation of both increased delivery of terrestrial organic matter and larger clastic grain sizes. C/N ratios and the proportion of clastic particles >32 μm in size together suggest reduced moisture availability, increased catchment erosion and lake level decline between ~31.5 and 18.5 cal. kyr BP.

Trends between the percentage of coarse particles (>32 μm), MS and Ti-abundance indicate declining erosion and sediment delivery from ~18.5 cal. kyr BP until an abrupt reversal at ~0.6 cal. kyr BP (Figure 4.19). Declining erosion from ~18.5 cal. kyr BP likely reflects increasing catchment biomass particularly as further proxy evidence
explored below suggest increased productivity at the onset of climatic amelioration following termination of the Last Glacial Coldest Period (LGCP). Lesser changes are again complicated by a likely diagenetic effect in MS and Ti-abundance. For instance, between ~15.7 and 14.6 cal. kyr BP increasing proportions of sediment exceed 32 µm in size. Increasing C/N during this period is further evidence of climatic deterioration reducing aquatic productivity and/or increasing influx of terrestrial OM. However, peaks in MS and Ti-abundance occur later between ~13.2 to 11.3 cal. kyr BP and ~13.6 to 11.3 cal. kyr BP respectively when aquatic productivity had increased, as implied by greater TS, TOC and TN concentration and lower C/N of organic sediment (see below). Changing lake level can explain the changes in dominant OM source (e.g., terrestrial vs. aquatic) with higher lake levels recording a corresponding increase in aquatic OM. Thus, the period ~15.7 to 14.6 cal. kyr BP likely demonstrates reduced lake level favouring terrestrial influx and focussing coarser particles on central basin sediments. Subsequent increases in lake level would necessitate a wetter climate and could therefore result in enhanced Fe-dissolution from catchment soils and deposition of ferromagnetic minerals via pyrite formation related to greater aquatic productivity (see below). Further increases in MS and Ti-abundance between ~8.0 to 5.6 cal. kyr BP and ~7.8 to 5.7 cal. kyr BP respectively, coincide with a subtle increase in the percentage of sediment >32 µm between ~7.2 and 6.2 cal. kyr BP. Given that the catchment would likely have retained greater terrestrial biomass during the Holocene, a reduction in sediment influx at this time is unsurprising. The most marked feature within particle-size distribution over the last ~10 kyr is a marked decline from ~3.4 cal. kyr BP until the rise in all erosional proxies at ~0.6 cal. kyr BP. The latter coincides with a marked decline in terrestrial OM from a mixed to largely aquatic provenance as shown by C/N of OM. A shift to increased relative aquatic productivity would result in deposition of finer organic silts and clays as expressed in the particle size data.

Unlike during earlier erosional events, increased delivery of coarse sediment after ~0.6 cal. kyr BP is not associated with an increase in the proportion of terrestrial vegetation. For instance, C/N ratios remain relatively low and stable at 15.9 ± 2.7 (μ ± 1σ, n = 20) over the last 650 yrs (Figure 4.19). Instead, the timing is coeval with that proposed by the Short Prehistory paradigm for the arrival of Polynesian migrants throughout Northland at ~0.8 cal. kyr BP (Anderson, 1991). Indeed a mechanism of catchment clearance rather than lake-level variation would explain both reduced terrestrial OM-influx and coeval increased erosion and sediment influx to Lake Pupuke. Loss of catchment cover could increase leaching of terrestrial minerals and nutrients thereby coupling MS and Ti-abundance to changes in clastic influx. Accentuated MS and Ti-abundance from ~130 cal. yr BP until today also lacks a corresponding change in catchment vegetation suggesting enhanced anthropogenic activity within the catchment possibly associated with European arrival. For instance, Augustinus et al (2006) infers the arrival of European migrants at ~110 cal. yr BP with the first appearance of non-native pollen (e.g., Pinus spp., Plantago lanceolata).

Changes in erosional influxes are also attested by changes in sediment indices. A strong inverse correlation between trends in water content (Wc) and dry bulk density (DBD) was noted in Chapter 3 (3.6. Lithology and Stratigraphy). Denser sediments are therefore characterised by lesser water content as would be expected if they also possess lesser organic and more clastic content (rDBD,Wc = -0.97, P < 0.001, n = 1420). Inspection of
W<sub>c</sub> by total organic Carbon (TOC) abundance further supports use of W<sub>c</sub> as a proxy for OM content. Stable, low W<sub>c</sub> from ~48.2 to 31.5 cal. kyr BP corresponds to stable, low TOC, whilst increasing W<sub>c</sub> from ~18.5 cal. kyr BP corresponds to increasing TOC from ~18.5 cal. kyr BP. As DBD and W<sub>c</sub> are inversely correlated troughs in W<sub>c</sub> likely correspond to peaks in clastic influx. Erosional events from ~31.5 to 18.5 cal. kyr BP, ~15.5 to 13.8 cal. kyr BP, ~7.8 to 5.7 cal. kyr BP, and from ~0.6 cal. kyr BP to today correspond to marked drops in W<sub>c</sub>, further suggesting the latter represent periods of heightened erosion and sediment delivery. A feature particularly evident in composite DBD is a marked change at ~18.5 cal. kyr; older sediment contains more clastic material (0.38 ± 0.06 g cm<sup>3</sup> [μ ± 1σ, n = 699]) whilst younger sediment is less dense reflecting earlier inferences on markedly reduced erosion after ~18.5 cal. kyr BP (0.20 ± 0.06 g cm<sup>3</sup> [μ ± 1σ, n = 721]) (Figure 4.19).

Inferred changes to erosion also help to explain observed changes in mass accumulation rate (MAR) noted in Chapter 3 (3.6.4. Mass Accumulation Rate). In particular, an increased MAR between ~23.5 and 18.4 cal. kyr BP corresponds to greatest DBD, coarser (>32 μm) sediment and increased MS. Similarly, heightened erosion between ~15.5 and 13.8 cal. kyr BP contributes partially to the observed rise in MAR between ~14.8 and 12.7 cal. kyr BP. However, the latter also stresses the likelihood of other controls on MAR within the composite sequence. For instance, a weak but significant correlation between MAR and percentage of sediment >32 μm highlights that a large proportion of changes to MAR lack a corresponding change in catchment erosion or allochthonous sediment influx (r<sub>MAR,>32</sub> = 0.13, P > 0.10, n = 218). Instead, variations in aquatic productivity have substantially altered rates of sedimentation from ~18.5 cal. kyr BP suggesting limited productivity prior to coeval climatic amelioration. Nonetheless, from examination of physical sedimentary characteristics and changes in sedimentation there appear to have been 4 events of heightened erosion in Lake Pupuke over the last ~48 kyr (presented in Table 4.6).

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<sup>-6</sup> (SI); >32 μm, 18.15 %; and Ti-abundance, 0.0075 cps/inc.

<table>
<thead>
<tr>
<th>Interval of heightened erosion (cal. kyr BP ± 95% uncertainty)</th>
<th>Erosional Proxy (average for interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset</td>
<td>Finish</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>0.6 ± 0.2</td>
<td>Today</td>
</tr>
<tr>
<td>7.8 ± 0.8</td>
<td>5.7 ± 0.8</td>
</tr>
<tr>
<td>15.5 ± 1.1</td>
<td>13.8 ± 0.8</td>
</tr>
<tr>
<td>31.5 ± 1.6</td>
<td>18.5 ± 1.4</td>
</tr>
</tbody>
</table>
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.
4.5.2 Paleoproduction

Carbon and Nitrogen are major constituents of OM such that the total organic Carbon (TOC) and Nitrogen (TN) concentrations of lacustrine sediment record changes in paleoproduction (Talbot, 2001). To a lesser extent, the concentration of total Sulphur (TS) can also record changes in productivity although significant REDOX effects complicate interpretations of downcore TS (Werne et al., 2003). As noted above productivity can be partitioned into autochthonous and allochthonous systems through inspection of C/N ratios, with TOC and TN dependent on both sources and TS largely aquatic in origin (Talbot and Laerdal, 2000; Russell and Werne, 2009). Changes in the proportion of terrestrial vs. aquatic productivity can be aligned to changing lake level, whilst changes in overall productivity offer a record of changing environmental conditions, particularly temperature, precipitation and nutrient availability.

4.5.2.1 Changes to catchment vegetation

The average C/N throughout the composite sequence (24.41 ± 8.33 [μ± 1σ]) reflects a mixed terrestrial and aquatic source of OM supporting earlier insights that the lake has existed in substantive form throughout the last ~48 kyr, although marked variation exists (Figure 4.19). The retention of fine laminae (<1 mm) lacking evidence of bioturbation or wave/current reworking throughout the composite sequence suggest any past changes to lake level were not substantive. For instance at least ~30 m depth is necessary to prevent wave-induced mixing under present boundary conditions (see Chapter 2). However, the large proportion of catchment currently occupied by Lake Pupuke (~62 %) would mean that even subtle changes in lake level would substantially alter catchment area available to colonisation by terrestrial flora, and therein the balance of terrestrial and aquatic productivity.

A clear increase in the proportion of terrestrial OM delivered to lake sediments occurs between ~33.8 and 16.5 cal. kyr BP during earlier identified increased erosion (~31.5 and 18.5 cal. kyr BP). Average C/N ratios prior to ~33.8 cal. kyr BP are 21.71, rising to 30.42 during the latter dominance of terrestrial OM and promptly falling to 21.90 from ~16.5 cal. kyr BP until today. Given the lake has only recently eutrophied (~5 to 6 cal. kyr BP; see below and Chapter 5), it is unlikely that greater supply of limiting nutrients during an intensification of erosion in the LGCP, would restrict aquatic productivity, particularly as the LGCP was likely to be moderately cooler in Auckland (~4-5 ºC [Newnham et al., 2007a]). Instead, to accommodate the likelihood of fertilization by nutrient inwash, a reduction in lake volume between ~31.5 and 18.5 cal. kyr BP is necessary to explain observed reductions in the proportions of aquatic OM within composite sediments. Thus synchronous increases in C/N ratios and proxies for erosion between ~18.5 to 31.5 cal. kyr BP suggest a period of lower lake level corresponding to enhanced sediment delivery to Lake Pupuke (Figure 4.19).

The latter argument is however, too simplistic to explain changes in C/N following reduced erosion from ~18.5 cal. kyr BP. For instance, from 17.8 to 16.5 cal. kyr BP, C/N ratios increase substantially to a maximum of ~75
Instead reduced erosional influx suggests increased catchment vegetation cover, indicative of an amelioration of climate following termination of the LGCP. The dominance of OM influx by terrestrial productivity suggests lake levels did not immediately respond but rather the onset of declining C/N ratios at ~16.5 cal. kyr BP denotes the point at which lake levels rose thereby facilitating greater aquatic productivity and reducing the C/N of lacustrine OM. Using the same logic, an increase in C/N ratios between ~15.5 cal. kyr BP and ~14.2 cal. kyr BP may record a brief reversal and lake low stand followed by a return to deeper water conditions by ~13.7 cal. kyr BP (Figure 4.19). Thereafter until today, C/N ratios decline steadily from 32 to 10, indicating a mixed source of OM with increasing proportions of aquatic OM. Low C/N values from ~3.3 cal. kyr BP until today (16.58 ± 2.65 [μ ± 1σ, n = 52]) imply a further increase in the proportion of OM sourced from algae and aquatic macrophytes. This increasing algal content likely reflects a recent increase in the trophic status of Lake Pupuke.

### 4.5.2.2 Changes to biological productivity

High resolution (~180 yr intervals, n = 269) sedimentary TOC and TN concentrations permit the precise identification of changes in paleoproductivity throughout the Pupuke composite sequence. Variation therein exceeds 19.41 wt. % (TOC) and 1.74 wt. % (TN) which exceeds modern seasonal variability (9.38 wt. % and 0.80 wt. % for TOC and TN respectively). Little change occurs to TOC and TN concentrations prior to ~16.5 cal. kyr BP whereupon sedimentary OM-content more than doubles (Figure 4.20). For instance, respective averages in TOC and TN prior to ~16.5 cal. kyr BP are 9.74 and 0.46 wt. % compared to 17.16 and 1.00 wt. % to today. As C/N ratios decline from ~16.5 cal. kyr BP, increasing proportions of OM are aquatic in origin thereafter. Consequently, changes to TOC and TN appear driven by aquatic productivity with periods of higher C/N coincident with decreased OM-content prior to ~16.5 cal. kyr BP. Two older events of reduced C/N and TOC can also be discerned which enforce this insight and suggest a severe reduction in catchment productivity during the LGCP: (1) a marked decline in TOC between ~27.8 and 26.0 cal. kyr BP; and (2) between ~21.0 and 19.0 cal. kyr BP. Both events are associated with large drops in TOC (9.42 and 7.02 wt. % respectively) and lack of influx of terrestrial OM as inferred from markedly lower C/N values (refer to Figure 4.20). Thus, the declines in TOC correspond to declining terrestrial productivity and point to a marked deterioration in the terrestrial environment. The absence of an effect in TN suggests aquatic productivity was already reduced during these intervals, in line with an inferred drop in lake level. From ~19.0 cal. kyr BP increasing TOC and C/N, coupled to limited changes in TN, also imply a delayed response to climate amelioration associated with a reduction in erosion at the end of the LGCP. Furthermore TN values do not rise until ~16.5 cal. kyr BP suggesting an intervening period of ~2-2.5 kyr for lake level and aquatic productivity to increase. Importantly, the brief rise in C/N ratios between ~15.5 and 14.2 cal. kyr BP corresponds to a decrease in TOC and TN, further underscoring the likelihood of the latter representing a period of reduced aquatic productivity and increased erosion, in line with a brief drop in lake level. Although, latter drops in TOC and TN begin and finish more recently than corresponding C/N change (~14.4 to 13.8 cal. kyr BP) pointing to a delayed lacustrine response.
Concentrations of TOC and TN continue to rise from ~13.8 cal. kyr BP although another brief decline in productivity occurs between ~12.8 and 12.0 cal. kyr BP (Figure 4.20). A similar magnitude and duration of declining TOC and TN concentration in the latter, suggest a similar mechanism to declining productivity between ~14.4 and 13.8 cal. kyr BP. However, a lack of discernible change in C/N ratios at this time indicates reduced biomass within both catchment and water column (Figure 4.20). Subsequently, concentrations of TOC and TN rise markedly between ~10.2 and 8.0 cal. kyr BP implying a period of higher productivity before promptly falling between ~7.6 and 5.7 cal. kyr BP. From ~5.7 cal. kyr BP, TOC and TN both rise and remain high indicating a return to increased productivity. Notably prior to ~6.2 cal. kyr BP, TOC and TN are very closely correlated despite marked changes in OM-provenance as inferred from C/N variation. However, from ~6.2 cal. kyr BP to today, relative increases in TN exceed those of TOC. Whilst C/N ratios continue to decline and increasing algal contributions have resulted in a greater concentration of TN relative to TOC, markedly reduced C/N ratios do not appear until ~3.3 cal. kyr BP (Figure 4.20). Therefore this could record the preferential mineralisation and loss of TOC from sedimenting OM, as presently occurs through methanogenesis under reducing conditions generated by thermal stratification (see Chapter 2). From ~6.2 cal. kyr BP to today, it seems highly likely that an increase in algal productivity in addition to a change in the diagenesis of sedimentary OM has occurred, possibly in response to the onset of intense thermal stratification.

The application of TOC and TN as paleoproductivity indicators is hindered by the potential for changes in concentration to arise through dilution or concentration of OM by changing erosion and sediment delivery rather than a change in productivity (Meyers and Teranes, 2001). Normalisation of TOC and TN by MAR to Carbon and Nitrogen accumulation rates (CAR, NAR) enable changes in productivity to be correctly identified beyond changes in erosion and sediment delivery. Trends in CAR, NAR and MAR are presented in Figure 4.20. Changes in MAR appear to drive much of the changes in CAR ($r_{\text{MAR,CAR}} = 0.88$, $R^2 = 0.77$, $P < 0.001$, $n = 270$) and NAR ($r_{\text{MAR,NAR}} = 0.80$, $R^2 = 0.60$, $P < 0.001$, $n = 270$). Enhanced MAR between ~23.3 and 18.0 cal. kyr BP is ascribed to increased erosion and sediment delivery, driving a corresponding increase in CAR and NAR either through the influx of greater allochthonous organic matter and/or through a likely artefact of flux calculation – elemental fluxes are the product of concentration (wt. %) and MAR meaning any change to MAR will be expressed in elemental flux even if no change in elemental concentration occurs. The peak in MAR between ~14.8 and 12.7 cal. kyr BP does not coincide directly with enhanced erosion. Instead, increased erosion between ~15.6 and 13.2 cal. kyr BP corresponds to the initial rise in MAR. Declining percentage of coarse sediment >32 μm from ~14.5 to 13.1 cal. kyr and corresponding increases in Wc, TOC and TN, suggest a period of limited erosion and substantially higher productivity coincident with the peak in MAR at ~13.3 cal. kyr BP (Figure 4.20).

An initial increase in catchment erosion is therefore followed by an abrupt increase in biological productivity. Likewise, increased MAR between ~10.0 and ~7.6 cal. kyr BP corresponds to relatively low MS, finer clastic particles and reduced Ti-abundance excluding erosion as a causal mechanism. Instead a coeval increase in TOC and TN during this period indicates the onset of the Holocene and a climatic optimum for productivity,
before a drop in productivity and increase in erosion and sediment delivery commencing ~7.6 cal. kyr BP. Despite the drop in CAR and NAR at ~7.6 cal. kyr BP, MAR continues to remain elevated supporting earlier inferences that the period ~7.6 to 5.7 cal. kyr BP is one of increased erosion. From ~5.7 cal. kyr BP, a greater concentration of TOC and TN is coupled with increasing MAR indicative of substantial increases to aquatic biomass. In line with changes to provenance that imply an increasing algal component, this suggests marked eutrophication of Lake Pupuke in the mid Holocene. The last ~650 yrs are characterised by an exponential rise in CAR and NAR whose coincidence with peaks in erosional influx suggest greater aquatic biomass resulted from catchment modification and influx of terrestrial nutrients.

A complex series of changes in terrestrial and aquatic productivity can be reconstructed for the composite sequence (refer to Figure 4.20 and Table 4.7). This offers remarkable insight to the causes of altered mass accumulation within Lake Pupuke over the last ~48 kyrs, including increased productivity preceded by enhanced erosion at ~13.8 cal. kyr BP, an early Holocene peak between ~10.0 and 7.6 cal. kyr BP and increased productivity corresponding to the recent eutrophication of Lake Pupuke beginning ~5.0-6.2 cal. kyr BP:

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

<table>
<thead>
<tr>
<th>Biological Productivity</th>
<th>Interval (cal. kyr BP ± 95% uncertainty)</th>
<th>Productivity Proxy (average for interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>Finish</td>
</tr>
<tr>
<td><strong>Major changes during the last ~48.2 cal. kyr BP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>18.5 ± 1.4</td>
<td>Today</td>
</tr>
<tr>
<td>Low</td>
<td>48.2 ± 4.7</td>
<td>18.5 ± 1.4</td>
</tr>
<tr>
<td><strong>Millennial-scale change during the last ~18.5 cal. kyr BP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>5.7 ± 0.8</td>
<td>Today</td>
</tr>
<tr>
<td>Falling</td>
<td>7.6 ± 0.8</td>
<td>5.7 ± 0.8</td>
</tr>
<tr>
<td>High</td>
<td>12.0 ± 0.7</td>
<td>7.6 ± 0.8</td>
</tr>
<tr>
<td>Transitional</td>
<td>12.8 ± 0.7</td>
<td>12.0 ± 0.7</td>
</tr>
<tr>
<td>High</td>
<td>13.8 ± 0.8</td>
<td>12.8 ± 0.7</td>
</tr>
<tr>
<td>Transitional</td>
<td>18.5 ± 1.4</td>
<td>13.8 ± 0.8</td>
</tr>
<tr>
<td><strong>Millennial-scale change from ~48.2 to 18.5 cal. kyr BP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>21.0 ± 1.4</td>
<td>19.0 ± 1.4</td>
</tr>
<tr>
<td>*Low</td>
<td>27.6 ± 2.3</td>
<td>26.0 ± 2.2</td>
</tr>
</tbody>
</table>

* Note these values are artificially high due to unusually high influx of minerogenic sediment under increased erosion and sediment influx, which has driven a corresponding increase in CAR and NAR with despite a drop in TOC and TN.
Figure 4.2: 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.
4.5.3 Total Sulphur: A Novel Proxy for Paleoproductivity and Mixing

The abundance of sulphur in lacustrine sediments has been shown to be a powerful proxy for paleoclimate in paleolimnological reconstructions (Mayer and Schwark, 1999; Mora and Hinnov, 2005). Almost all Sulphur reaching a lake is delivered by weathering and oxidation reactions in catchment soils (Russell and Werne, 2009). S-input therefore varies with changes to precipitation and runoff although subsequent sedimentation into bottom sediments is dependent upon the conversion of dissolved sulphate to reduced sulphur by sulphate reducing bacteria (SRB) under anoxic conditions (producing H₂S) (Werne et al., 2003). Greater sulphur will be retained by sediments richer in iron and capable of producing iron pyrite (FeS₂) (Berner, 1970). Similarly, under reducing conditions, sulphur will bind with OM to generate stable organic sulphur (Werne et al., 2004). Thus the concentration of total sulphur (TS) might offer a record of productivity and reducing potential (Russell and Werne, 2009). However, the complexities inherent to the lacustrine S-cycle and the spatio-temporal heterogeneity of lacustrine conditions (e.g., partitioning of TS within the water column through environmental interactions dependent upon the supply of OM, dissolved sulphate and iron as well as changes to REDOX conditions) have hindered application of TS to paleolimnological study (Russell and Werne, 2009).

Modern sedimentary concentrations of TS within Lake Pupuke are driven primarily by productivity with a spring peak in TS and TOC (Section 4.3. The Modern Geochemical Framework of Lake Pupuke). Relatively high summer concentrations of TS during the seasonal TOC-minima also demonstrate the functional role of REDOX state; heavily reducing conditions within deeper waters, favouring sulphate reduction to iron pyrite. Sulphate reducing bacteria (SRB) are inhibited from reducing dissolved sulphate by greater oxygenation thereby explaining a drop in TS-concentration during Autumn/Winter months (e.g., during overturn and benthic ventilation). An examination of changes in TS-concentration and flux over the composite sequence could therefore contribute further insight into productivity and the strength of water column mixing. Any discrepancy with highlighted periods of changing productivity can help identify likely periods of enhanced and/or weak benthic anoxia (refer to Figure 4.21).

Downcore variation in TS exceeds modern seasonal variation (2.58 wt. % compared to 0.29 wt. % respectively) suggesting that marked change has occurred to paleoproductivity and/or mixing over the last ~48 kyr (Figure 4.21). A significant and moderate, positive correlation with TOC-concentration suggests an important link to productivity ($r_{TS,TOC} = 0.55, P < 0.001, n = 263$). For instance, clear similarities include increasing TS and TOC concentrations from ~16.5 to 14.7 cal. kyr BP followed by reduced concentrations until ~13.6 cal. kyr BP whereupon TS values rise to their series maximum at ~13.0 cal. kyr BP coeval with increases to biological productivity. Increased erosion and a likely drop in lake level between ~12.8 and 12.0 cal. kyr BP is marked by declining TS and TOC concentrations suggesting a consequent drop in aquatic productivity. Peak TOC concentrations between ~10.2 and 8.0 cal. kyr BP are also marked by exceptionally high concentrations of TS suggesting greater biomass and heavy reducing conditions (e.g., deep lake). However, marked dissimilarities between TOC and TS are readily apparent. For instance, despite relatively low concentrations of TS in
composite sediments prior to ~16.5 cal. kyr BP there is a marked rise of ~0.98 % between ~31.4 and 31.7 cal. kyr BP which continues until ~48.2 cal. kyr BP. Changes to TS-concentration are likely to have occurred through changing REDOX conditions in pore-waters such that reduced TS concentration corresponds to lesser reducing potential (Russell and Werne, 2009). A drop in TS between ~31.5 and 16.5 cal. kyr BP therefore supports an inferred reduction of aquatic productivity and lake level over the same time interval. Lowered lake level could increase benthic oxygenation by enhancing mixing, impairing the capacity for SRB to reduce dissolved sulphate to H_2S, and limiting precipitation of FeS_2. The period ~31.7 to 48.2 cal. kyr BP is therefore likely to have been accompanied by a deeper lake with sufficient depth to generate strong reducing conditions.

Another discrepancy between TOC and TS records is the marked rise in TOC following a highly disturbed phase between ~7.6 and 5.7 cal. kyr BP which is not accompanied by a rise in TS (Figure 4.21). Thus, increased biomass occurred either during a decline in lake level or an increase to lake mixing (e.g., to prevent reduction of dissolved sulphate). The decline of erosional influx from ~5.7 cal. kyr BP precludes a drop in lake level as this would have focussed coarser particles on coring locations (Section 4.5.1. Paleoerosion). Increased mixing from the mid-Holocene is therefore likely to be the cause of relatively low TS from ~5.7 cal. kyr BP. A further reduction in TS also occurs at ~1.8 cal. kyr BP, also during a period of relatively stable, high TOC-concentration (Figure 4.21). This is further evidence of enhanced mixing and a likely increase in windiness and/or thermal stratification at Lake Pupuke during the Holocene, both of which can deliver greater dissolved Oxygen to deeper water (e.g., by waves/currents and overturn respectively).

Trends in Sulphur accumulation rate (SAR) also largely mirror those of Carbon (CAR) further underscoring the response of composite TS-concentrations to changes in paleoproductivity (Figure 4.21). Higher lake level from ~48.2 to 31.5 cal. kyr BP is inferred from higher SAR whereupon lowered SAR until ~16.5 cal. kyr BP indicates reduced benthic anoxia and/or aquatic productivity (with an apparent MAR-artefact resulting in a brief increase between ~23.5 and 18.4 cal. kyr BP). Whilst SAR rises from ~16.5 cal. kyr BP until today, marked increases do not occur until ~13.8 cal. kyr BP (peaking at ~13.0 cal. kyr BP), supporting earlier arguments for markedly greater aquatic productivity driving a coincident peak in MAR at ~13.3 cal. kyr BP. Furthermore, enhanced aquatic productivity is also apparent in greater SAR between ~10.2 and 8.0 cal. kyr BP as well as a recent likely eutrophication of Lake Pupuke from ~5.0-6.2 cal. kyr BP to today.
Chapter Four

Figure 4.2

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.
### 4.5.4 Change to Mixing and Benthic REDOX

Several sedimentary components offer an insight to changes in the degree of water column mixing and benthic REDOX conditions. The importance of reducing conditions in the formation of iron pyrite and organic sulphur compounds from dissolved sulphate has been discussed above. However, greater reducing potential also favours greater relative dissolution of manganese (Mn) over iron (Fe) in lacustrine sediments (Shanahan et al., 2008). Thus the ratios of Mn/Fe offer the potential to record changing paleo-REDOX. The primary controls on the latter will therefore be depth (greater depth permitting stable benthic anoxia) and thermal stratification (mixing is presently limited to overturn during July and August).

An apparent drop in Mn/Fe from 16.5 cal. kyr BP until today supports earlier inferences of a delayed rise in lake level following earlier termination of the last Glacial at ~18.5 cal. kyr BP (Figure 4.22). In this case lowered lake level would permit greater benthic oxygenation by wave-induced mixing and therefore greater abundance of Mn relative to Fe. Reductions in the Mn/Fe ratios from ~14.0-13.2 cal. kyr BP indicate lesser mixing and greater benthic anoxia. Coupled to an inferred drop in erosion from ~13.8 to 12.8 cal. kyr BP this supports an inferred rise in lake level as does a drop in Mn/Fe between 11.2 and 9.6 cal. kyr BP. A more marked drop in Mn/Fe ratios occurs between ~7.1 and 5.8 cal. kyr BP and suggests a period of very limited mixing or deeper lake level, and is coeval with an inferred rise in erosion and disturbance to terrestrial vegetation (e.g., drop in C/N ratios and increase in mean particle size) (Section 4.5.1. Paleoerosion).

Increased Mn/Fe ratios from ~5.6 cal. kyr BP indicate an abrupt return to greater seasonal oxygenation of deeper water and benthic sediment in the mid Holocene. Thereafter, higher Mn/Fe ratios are expressed to today and a present hydrological regime governed by thermal stratification. This suggests the capacity for overturning waters in July and August to better oxygenate benthic sediments at holomixis. In turn this suggests that prior to the onset of thermal stratification, wave-induced mixing resulted in lesser oxygenation of benthic waters. Importantly this then offers a mechanism to explain the observed natural eutrophication of Lake Pupuke ~5-6 cal. kyr BP because stronger seasonal mixing associated with thermal stratification would then redistribute essential nutrients to surface waters, and resulting in the contemporary pattern of Spring algal blooms following overturn (see Chapter 2) and offering a causative mechanism for increasing algal components of OM from ~6.2 cal. kyr BP to today (e.g., declining C/N ratios) (Figure 4.22).

Changes in the degree of lake mixing can also be revealed by inspection of the composite δ¹⁵N series. The modern N-cycle within Lake Pupuke is linked to denitrification, in particular the production of ammonia from detrital OM (principally as NH₄⁺). In Chapter 2 a strong correlation was demonstrated between dissolved TN and NH₄⁺ concentration ($r_{TN,NH4} = 0.83$, $p < 0.01$, $n = 19$). Reduction of nitrate and nitrite to ammonia occurs only under particularly stable anoxic conditions (Talbot, 2001). Thus denitrification within Lake Pupuke reflects the seasonal pattern of thermal stratification with peak NH₄⁺ concentration expressed by hypolimnetic waters during peak summer stratification. The onset and magnitude of denitrification therefore offers a proxy for onset and strength of thermal stratification within composite sediments.
Figure 4.2: 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 δ¹⁵N-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).
Increasing TN-concentration in line with rising TOC-concentration throughout the last ~18.5 kyr suggests little diagenetic loss of TN relative to TOC and therein, limited impact of denitrification upon sedimentary TN-concentration. However, subtle changes in denitrification are likely to be recorded in the isotopic ratios of $^{15}\text{N}/^{14}\text{N}$ ($\delta^{15}\text{N}$) whereby the lower activation energy of $^{14}\text{N}$ ensures its preferential incorporation into ammonia, leaving sediment more enriched in $^{15}\text{N}$ (Talbot, 2001). For instance, permanent stratification of oceanic waters enables a diagenetic $^{15}\text{N}$-enrichment of 3-7 ‰ in marine organic sediment (Altabet and Francois, 1994). Thus, changes in the N-isotopic composition of Pupuke composite sediment can also be used to infer changes to reducing potential throughout the composite sequence whereby greater and lesser reducing potential results in enrichment and depletion of $\delta^{15}\text{N}$ respectively. In support of our earlier argument for the onset of intense thermal stratification to have begun at ~5.6 cal. kyr BP and continuing until today, composite $\delta^{15}\text{N}$ values undergo substantial enrichment (~1.92 ‰) at ~5.5 cal. kyr BP. Indeed $\delta^{15}\text{N}$ values remain heavily enriched from ~5.5 cal. kyr BP until today stressing the continued likely effects of strong thermal stratification throughout the mid-to-late Holocene (Figure 4.22). Stratification acts to limit the availability of dissolved inorganic Nitrogen (DIN) within the epilimnion causing a corresponding enrichment of algal OM in $\delta^{15}\text{N}$, whilst simultaneously leading to the denitrification and enrichment of $\delta^{15}\text{N}$ in detrital sediment within the hypolimnion (e.g., Talbot and Laerdal, 2001).

![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.]
Examination of the linear relationships between TOC and TN in Pupuke composite sediments further underscores the likelihood of denitrification occurring after ~5.6 cal. kyr BP (Figure 4.23). Although statistically insignificant, the relationship between ~5.6 cal. kyr BP and today possesses markedly greater inorganic Nitrogen than older sediment (positive intercept of 0.23 respectively [equivalent to wt. % TN contamination]). Greater inorganic Nitrogen content likely represents the retention of ammonia by clays and colloids as occurs through ammonification, a process capable of substantially enriching $\delta^{15}$N but also dependent on highly reducing conditions (e.g., associated with a stratified water column) (Talbot, 2001). If only samples younger than ~3.2 cal. kyr BP are employed, a positive intercept of 0.08 (wt. % contamination of TN) is coupled to a significant correlation coefficient ($r_{TOC,TN} = 0.56, P < 0.05, n = 52$) suggesting whilst the onset of denitrification may lie at ~5.6 cal. kyr BP, production and retention of ammonia appears markedly greater from ~3.2 cal. kyr BP (Figure 4.23).

The onset of intense stratification at ~5.6 cal. kyr BP can therefore be aligned to increasing algal productivity through the generation of essential nutrients under seasonal anoxic conditions and return to surface waters by more intense mixing associated with holomixis. For instance, XRF-inferred Fe-abundance, normalised to erosional influx (e.g., Fe abundance divided by detrital Ti), increases from ~6.4 cal. kyr BP indicating greater autochthonous production of Fe-compounds (Figure 4.22). The onset of thermal stratification offers a causative mechanism, primarily through precipitation of iron pyrite under reducing conditions present in the hypolimnion. Precipitation of iron pyrite typically results in displacement of iron-bound phosphate to anoxic overlying waters (Wetzel, 2001). Overturning circulation will then return dissolved phosphate to the epilimnion. As phosphate is a key limiting micronutrient within lacustrine ecosystems, its regeneration and supply to surface waters would fertilize aquatic producers (Wetzel, 2001). In addition, denitrification of organic matter under benthic anoxia would result in the production of ammonia (Wetzel, 2001). Ammonia is readily fixed to dissolved nitrite and then nitrate by nitrifying bacteria, particularly cyanobacteria, which are abundant within the water column and as colonizing mats within Lake Pupuke (e.g., Holmes, 1994). Wetzel (2001) notes that rates of $N_2$-fixation are enhanced when productivity is increased through phosphate fertilization. Thus release and return of phosphate through seasonal stratification could increase $N_2$-fixation and nitrification of ammonia within the epilimnion following reduction of organic Nitrogen to ammonia in anoxic bottom waters. Consequently, the onset of thermal stratification in the mid Holocene can explain a coincident rise in aquatic productivity through regeneration of orthophosphate and ammonia, enhanced nitrification at the oxycline and more intense mixing returning essential nutrients to the productive photic zone. Stratification would favour seasonal Spring algal blooms as presently occurs in response to mixing (Cassie, 1989; Holmes, 1994). Highly seasonal algal productivity would have increased competition for DIN, in turn reducing algal discrimination against heavier $^{15}$N and enriching organic sediment in $\delta^{15}$N. In addition, the diagenetic enrichment of composite $\delta^{15}$N has intensified from ~3.2 cal. kyr BP until today, under heavily reducing conditions necessary for ammonification. Enhanced ammonification is demonstrated by increased proportions of inorganic Nitrogen amongst corresponding sediment which likely corresponds to greater retention of ammonia by adsorption onto clays (e.g., Talbot, 2001).
4.5.5 Carbon Stable Isotopes: A complex story of changing $\rho$CO$_2$, productivity and mixing

Lacustrine stable Carbon isotopic composition ($\delta^{13}$C) varies in response to the changing availability of dissolved inorganic Carbon (DIC) incorporating responses to changes in alkalinity, productivity and atmospheric Carbon availability ($\rho$CO$_2$) (Meyers and Lallier-Vergès, 1999). Numerous paleolimnological investigations have reconstructed the marked drop in $\rho$CO$_2$ during Marine Oxygen Isotope Stage 2 (MIS 2; $\rho$CO$_2$ decline of 80-100 p.p.m.v. [Leuenberger et al., 1992]) as a marked enrichment of $\delta^{13}$C in lacustrine OM (Meyers and Horie, 1993; Ficken et al., 1998; Street-Perrott et al., 2004; Morley, 2005). The latter is also coincident with the enhancement of glacial conditions described as the Last Glacial Coldest Period in New Zealand (LGCP) (e.g., Alloway et al., 2007). In addition to changing atmospheric CO$_2$-availability, changes to the availability of dissolved inorganic Carbon (DIC) will also become incorporated into lacustrine $\delta^{13}$C records (Meyers and Teranes, 2001). For instance, reduced DIC will favour lesser discrimination against heavier $^{13}$C with a consequent enrichment of sedimentary $\delta^{13}$C (Meyers and Teranes, 2001). Marked reduction in DIC coupled to increased pH will favour uptake of dissolved bicarbonate whose $\delta^{13}$C-signature is markedly less depleted than atmospheric CO$_2$ (-1 ‰ compared to -7 ‰ respectively [O’Leary, 1988; Keeley and Sandquist, 1992]). As with changes to TOC-concentration, diagenetic changes within $\delta^{13}$C are also possible with greater mineralisation favouring enrichment of remnant TOC (Meyers and Lallier-Vergès, 1999). Thus, changes in $\rho$CO$_2$, alkalinity, DIC availability and bacterial heterotrophy can alter the $\delta^{13}$C of organic sediment produced by aquatic flora.

The Pupuke composite sequence exhibits marked variation in $\delta^{13}$C with little similarity to changing overall productivity ($f_{\delta^{13}C,TOC} = -0.14, P > 0.001, n = 266$) (Figure 4.24). The most notable feature is a broad enrichment of sedimentary $\delta^{13}$C between ~28.8 and 18.3 cal. kyr BP. The period ~31.5 until 18.5 cal. kyr BP is characterised by lower TS and TN concentration supporting an inferred drop in aquatic productivity so that enriched $\delta^{13}$C is unlikely to reflect heightened productivity during the latter period. Similarly, a corresponding shift to increasing proportions of terrestrial OM within composite sediment would favour depletion of sedimentary $\delta^{13}$C as atmospheric reservoirs are typically well mixed and less limiting than aquatic (Meyers and Teranes, 2001). Instead, the coincident timing of enriched sedimentary $\delta^{13}$C with lowered $\rho$CO$_2$ during the LGCP hints at greater incorporation of heavier $^{13}$C by primary producers in response to the lesser availability of atmospheric CO$_2$ and by association, DIC. Little variation about this enriched signature and limited corresponding variability about paleo-$\rho$CO$_2$ during this interval further hints at composite sediment geochemistry offering a record of changing availability of atmospheric CO$_2$ prior to ~18.5 cal. kyr BP. An inferred drop in lake level between ~31.5 and 18.5 cal. kyr BP can then be tied to enhanced glacial conditions during the LGCP (see above).

A transitional period of increasingly depleted $\delta^{13}$C from ~18.3 cal. kyr BP continues until ~9.3 cal. kyr BP in line with increasing $\rho$CO$_2$. However, a marked enrichment of ~2‰ occurs between ~13.8 and 13.6 cal. kyr BP (Figure 4.24). Little change to corresponding C/N ratios precludes the likelihood of varying OM-source as cause for $\delta^{13}$C-variation. Instead, a coeval peak in paleoproductivity indicators (TOC, TN, and TS concentration and fluxes) was earlier aligned to increased mass accumulation between ~14.8 and 12.7 cal. kyr BP. Increased productivity results in greater demand on DIC. Consequently, the latter $\delta^{13}$C isotope excursion could represent
reduced DIC-availability and greater uptake of bicarbonate by aquatic flora with a consequent $^{13}\text{C}$-enrichment of organic Carbon. Enrichment of sedimentary $\delta^{13}\text{C}$ between $\sim$9.3 and 8.0 cal. kyr BP also corresponds to increased productivity and sedimentation of OM. Thus marked climatic improvement resulting in greater productivity between $\sim$10.2 and 8.0 cal. kyr BP likely also resulted in uptake of isotopically heavier bicarbonate during the early Holocene.

Middle and late Holocene $\delta^{13}\text{C}$-enrichment events between $\sim$6.5 and 5.7 cal. kyr BP, $\sim$4.2 and 2.9 cal. kyr BP, and $\sim$1.8 and 1.5 cal. kyr BP are also associated with increasing aquatic productivity and the likely onset of stratification in the middle Holocene (Figure 4.24). In 4.2, The Modern Geochemical Framework of Lake Pupuke it was noted that sedimentary organic Carbon collected during thermal stratification is enriched relative to organic sediment collected during overturn (-20.54 ‰ compared to -24.91 ‰). Presumably, the onset of seasonal stratification results in isolation of the hypolimnetic DIC reservoir which limits the availability of DIC within the epilimnion from September until June thereby forcing primary producers to fix more dissolved $^{13}\text{CO}_2$ or $^{13}\text{HCO}_3^-$. Surface waters in Lake Pupuke can exhibit pH $>$ 9.0 during heightened spring and summer productivity with a consequent change in alkalinity supporting increased uptake of bicarbonate by primary producers resulting in greater incorporation of enriched $^{13}\text{C}$ (Section 2.4.1.4. pH). The likely onset of intense thermal stratification in Pupuke at $\sim$6 to 5 cal. kyr BP then offers a mechanism to explain $^{13}\text{C}$-enriched sediment. Coupled to greater algal productivity particularly from $\sim$3.3 cal. kyr BP, the younger periods of $^{13}\text{C}$-enrichment likely reflect lesser DIC amongst surface waters either through enhanced productivity and/or weaker overturn resulting in lesser mixing of hypolimnetic DIC, and a consequent uptake of heavier isotopic forms of DIC.

Earlier we noted marked changes in TOC and TN concentration and isotopic composition at $\sim$28.5, $\sim$16.5 and $\sim$6.0 cal. kyr BP (Section 4.5.8. Geochemical Zonation Analyses). Inferring physical proxy boundaries are closely aligned to those identified through biplot zonation suggesting geochemical cycles are intimately linked to erosional and lake-level variability, and therein confirming the likelihood of marked paleoenvironmental change recorded by the $\delta^{13}\text{C}$ composition of composite sediment. Subsequent proxy investigations in Chapters 5 and 6 will add further detail prior to a comparison with the NZ-INTIMATE climate event stratigraphy to determine if the above events are local to Lake Pupuke or representative of the regional Northern North Island (NNI) (see Chapter 7).
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 $\delta^{13}C$ from $-28.8$ to $18.3$ cal. kyr BP records the global drop in $pCO_2$ 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 $\delta^{13}C$ from the middle Holocene are driven by varying intensities of thermal stratification, moreover overturn, limiting the recirculation and availability of DIC in the epilimnion.
4.6 Summary

Bulk geochemical and physical proxies for erosion, productivity and benthic REDOX record marked changes to Lake Pupuke during the last ~48 kyr. A key feature of the Pupuke composite sequence is the absence of total lake desiccation and continuous deposition of undisturbed, finely laminated lacustrine sediment. Inferences of paleoerosion do, however, suggest marked changes to lake level associated with changes in effective precipitation. Higher lake level corresponds to the interval ~48.2 to ~28.5 cal. kyr BP with reduction commencing ~31.5 cal. kyr BP, suggesting preceding years were particularly mild and relatively humid. Inferred lowest lake level is associated with the Last Glacial Coldest Period (LGCP) as reconstructed from a greater abundance of coarse clastic particles, terrestrial organic matter and reduced aquatic productivity and benthic REDOX to occur between ~28.5 and 18.5 cal. kyr BP. Thereafter, during the transition from full glacial to present interglacial (Last Glacial Interglacial Transition [LGIT; ~18.5 to 10.2 cal. kyr BP]), a brief paleoclimate deterioration from ~15.5 to 13.8 cal. kyr BP is recorded by reduced coeval aquatic productivity. This event precedes a period of abundant productivity coupled to massive increases in organic sedimentation from ~13.8 to 13.0 cal. kyr BP, peaking at ~13.4 cal. kyr BP. The LGIT is a variable period of transitional paleoclimate which terminates with the initiation of abundant floral productivity during the early Holocene (~10.2 to 8.0 cal. kyr BP), a period characterised by higher lake level and denoted by markedly greater organic Carbon and Nitrogen influx.

Marked variations in effective precipitation could play a significant role in explaining changes to productivity within Lake Pupuke in a similar fashion to other parts of the Northern North Island (NNI) (e.g., Newnham et al., 1993; Newnham, 1999), not just during heightened glacial activity in the LGCP or variable ameliorating climate in the LGIT, but throughout the Holocene. For instance, marked changes in the trophic status of Lake Pupuke, including its natural eutrophication from ~6.0-5.0 cal. kyr BP, are associated with substantial changes to benthic REDOX state at the onset of intense thermal stratification ~5.6 cal. kyr BP. A causative mechanism has been suggested here which focuses on the greater seasonality of REDOX conditions associated with stratification, principally the regeneration of essential nutrients through benthic anoxia for much of the year coupled to nutrient recirculation into a productive epilimnion during seasonal overturn. Changes in the degree of mixing and benthic REDOX are likely responsible for subtle changes to paleoproductivity including a marked increase in algal productivity from ~3.3 cal. kyr BP until today associated with more intense ENSO-variability and greater seasonality across the NNI in the late Holocene (Shulmeister et al., 2001; Newnham et al., 2007a). Most recently, the arrival of Polynesian migrants and associated clearance of terrestrial vegetation is evidenced by reduced terrestrial productivity, increased leaching of catchment minerals through reduced vegetation cover and greater erosional influx commencing ~0.6 cal. kyr BP. Continued, abundant aquatic productivity distinguishes this event from any other natural response during the last ~48 cal. kyr BP at Lake Pupuke, underscoring the likelihood of an anthropogenic rather than natural cause. Further increased terrestrial minerogenic influx is proposed with the arrival of European migrants and more intensive catchment activity at AD 1840.
CHAPTER FIVE

The Paleolimnology of Lake Pupuke inferred from Diatom Fossil Assemblies

5.1 Introduction to Paleoecology

Microalgae are particularly robust proxies for past environment owing to their cosmopolitan distribution and contribution to biomass in many aquatic ecosystems, broad ecological and environmental tolerances, rapid regeneration times and comprehensively studied ecologies (Korhola, 2007). Application of biotic indicators to geochemical and physical data confers multiproxy paleolimnologic approaches with the greatest reliability and insight to past environment (Birks and Birks, 2006). The Pupuke composite sediment series has thus been subsampled for diatom analysis from which to reconstruct qualitative and quantitative paleohydrology during the last ~48.2 kyrs. The complex nature of diatom responses to changing hydrology and wide range of analytical approaches available require a full review of diatom-inferred paleolimnology. A complimentary overview and synthesis of diatom paleolimnology with earlier geochemical and physical inferences is offered in Chapter 7. Thus, in this chapter diatom microfossil remains will be examined at Lake Pupuke to reveal further insight into reconstructed climate and lake environment beyond the prior interpretation of bulk geochemical and physical proxy indicators (Chapter 4).

5.1.1 Diatoms as Paleoecologic Indicators

Diatoms are autotrophic unicellular algae of the order Bacillariophyta (three classes: Fragilariophyceae, Bacillariophyceae and Coscinodiscophyceae) capable of growth in oceanic and freshwater habitats (Round et al., 1990). Notable diatom characteristics include their bipartite siliceous thecae (valves) that comprise a singular frustule, ubiquity throughout oceanic and freshwater photic zones, rapid rate of reproduction and established autecologies (Round et al., 1990). Siliceous valves are held together by siliceous belts or girdles (Figure 5.1) (Round et al., 1990). This incorporation of amorphous silica into frustules enables diatom microfossils to readily preserve in many aquatic sedimentary environments (with the exception of highly alkaline waters in which silica is readily soluble [>9 pH] [Battarbee, 1986]). Coupled to narrow ecological tolerances and well defined environmental optima, many diatom taxa are ideal environmental indicators (e.g., pH, dissolved nutrients, depth, clarity, diurnal and seasonal temperature) and have been applied to paleoclimatic research through two main approaches: (1) reconstruction of climatic change via changes to an ancillary environmental parameter (e.g., a change in temperature is inferred from reconstructed changes to pH); or (2) directly via the application of a
temperature transfer function (Stoermer and Smol, 1999). Diatoms often only weakly respond to direct changes in temperature and instead many researchers focus on applying transfer functions to other limnological parameters (Stoermer and Smol, 1999). With their dependence upon dissolved nutrients (in particular dissolved nitrate/nitrite, phosphate and silica) diatoms are excellent trophic indicators offering detailed insights into the seasonal and spatial gradients in nutrient cycling through time (Battarbee et al., 2001). In this chapter diatom fossil assemblages extracted from the Lake Pupuke composite sequence are applied to a transfer function that describes changes in trophic status amongst freshwater lakes in the North and South Islands of New Zealand (e.g., Reid, 2005) to better describe changes in paleolimnology at Lake Pupuke over Marine Oxygen Isotope Stages (MIS) 1, 2 and 3.

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, Fragilariophyceae (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, Bacillariophyceae (e.g., Pinnularia) with a naviculoid raphe running along the central axis of the valve which is divided into two separated by the central area; (C') a pennate diatom, Bacillariophyceae (e.g., Nitzschia) with an eccentric raphe (Source: Jones, 2007: 477).
5.1.2 Interpretation of Fossil Diatom Assemblages

Diatom surface morphology and architecture is so elegant and varied that frustules can be readily identified to a family and species (Round et al., 1990). Diatoms are also one of the most diverse classes of algae with over 50,000 species spread throughout 100 genera (Mackay et al., 2003). This high level of diversity is at once beneficial and detrimental to their application in paleolimnology because it results in highly sensitive ecological responses, and simultaneously, a high level of endemism in many systems, particularly in old or isolated basins (e.g., Lake Tanganyika [Cocquyt and Jahn, 2005], Lake Baikal [Morley, 2005], Lake Malawi [Stone et al., 2010]). In the context of New Zealand, where geographic isolation has permitted the evolution of many endemic species, subsequent colonisation by invasive taxa has pushed some native flora to extinction or isolation (Reid, 2005). This prevents a relationship from being constructed between such taxa and past environment. Thus when examined in a paleolimnological series a researcher cannot employ their remains, reducing the reliability of subsequent inferences (Battarbee et al., 2001).

The application of a biogenic proxy indicator is also hindered by questions of sedimentary bias and whether post-depositional changes have altered a microfossil assemblage (Battarbee et al., 2001). As noted earlier, diatomaceous silica is subject to dissolution involving selective removal of weakly silicified frustules resulting in a bias to denser forms (e.g., Morley, 2005). It is therefore important to consider the effect of dissolution upon a stratigraphic diatom record (Barker et al., 1994). Contemporary monitoring of Lake Pupuke has revealed an annual average pH of ~7.8 although benthic pH averages a lesser value of 7.7 (see Chapter 2 [2.4.1.4. pH]). However, pore-water pH might very well have varied over the last ~48 cal. kyrs at Lake Pupuke in line with changes to benthic anoxia, temperature and salinity (see Chapter 4). Thus it is essential to monitor changes in diatom assembly preservation. Fortunately, diatom dissolution is readily evident via the changes induced to architecture and surface features present on frustules. The latter, taphonomy, is increasingly understood to reflect the overall accuracy of any such environmental reconstruction (Sayer et al., 2010).

Taphonomy describes the incorporation of a death assemblage (thanatocoenose) of littoral, benthic and planktonic diatom communities at the mud-water interface (Barker, 1990). Bias can become incorporated into the fossil assembly via the over- or under-representation of different communities due to: (1) spatial variation in frustule transport (e.g., changes due to mixing); (2) variable preservation by mechanical action, dissolution or detritivory (e.g., due to greater or lesser silicification); and (3) post-depositional mobility (e.g., due to benthic reworking or pore-water current) (Barker, 1990). The relative importance of (1) to (3) vary with salinity and oxygenation; saline lakes possess higher pH (>9.0) which renders diatom frustules soluble, whereas oxygenated sediments favour grazing and detritivory of diatom remains (Battarbee et al., 2001). The absence of desiccation within the Lake Pupuke composite sequence removes much of the bias expected from disappearance of frustules due to erosion. The presence of fine (< 1mm), organic-rich sediment laminae indicates an absence of bioturbation and likelihood of benthic anoxia preventing much detrital grazing (see Chapter 3). Thus the diatom record within Lake Pupuke is likely to be very well preserved and indicative of past environment.
Diatom taxonomic variation coupled to their environmental requirements allows subtle changes in water quality to be recorded from past diatom abundance (Batterbee et al., 2001). Various classifications of life-form differences exist, with the most robust categories relating to habitat preference (Table 5.1) (Round et al., 1990). Changes in dominant taxa and their habitat preferences can be used to elicit qualitative paleoenvironmental change (Jones, 2007). As diatoms are primary producers their growth is limited to the photic zone. A shift to periphytic or benthic forms is indicative of greater littoral habitat, whilst dominance of planktic or facultative planktic taxa requires a deep water column (Jones, 2007). Likewise, meroplanktic taxa occupy a position between the prior two classes, requiring turbulence to suspend resting cells (spores) from surface sediment and back into the water column. The presence of meroplanktic diatoms within a sedimentary record can imply shallowing, nutrient scarcity and/or benthic oxygenation (Cochran, 2009). Importantly, changes in littoral or pelagic habitat can reflect shallowing or deepening depending on basin morphology. In a typical scenario, shallowing permits bottom sediments to receive more light and oxygenation favouring greater blooms of periphytic diatoms. However, maar crater lakes often possess steep sides preventing marked changes to littoral habitat unless sufficient lake shallowing occurs to permit deep benthic sediments to become colonised, or sufficient increases occur to lake depth to flood surrounding gentler sloping crater shelves. To reliably infer shallowing one must therefore observe an increase in aerophilous, non-lacustrine diatoms which inhabit soils and ephemeral pools, and whose abundance reflects changes in the proportion of exposed catchment (Dam et al., 2001).

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

<table>
<thead>
<tr>
<th>Adult Life-form</th>
<th>Classification</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial</td>
<td>Aerophilous</td>
<td>Life cycle spent sub-aerial, moist or dry surfaces (associated with soil)</td>
</tr>
<tr>
<td>Periphyton (attached benthic)</td>
<td>Epilithic</td>
<td>Life cycle spent attached to rock</td>
</tr>
<tr>
<td></td>
<td>Epipellic</td>
<td>Life cycle spent attached to mud/silt</td>
</tr>
<tr>
<td></td>
<td>Epispamnic</td>
<td>Life cycle spent attached to sand</td>
</tr>
<tr>
<td></td>
<td>Epiphytic</td>
<td>Life cycle spent attached to aquatic macrophyte</td>
</tr>
<tr>
<td>Plankton (non-attached)</td>
<td>Planktic/Euplanktic</td>
<td>Entire life cycle spent suspended in water column</td>
</tr>
<tr>
<td></td>
<td>Facultative Planktic/Meroplanktic</td>
<td>Most of life cycle spent suspended in water column</td>
</tr>
<tr>
<td></td>
<td>Tychoplanktic</td>
<td>Life cycle spent in shallow/turbulent water column</td>
</tr>
</tbody>
</table>

Auteological relationships between taxonomic abundance and environmental conditions in contemporary environments have been well researched. Hence robust inferences can be made on a suite of water quality variables (e.g., pH [Psenner and Schmidt, 1992], salinity [Barker et al., 2003], total Phosphate [TP; Hall and Smol, 1992], total Nitrogen [TN; Bennion et al., 2001], intensity of stratification [Bradbury et al., 1993]) based on the relative abundance of diatom taxa through time. Three approaches can be applied (Battarbee et al., 2001):
(1) Qualitative inferences: from the use of autoecological information and/or classification schemes (e.g., Hustedt pH [Table 5.2] or salinity scheme) providing nominal data;

(2) Semi-quantitative inferences: from the use of compound indices which rank species along an environmental gradient providing ordinal data;

(3) Quantitative inferences: from the calibration of contemporary relationships between diatom abundance and a set of environmental parameters for a suite of modern hydrological systems, and the regression of past environmental conditions using the inverse of this relationship applied to estimates of past taxonomic abundance (e.g., a multivariate approach [Battarbee et al., 2001]). This approach employs transfer functions to yield diatom-inferred (DI) water quality as continuous data.

Table 5.2: Classification of diatom taxa by trophic and pH status (modified from Van Dam et al., 1994).

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Code</th>
<th>Classification</th>
<th>Status</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trophic State</td>
<td></td>
<td>Oligotrophic</td>
<td>&lt;0.015 mg L TP</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mesotrophic</td>
<td>0.015-0.030 mg L TP</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eutrophic</td>
<td>0.030-0.055 mg L TP</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hypereutrophic</td>
<td>&gt;0.055 mg L TP</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acidobiontic</td>
<td>Optimal occurrence at pH &lt;5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acidophilous</td>
<td>Mainly occurring at pH &lt;7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Circumneutral</td>
<td>Mainly occurring at pH ~7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkaliphilous</td>
<td>Mainly occurring at pH &gt;7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkalibiontic</td>
<td>Exclusively occurring at pH &gt;7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Indifferent</td>
<td>No apparent pH optimum</td>
<td></td>
</tr>
</tbody>
</table>

Here approaches (1) to (3) are employed to reconstruct past environment from diatom assemblages within the Pupuke composite sequence. These environmental reconstructions are built upon relationships in extant taxa and uncertainty will remain for those species no longer extant in the region for which no modern calibrated relationship between abundance and environment can be established (‘no-analogue’ error [Battarbee et al., 2001]).

Qualitative knowledge of diatom environmental preferences can be used to rank taxa along a corresponding environmental gradient whereby each taxon can be assigned a score by which to construct an environmental index. The latter can be constrained by presence/absence or weighted by taxonomic abundance. Van Dam et al (1994) analysed 776 species of freshwater diatoms for their tolerance of 7 environmental parameters: (1) pH; (2) salinity; (3) Nitrogen uptake metabolism; (4) Dissolved Oxygen; (5) saprobity; (6) trophic state and (7) moisture availability (Table 5.3). Of these, pH and salinity can also be modelled in New Zealand using a transfer function approach (see below). Others have successfully applied this classification scheme to paleoecologic series demonstrating its capacity to reconstruct changing paleolimnology (Ruggiu et al., 1998; Cochran et al., 2006; Hutchinson et al., 2008; O’Dwyer and Taylor, 2009; Spierenburg et al., 2010).
Table 5.3: Classification of ecological indicator values (Source: Van Dam et al., 1994: 120).

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Code</th>
<th>Classification</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Uptake</td>
<td>N</td>
<td>1</td>
<td>Nitrogen-autotrophic taxa, tolerating very small concentrations of organically-bound Nitrogen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Nitrogen-autotrophic taxa, tolerating elevated concentrations of organically-bound Nitrogen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Facultatively Nitrogen-heterotrophic taxa, needing periodically elevated concentrations of organically bound Nitrogen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Obligately Nitrogen-heterotrophic taxa, needing continuously elevated concentrations of organically bound Nitrogen</td>
</tr>
<tr>
<td>Oxygen requirements</td>
<td>O</td>
<td>1</td>
<td>Continuously high (~100 % saturation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Fairly high (&gt;75 % saturation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Moderate (&gt;50 % saturation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Low (&gt;30 % saturation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Very low (~10 % saturation)</td>
</tr>
<tr>
<td>Saprobity</td>
<td>S</td>
<td>1</td>
<td>Oligosaprobous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>B-mesosaprobous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>α-mesosaprobous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>α-meso/polysaprobous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Polysaprobous</td>
</tr>
<tr>
<td>Trophic State</td>
<td>T</td>
<td>1</td>
<td>Oligotrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Oligo-mesotrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Mesotrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Meso-eutrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Eutrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Hypereutrophic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>Oligo- to hypereutrophic</td>
</tr>
<tr>
<td>Moisture availability</td>
<td>M</td>
<td>1</td>
<td>Never, or only very rarely, occurring outside water bodies</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Mainly occurring in water bodies, sometimes on wet places</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Mainly occurring in water bodies, also rather regularly on wet and moist places</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Mainly occurring on wet and moist or temporarily dry places</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Nearly exclusively occurring outside water bodies</td>
</tr>
</tbody>
</table>

Water Quality Class | Oxygen saturation (%) | BOD (mg L) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I, II-III</td>
<td>&gt;85</td>
<td>&lt;2</td>
</tr>
<tr>
<td>II</td>
<td>70-85</td>
<td>2-4</td>
</tr>
<tr>
<td>III</td>
<td>25-70</td>
<td>4-13</td>
</tr>
<tr>
<td>III-IV</td>
<td>10-25</td>
<td>13-22</td>
</tr>
<tr>
<td>IV</td>
<td>&lt;10</td>
<td>&gt;22</td>
</tr>
</tbody>
</table>

These indices were however, developed in the Northern Hemisphere and often using eurytopic taxa with wide environmental tolerances (e.g., *Caloneis* spp., *Fragilaria* spp.). Similarly, the relationships between taxa and environment might be subject to variation within New Zealand, particularly because of a high degree of endemism characteristic of Australasian diatom floras (Tyler, 1996; Vyverman et al., 1998; Sabbe et al., 2001; Reid, 2005). Nonetheless species-environment responses are assumed to hold for different geographic regions and the time frame examined here.

### 5.1.3.1 Species Diversity

Species richness or alpha diversity is an important proxy for habitat and niche availability, greater diversity attached to environments with greater habitat and niche availability (Hill, 1973). A measure of species diversity is an indicator of past changes to habitat availability through, for instance, changes in paleohydrology (e.g., water quality, depth, stratification and disturbance) (Battarbee et al., 2001). Several indices can be used to record species richness, although the Shannon-Weiner (H) and Hill’s (N2) index are most widely applied due to their capacity to combine information on species abundance with measures of richness (Fowler et al., 1998):
Chapter Five

\[ H = -\sum p_i \ln(p_i) \]

(Calculation of the Shannon-Weaver alpha diversity index)

\[ N2 = 1/\sum p_i^2 \]

(Calculation of Hill’s N2 alpha diversity index)

where \( p_i \) is the proportion of individuals in species \( i \). Higher and lesser \( H \) and \( N2 \) values correspond to greater and lesser alpha diversity respectively.

Whilst individual diatom samples can yield information on paleolimnology, changes in diatom community structure between samples can offer an insight into the relative stability of individual sample assemblages (e.g., hydrologic states) (Barker, 1990). Beta diversity offers a proxy for disturbance in a single estimate of species turnover: the greater the turnover and exchange of species, the greater the beta diversity and hence more marked the change to community structure (Barker, 1990). Amongst beta diversity indices, the most commonly used is based on the ratio of the total number of species in a collection of samples (\( S \)) and the average richness per sample (\( \bar{a} \)) (Fowler et al., 1998): \[ \beta = S/\bar{a} - 1 \]

(Calculation of beta diversity)

\( \beta \) scores of 0 refer to samples with no species heterogeneity or turnover. However, \( S \) will likely increase with increasing numbers of samples irrespective of changes to composition (e.g., a greater number of samples will likely record greater environmental change and therein, greater \( S \)) (Fowler et al., 1998). A modified index for diatom assemblage heterogeneity (SIMI) after Hoagland et al (1982) is used here:

\[ \text{SIMI} (a,b) = \frac{(\sum P_{ai} \cdot P_{bi})}{\left(\sqrt{\sum P_{ai}^2} \cdot \sqrt{\sum P_{bi}^2}\right)} \]

(Calculation of the Hoagland et al (1982) similarity index)

where SIMI is the degree of similarity between communities \( a \) and \( b \), in which \( P_{ai} \) and \( P_{bi} \) are the proportions of individuals represented by the \( i \)-th taxon in communities \( a \) and \( b \) respectively. Values are summed for every species present in adjacent samples. Values range from 0 to 1 with lowest values accorded to communities that have no taxa in common and a maximum value of 1 recording those communities with identical proportions of the same species between samples (Hoagland et al., 1982).
5.1.3.2 Autecologies of Dominant Taxa

The autecologies of dominant taxa (>30 %) are described below. Three taxa dominate the Pupuke composite sequence: *Aulacoseira granulata* var. *ambigua*, *Discotella stelligera* and *Staurosira microstriata*. The interplay of these three species record the dominant hydrological changes experienced over the last ~44 kyrs at Lake Pupuke. Nonetheless less abundant species can also provide insights into paleoenvironment and hence subdominant (>5 %) taxa are described in Appendix B. A summary of ecological preferences is also given in Table 5.4.

*Aulacoseira granulata/ambigua*: is a small (<10 to 30 μm), freshwater, circular, planktonic taxon previously allocated to the *Melosira* genus (Cochran, 2009). The species is alkaliphilous and prefers eutrophic, alkaline systems (Cochran, 2009). The species has moderate Oxygen requirements (>50 % saturation) and is β-mesosaprobous (Van Dam et al., 1994). The genus commonly blooms in Spring and late Summer under high dissolved Si and TP concentrations. The species is associated with nutrient-starved conditions where its capacity to generate resting stages (inoculae) enables rapid population growth following turbulent mixing (Cassie, 1989). Cassie (1989) and Holmes (1994) note peak abundance of *A.granulata* during holomixis within Lake Pupuke (July and September) whereby it demonstrated a remarkable ability to endure extended periods of benthic anoxia and aphotic conditions. Consequently it is an ideal indicator taxon for development of thermal stratification within Lake Pupuke.

*Discotella stelligera* (previously recorded as *Cyclotella stelligera*): is a small (<10 to 40 μm), freshwater, circular, planktonic taxon (Round et al., 1990). *D.stelligera* is a spring-summer blooming species that prefers circumneutral, oligotrophic systems (Cochran, 2009). The species is widespread within New Zealand lakes and appears indifferent to depth or temperature though it demonstrates a preference for greater open-water than littoral habitat (Reid, 2005). The species has moderate Oxygen requirements (>50 % saturation) and is α-mesosaprobous (Van Dam et al., 1994).

*Staurosira microstriata*: is a small (<10 to 30 μm), freshwater, elliptical taxon indicative of open-water and benthic habitats and mesotrophy (Round et al., 1990). The taxon mostly occurs at pH >7 (alkaliphilous) (Van Dam et al., 1994). The genus is held within the class Fragilariaceae which are described by Haworth (1976) as pioneer species whose appearance often heralds the onset of deglaciation in the Northern Hemisphere. Cochran (2009) classifies this taxon as tychoplanktonic owing to its association with turbulent, well-mixed, and/or very shallow lakes in New Zealand. This reflects the taxon’s demand for continuously high Oxygen requirements (~100 % saturation) and limited sensitivity to BOD (β-mesosaprobous) (Van Dam et al., 1994). Other Fragilariaceae within Lake Pupuke presently occur throughout and after holomixis (July to September) because they are capable of rapid growth in a limited period of higher nutrient load (Cassie, 1989; Holmes, 1994). Abundance of *S.microstriata* can therefore imply a limited growth period as well as increased nutrient availability (e.g., through mixing) (Cochran, 2009).
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).

<table>
<thead>
<tr>
<th>Taxon</th>
<th>Indicator</th>
<th>R</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>T</th>
<th>M</th>
<th>Habitat Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aulacoseira granulata/ambigua</td>
<td></td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>Facultative Planktic/Meroplanktic</td>
</tr>
<tr>
<td>Cocconeis placentula</td>
<td></td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>Benthic (epiphytic)</td>
</tr>
<tr>
<td>Cyclotella planctonica*</td>
<td></td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>Planktic/Euplanktic</td>
</tr>
<tr>
<td>Cymbella microcephala</td>
<td></td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>Benthic (epilithic)</td>
</tr>
<tr>
<td>Diatomella balfouriana*</td>
<td></td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>Benthic/Aerophilic</td>
</tr>
<tr>
<td>Discotella stelligera</td>
<td></td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>Planktic/Euplanktic, Aerophilic</td>
</tr>
<tr>
<td>Epithemia adnata</td>
<td></td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>Benthic (epiphytic)</td>
</tr>
<tr>
<td>Epithemia sorex</td>
<td></td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>Benthic (epiphytic)</td>
</tr>
<tr>
<td>Gomphonema exiguum</td>
<td></td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>Benthic (epiphytic/epilithic)</td>
</tr>
<tr>
<td>Nitzschia amphibia</td>
<td></td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>Benthic (epiphytic/epilithic)</td>
</tr>
<tr>
<td>Staurosira microstriata*</td>
<td></td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>Tychoplanktic</td>
</tr>
<tr>
<td>Staurosira pinnata</td>
<td></td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>7</td>
<td>3</td>
<td>Tychoplanktic</td>
</tr>
<tr>
<td>Stephanodiscus alpinus*</td>
<td></td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>Planktic/Euplanktic</td>
</tr>
<tr>
<td>Synedra capitata</td>
<td></td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>Benthic (epiphytic, epilithic)</td>
</tr>
</tbody>
</table>

* denotes those taxa for whom species-specific estimates of indicator optima were unknown and whose value is an average of the genus.

5.1.4 Reconstruction of Water Chemistry from Diatom Abundance: Transfer Functions (Quantitative Approaches)

Quantitative, numerical approaches to paleolimnology have undergone marked improvement over the last three decades (Mackay et al., 2003). Initial applications involved the quantitative reconstruction of changing pH in limnic and lotic ecosystems following alarming acidification during the late 20th Century (e.g., thePaleoecologic Investigation of Recent Lake Acidification [PIRLA, USA (Charles and Whitehead, 1986)] and Surface Water Acidification Program [SWAP, UK (Battarbee and Renberg, 1990)]. The quantitative approaches employed by these projects were based on diatom-inferred transfer functions (DI-TF). DI-TF approaches aim to express environmental parameters by the abundance of numerous diatom taxa within a contemporary suite of water bodies (a calibration dataset) (Mackay et al., 2003). Surface sediment diatom assemblages and corresponding water chemistry are used to calibrate a linear regression between taxonomic abundance and environmental conditions, resulting in a mathematical function that can be applied to fossil diatom abundance to reconstruct past water chemistry (Mackay et al., 2003).
Whilst applied centres of research in North America and Europe have stimulated the use of similar multivariate approaches globally, in New Zealand, thus far only two diatom TFs have been developed: one for brackish/saline taxa (Cochrane, 2002) and another for freshwater taxa (Reid, 2005). Here Reid’s (2005) diatom TF is applied to reconstruct a suite of water quality parameters from the Pupuke composite sequence (e.g., electrical conductivity [EC], annual mean of pH, dissolved (soluble) reactive Phosphorus [DRP], isothermal total Phosphorus [TP] and chlorophyll-a [Chl a]).

5.1.4.1 Quantitative Paleoenvironmental Reconstruction Approaches

Indicators of paleolimnology respond to multiple, interacting environmental factors (Legendre and Legendre, 1998). Biogenic proxy data possesses a characteristic multidimensionality with species and combined assemblages exhibiting several superimposed trends (Kovach, 1995). To aid paleoecological interpretation of proxy change it is essential to reduce dimensionality to the dominant trends in a dataset (Kovach, 1995) (Kent and Coker, 1992). Factor analyses achieve this by arranging species or samples along a series of composite axes (composed of species or sample variance) (Kent and Coker, 1992). Ordination is the most frequently applied paleoecologic factor analysis (Legendre and Legendre, 1998). Ordination generates a series of compound axes which arrange sample sites (e.g., core samples) along principal axes derived from species composition (e.g., those that exhibit the greatest variance by species) (Legendre and Legendre, 1998). Most ordination approaches utilise eigenanalysis to extract new axes from linear transformations of multivariate data by assessing covariance and correlation between factors (Legendre and Legendre, 1998). Each axis possesses a corresponding eigenvalue which reflects the proportion of total variance within the dataset explained by that axis (Legendre and Legendre, 1998). Selecting two axes (typically axes 1 and 2 [λ1, λ2]), a biplot can be presented to demonstrate similarity in sample, species or environmental variables by proximity in the two-dimensional space (e.g., correlation to λ1, λ2) (Legendre and Legendre, 1998). If for instance contemporary water chemistry is sampled alongside diatom community assemblages and diatom samples are plotted by λ1 and λ2 such that pH best approximates λ1 (e.g., pH is plotted as a vector whose direction follows Axis 1 closely), then diatom community structure is most heavily influenced by a gradient in pH or covariate of pH (see below).

Ordination approaches vary in response to the distribution of variance within a dataset employing a linear or unimodal species response model (Lepš and Šmilauer, 2003). A unimodal response curve best approximates ecological variation in species abundance along a full environmental gradient, with a well defined optimum bounded by a tolerance range that reflects a Gaussian curve (e.g., 68.26 % of variance within 1σ of the environmental optimum) (Pielou, 1984). Often however, if an environmental gradient is only partly expressed (or sampled) a linear model will best approximate a species abundance response (Pielou, 1984). The choice between whether to apply a unimodal or linear ordination is arbitrary and depends on the length of the principal axis (λ1). If >2σ, a unimodal species response is more likely; if <2σ, the relevant species or sample data likely exhibit a linear response to environmental change (Birks, 1998; Lepš and Šmilauer, 2003).
Ordination techniques can further be defined as unconstrained or constrained, depending on whether species data are constrained by corresponding environmental data (Kent and Coker, 1992). Species responses to environmental gradients in unconstrained (indirect) ordinations can be inferred only if a priori knowledge of an underlying environmental gradient is available (Kent and Coker, 1992). However, to develop a diatom TF, constrained (direct) methods must be applied to contemporary diatom assemblage and water chemistry data present in a calibration dataset (Kent and Coker, 1992). Ordination can then be used to demonstrate which environmental variables are of greater importance in explaining species variance and whether species distributions are dominantly unimodal or linear. Multivariate linear regression can then be applied to generate a relationship between significant environmental variables and abundance for each species (a so-called ‘calibration’ stage) (Legendre and Legendre, 1998). Finally, regression functions are inverted and applied to paleoecological species abundance data to calculate environmental values for those parameters significant in explaining contemporary species abundance (a so-called ‘regression’ stage) (Legendre and Legendre, 1998).

Unconstrained ordination methods can also be useful in explaining underlying trends within a diatom sequence by demonstrating which taxa dominate sample assemblage responses through time (see below). Unconstrained ordination techniques include principal components analysis (PCA; linear) and detrended correspondence analysis (DCA; unimodal). The latter corrects for an arch effect exhibited by species scores which possess a unimodal distribution when confined to two principal axes (e.g., a unimodal response and complete species turnover occurs through time [Hill and Gauch, 1980]). Constrained ordination approaches include redundancy analysis (RDA; linear) and canonical correspondence analysis (CCA; unimodal) as well as a detrended CCA form (DCCA; unimodal). In all approaches, the first axis ($\lambda_1$) explains the greater variance whilst the second ($\lambda_2$) corresponds to the next greatest factor (Hill and Gauch, 1980). Thus ordination results are typically presented as a biplot of the $\lambda_1$ and $\lambda_2$. Unconstrained biplots represent species as vectors extending in the direction of greatest abundance whilst constrained biplots present species as points indicating optima along corresponding axes (Hill and Gauch, 1980). In the latter, environmental parameters are displayed as vectors driving variation in species or sample scores (Hill and Gauch, 1980).

### 5.1.4.2 A New Zealand Transfer Function

The following provides a summary of the only freshwater diatom TF available for New Zealand (Reid, 2005). To be successfully applied, the present-day limnology of calibration sites within New Zealand must cover a gradient exhibited by our paleoecological dataset. However, the endemism of New Zealand’s diatom flora offers distinct problems of ‘no analogue’ likely to be exacerbated by the heavy impact of agriculture throughout the North Island which has made many contemporary freshwater systems highly eutrophic (Reid, 2005). Nevertheless, the wide gradient of trophic state exhibited by the calibration lakes and an intensive sampling regime of seasonal water chemistry (e.g., isothermal or mixed and stratified water chemistry) accrues this TF great explanatory power (Table 5.5 and 5.6). It therefore offers a unique insight into the paleolimnology of Lake Pupuke via reconstruction of past nutrient cycling (Dissolvable Reactive Phosphate [DRP], total Phosphate [TP]) amongst
other water quality parameters (pH, electrical conductivity, Chlorophyll a). The latter directly alter diatom abundance and community structure, and respond indirectly to changes in paleoclimate (e.g., through changing erosion and sediment influx and/or thermal stratification). Reid’s (2005) diatom TF offers a robust mechanism of corroborating paleolimnologic changes recorded in Chapter 4. However, all transfer functions despite varying capacities to model present and past water quality are limited to reconstructing ranges of water quality parameters present in the calibration dataset, extreme values will be very poorly modelled (Figure 5.2).

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

<table>
<thead>
<tr>
<th>Statistic</th>
<th>pH</th>
<th>EC (μS cm)</th>
<th>DRP (mg m⁻³)</th>
<th>TP (mg m⁻³)</th>
<th>Chlorophyll a (mg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>8.88</td>
<td>1115</td>
<td>175.41</td>
<td>171.25</td>
<td>26.07</td>
</tr>
<tr>
<td>Minimum</td>
<td>5.66</td>
<td>20</td>
<td>0.28</td>
<td>1.85</td>
<td>0.38</td>
</tr>
<tr>
<td>Mean</td>
<td>7.47</td>
<td>121</td>
<td>6.30</td>
<td>14.44</td>
<td>3.76</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.51</td>
<td>170</td>
<td>24.31</td>
<td>25.20</td>
<td>5.11</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Variable</th>
<th>Model</th>
<th>( r_{\text{jack}} )</th>
<th>Mean bias</th>
<th>Max bias</th>
<th>Gradient length</th>
<th>RMSEP</th>
<th>RMSEP/Gradient length</th>
<th>Calibration size</th>
</tr>
</thead>
<tbody>
<tr>
<td>( pH_{\text{ALL}} )</td>
<td>WA</td>
<td>0.72</td>
<td>-0.006</td>
<td>0.484</td>
<td>2.703</td>
<td>0.252</td>
<td>0.093</td>
<td>47</td>
</tr>
<tr>
<td>( EC_{\text{ISO}} )</td>
<td>WA-tol</td>
<td>0.79</td>
<td>0.025</td>
<td>0.244</td>
<td>1.420</td>
<td>0.151</td>
<td>0.106</td>
<td>48</td>
</tr>
<tr>
<td>( DRP_{\text{ISO}} )</td>
<td>WA-tol</td>
<td>0.78</td>
<td>0.048</td>
<td>0.344</td>
<td>1.309</td>
<td>0.166</td>
<td>0.127</td>
<td>48</td>
</tr>
<tr>
<td>( TP_{\text{ALL}} )</td>
<td>WA</td>
<td>0.50</td>
<td>-0.004</td>
<td>0.221</td>
<td>1.229</td>
<td>0.240</td>
<td>0.195</td>
<td>48</td>
</tr>
<tr>
<td>( Chl \text{a}_{\text{ISO}} )</td>
<td>WA</td>
<td>0.71</td>
<td>0.001</td>
<td>0.265</td>
<td>1.268</td>
<td>0.180</td>
<td>0.142</td>
<td>49</td>
</tr>
</tbody>
</table>

Reid (2005) sampled the surface sediments and water chemistry of 53 lakes throughout the North (\( n = 21 \)) and South (\( n = 32 \)) Island of New Zealand. Lakes were selected to cover wide environmental gradients whilst avoiding extremes of any single dominant parameter. A preference for deeper lakes (>10 m) with dominantly euplanktonic diatom assemblages aids this investigation as lithological indicators suggest retention of a deep water column favouring euplanktonic diatom communities throughout the Pupuke composite sequence (Chapters 3 and 4). Similarly, the range of altitudes (6-819 m a.s.l.), depths (11.9-134.5 m) and surface area (7.8-17273 ha) in calibration sites likely exceed the changes experienced by diatom assemblages at Lake Pupuke throughout the last ~44 kyrs.

Reid (2005) applied principal component analysis (PCA) to water chemistry data to identify those parameters that best explain variance amongst diatom assemblages as well as to exclude outlier basins. Gradient lengths confirmed the need for a unimodal factor analysis to investigate species-environment relationships so that a direct, detrended canonical correspondence analysis (DCCA) was applied to calibrate unimodal species-environment relationships to surface water hydrology (Reid, 2005). Five water quality variables (pH, EC, DRP, TP and Chl a) met the necessary conditions for transfer function development (e.g., Axis 1/Axis 2 [\( \lambda_1/\lambda_2 \)] ratios >0.5; >5 % total species variance explained) (see Dixit et al., 1991). Of the many data transformation techniques available, weighted averaging (WA) performed better at predicting calibration lake water quality for pH, TP and Chl a than weighted averaging with tolerance downweighting (WA-tol) and weighted averaging through partial least squares regression (WA-PLS). WA-tol performed best for computing EC and DRP (see Table 5.6; refer to jack-knifed correlation coefficients \( r_{\text{jack}}^2 \), root mean squared error of prediction [RMSEP], and residual bias).
Annual means of pH (pH\textsubscript{ALL}) and TP (TP\textsubscript{ALL}), and isothermal means of EC (EC\textsubscript{ISO}), DRP (DRP\textsubscript{ISO}) and Chl a (Chl a\textsubscript{ISO}) were modelled best (e.g., higher $r^2_{\text{jack}}$, lesser RMSEP and bias).

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., $\lambda_1/\lambda_2 > 0.5$; explain >5% of total species variance). With the exception of TP\textsubscript{ALL} each also performed well at predicting calibration water chemistry ($r^2_{\text{jack}} > 0.7$). Thus the latter was excluded from application to the Lake Pupuke composite sequence. 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).
5.2 Diatom Methodology

73 sediment samples were prepared for diatom analysis at 2 to 39 cm (~60 to 1520 yr) intervals throughout the Pupuke composite sequence. Aliquots of known weight (~0.5 dry wt. g) were extracted from each sample interval to allow calculation of diatom concentration and flux. Samples were prepared by the author and enumerated by Ursula Cochran (GNS Science, Wellington).

5.2.1 Laboratory Methods

Figure 5.3: Diatom laboratory procedure employed for Pupuke composite samples.
Laboratory diatom preparation is outlined in Figure 5.3. Diatom frustules were isolated by oxidation in excess hydrogen peroxide (~27% v/v H₂O₂), initially at room temperature over 24 hrs prior to heating in a water bath at 70 °C for a further 12 hrs. Composite sediments are highly organic (~10-30 wt.% TOC [Chapter 4]) and therefore required a large quantity of oxidising reagent (~75 ml) prior to an acid-leaching stage to attack further reduced organics adhering to isolated frustules (1N HNO₃). Samples were rinsed and centrifuged with deionised water (x4500 rpm, 5 min) between oxidation stages (x3). Wet samples were diluted to 20 ml with deionised water. An aliquot of 0.1 ml was then mixed with 5.0 μl of marker sphere solution (~6.27 x 10⁷ marker spheres per ml [~313500 marker spheres]). This solution was further diluted as necessary for slide production depending on diatom concentration.

73 glass slides were manufactured from microsphere-spiked diatom extract. A droplet of solution was mounted to a glass coverslip and dried in a hermetically-sealed chamber at room temperature. Dried coverslips were mounted to glass slides with Naphrax (refractive index 1.7) and fixed by heating to 130 °C on a hotplate.

5.2.1.1 Identification and Abundance

At least 300 diatom frustules were identified on each slide using a Leica DMLB light microscope at x1600 magnification by Ursula Cochran (GNS Science, Lower Hutt). Diatom identification was by reference to standard diatom floras (e.g., Hustedt, 1985; Round et al., 1990; Hartley, 1996; Krammer and Lange-Bertalot, 1991-2000) as well as more specific diatom floras (Wunsum et al., 1995; Houk and Klee, 2004; Schmidt et al., 2004a, 2004b). Identified taxa are listed in Appendix C. Diatom abundances are expressed as percentages, concentrations and fluxes.

5.2.1.2 Concentration and Flux

Taxonomic percentage abundance can readily be misinterpreted (e.g., changes to abundance of species A can arise from a change in that species or alternately, a change in abundance of species B). To allow estimation of absolute abundance the number of diatoms on each slide (N₄s), from the number of microspheres introduced (N₅₄ₑ), diatoms counted (N₅) and number of microspheres counted (N₅ₑ):

\[ N_{Ds} = \frac{(N_{Ms} \times N_5)}{N_{M}} \]

(Calculation of diatoms on slide)

Total diatoms present in a sample (N₁) are the product of N₄s * 200 (e.g., 0.1 ml aliquot of 20 ml dilute sample [see above]). The absolute quantity of diatoms per unit weight of sediment (N₅ₑ) can be calculated from N₁ and the weight of sediment digested (W) as follows:
\( N_{WT} = N_T / W \)

(Calculation of diatoms per unit weight of sediment)

Diatom fluxes \( (D_F \text{ [valves cm}^{-2} \text{ yr}^{-1}]) \) can be calculated from the product of \( N_{WT} \) (diatoms per unit weight \([g]\) of sediment) and mass accumulation rate \( (\text{MAR} \text{ [g cm}^{-2} \text{ yr}^{-1}]) \) as follows:

\[ D_F = N_{WT} \times \text{MAR} \]

(Calculation of diatom flux)

5.2.2 Numerical and Graphical Methods

Raw diatom counts were entered and converted to percentage abundances in Microsoft Excel. Taxa with >5 % abundance in one or more samples were included for graphical representation. Diatom stratigraphic plots were created in the software C2 v.1.6.5. (Juggins, 2010).

5.2.2.1 Diversity and Habitat Preference

Alpha diversity values were computed from diatom composite abundance data (percentage count) within the statistical software R by the Vegan package (Oksanen et al., 2010). Beta diversity values were computed in Microsoft Excel. Alpha diversity is described by Shannon-Weaver H and Hill’s N2 scores and beta diversity by the standard \( \beta \)-dissimilarity measure and Hoagland et al’s (1982) SIMI similarity index.

Data on taxonomic percentage abundance was combined with knowledge of contemporary habitat preferences within Pienitz et al (1991) to generate five percentage weighted habitat preferences: (1) planktic/euplanktic; (2) facultative planktic/meroplanktic; (3) tychoplanktic; (4) benthic; and (5) aerophilic (defined in Table 5.1).

5.2.2.2 Morphotype agglomeration

To limit the impact of different morphotypes in the ordination analyses and transfer function application (e.g., contributing to greater ‘no analogue’) several species morphotypes were combined to a single relevant species sum. For instance, Discotella stelligera were identified at greater and lesser than 10 \( \mu \text{m} \) in radial diameter. Four taxa were subsumed in this manner (Discotella stelligera [2 morphotypes], Staurosira aff. venter [5 morphotypes], Staurosira microstriata [2 morphotypes] and Staurosira pinnata [3 morphotypes]).

5.2.2.3 Diatom Zonation

Zonation of diatom percentage abundance was undertaken to simplify interpretation of the Pupuke composite sequence through constrained hierarchical agglomerative cluster analysis within R by the CHCLUST function of
the ‘Rioja’ package (Juggins, 2009). Clusters were calculated with Euclidean chord distance to generate a dissimilarity matrix (Juggins, 2009). To assess the likely significance of the clusters one can generate a model of the variance sum of squares explained by clusters under a random (null) distribution, a broken-stick distribution (Bennett, 1996). Variance explained by agglomerative clusters can be plotted against the variance likely to be explained by randomly assigning clusters. The point of intersection of both trends highlights the maximum parsimonious model (Juggins, 2009). A resultant cluster dendrogram and broken stick biplot was plotted against diatom stratigraphy (see 5.4. Diatom Results).

5.2.2.4 Diatom Ordination

Dominant structural changes to composite diatom assemblages can be revealed relatively easily in CONISS zonation. However, less apparent but significant underlying structure in diatom community data can also be revealed through PCA or DCA. Both are ideal indirect gradient techniques with which to explore species turnover as sample scores are expressed in standard deviation units (σ, SD), thereby enabling ready interpretation of between-sample (beta) diversity (Lepš and Šmilauer, 2003). Linear (PCA) and unimodal (DCA) analyses were performed in the statistical program R using the DECORANA function of the ‘Vegan’ package (Oksanen et al., 2010). DECORANA detrends ordination axes to remove notable artefacts of CA present in unimodal data (‘arch’, ‘trumpet’ curves [Hill and Gauch, 1980]) via non-linear rescaling of 26 axial segments through repeated iterations (n = 4) (Oksanen et al., 2010).

Diatom assemblage data were entered as percentage abundance estimates (by count). All species were included in ordinations but to limit the influence of rare taxa, abundance percentages have been square root transformed and all ordinations were performed by downweighting rare species within the Vegan package. Data transformation is essential to prevent the primary and secondary ordination axes simply reflecting variance in the most dominant species, and moreover to drive variation in axes by changes to minor species whose environmental optima/tolerances might be more indicative of surrounding paleoenvironment (Legendre and Legendre, 1998).

5.2.2.5 Diatom Transfer Function

Reid’s (2005) New Zealand diatom TF was applied to diatom percentage abundance estimates in the software package C2 v.1.6.5. (Juggins, 2010). Morphotypes were summed to a single taxon in several species (Section 5.2.2.2. Morphotype agglomeration). As per Reid (2005), a classical deshrinking WA model was applied to model pH and Chl a, whilst a classical deshrinking WA-tol model was applied to model EC and DRP. Outlier lakes were also identified and excluded from direct ordinations as per Reid (2005) (Table 5.7).
5.3 Diatom Results and Interpretation

The next section covers the results of diatom analysis. For ease of interpretation all values referred to as \( # \pm # \) refer to the mean \( \pm \) one standard deviation (e.g., \( \mu \pm 1\sigma \)).

### 5.3.1 Preservation

73 diatom microscope slides offered a minimum of 300 valves to count \( (321 \pm 16 \text{ valves per slide}) \). Of these, Cochran (2009) identified four samples that exhibited weathered valves: (1) D812 (29.7 cal. kyr BP, 973 cm composite depth); (2) D813 (30.4 cal. kyr BP, 992 cm composite depth); (3) D811 (30.8 cal. kyr BP, 1005 cm composite depth); and (4) D810 (31.3 cal. kyr BP, 1019 cm composite depth). Thus the interval \(~31.3\) to 29.7 cal. kyr BP demonstrates evidence for poorer preservation and greater mechanical erosion of diatom frustules.

### 5.3.2 Influx

Diatom fluxes have been estimated for each species from taxonomic concentration and MAR before combination as an assemblage sum in Figure 5.4. Diatom flux rates are exceedingly high at \(~6.7 \times 10^5\) to \(~3.67 \times 10^7\) valves \( \text{cm}^2 \text{ yr} \) reflecting the likely prevalence of a deep lacustrine environment throughout deposition of the composite sequence in Lake Pupuke.

Total diatom fluxes exhibit marked variability (Figure 5.4). Most notably, diatom fluxes prior to \(~31.9\) cal. kyr BP are exceptionally high \( (9.0 \pm 3.8 \times 10^6 \text{ valves cm}^2 \text{ yr}) \). Thereafter fluxes of diatom valves decrease and remain low \( (5.68 \pm 4.29 \times 10^6 \text{ valves cm}^2 \text{ yr}) \) until the late-to-mid Holocene \( (~3.3\) cal. kyr BP; \(1.23 \pm 8.5 \times 10^7 \text{ valves cm}^2 \text{ yr}) \) with the exception of several brief increases in flux between \(~22.5\) and \(~21.4\) cal. kyr BP \( (8.6 \pm 3.3 \times 10^6 \text{ valves cm}^2 \text{ yr}), \sim 13.9 \text{ and } 13.4 \text{ cal. kyr BP} (1.3 \pm 0.7 \times 10^7 \text{ valves cm}^2 \text{ yr}), \sim 8.2 \text{ and } 5.5 \text{ cal. kyr BP} (4.9 \pm 2.8 \times 10^6 \text{ valves cm}^2 \text{ yr}) \). The most recent influx increase from \(~3.3\) cal. kyr BP to today is the highest of the entire series \( (\text{max} = 3.67 \times 10^7 \text{ valves cm}^2 \text{ yr}) \).

The diatom flux peak from \(~13.9\) to \(~13.4\) cal. kyr BP \( (\text{max} = 2.5 \times 10^7 \text{ valves cm}^2 \text{ yr}) \) is also an important feature as the timing of this event is constrained by 5 samples. Similarly, a peak in diatom flux between \(~22.5\) and \(~21.4\) cal. kyr BP \( (\text{max} = 1.23 \times 10^7 \text{ valves cm}^2 \text{ yr}) \) forms another distinctive feature as this period was noted in
Chapter Four to coincide with a proposed enhancement of glacial conditions increased erosion during the LGCP. However, the most notable feature of the diatom influx profiles are the coincidence of many influx peaks with major tephra deposition events (Figure 5.4). Influx peaks at ~2.0 cal. kyr BP, ~6.9 cal. kyr BP, ~13.5 cal. kyr BP, ~21.9 cal. kyr BP, ~27.2 cal. kyr BP and ~29.1 cal. kyr BP are adjacent to tephras: Taupo (1.7 cal. kyr BP), Tahua (7.0 cal. kyr BP), Waiohau (13.6 cal. kyr BP), Okareka (22.0 cal. kyr BP), Kawakawa (27.1 cal. kyr BP) and Okaia (29.3 cal. kyr BP) respectively. Harper et al (1986) proposed positive diatom response to the supply of silica and other essential nutrients (e.g., Fe, P and S) from direct tephra fall to a water column and via subsequent reworking from the catchment.

5.3.3 Diversity

Cochran (2009) identified 62 species of freshwater diatoms within the Pupuke composite sequence (excluding an additional 7 morphotype subspecies). Despite this, most samples contained only a minor subset including up to 5 or fewer dominant and subdominant species (e.g., >5 % by count). The dominance of any single sample by only a few diatom species results in a low/moderate species richness as denoted by low Shannon-Weiner H and Hill’s N2 index scores (1.33 ± 0.35 and 3.93 ± 1.30) (Figure 5.4). The period ~21.9 cal. kyr BP to today records a higher species richness (1.51 ± 0.29 [Shannon-Weaver H] and 4.26 ± 1.51 [Hill’s N2]) whilst the period ~44.0 to 26.2 cal. kyr BP exhibits lesser alpha diversity (1.04 ± 0.23 [Shannon-Weaver H] and 3.37 ± 0.57 [Hill’s N2]). The intervening period marks a transition from reduced to greater diatom community richness (~26.2 to 21.9 cal. kyr BP; 1.34 ± 0.39 [Shannon-Weaver H] and 4.16 ± 1.22 [Hill’s N2]).

Diatom community structure exhibits a complex pattern of between-sample variability throughout the composite sequence. Sørensen’s dissimilarity index and Hoagland’s similarity index (SIMI) present a complementary message of limited variability prior to ~8.2 cal. kyr BP whereupon species abundances and richness becomes much more varied (Figure 5.4). Sørensen’s dissimilarity index exaggerates variability prior to ~27.2 cal. kyr BP whilst the Hoagland index better captures the stability of diatom communities prior to ~26.2 cal. kyr BP as recorded by values nearer 1 (0.99 ± 0.01). Between ~26.2 and 11.2 cal. kyr BP SIMI values become more variable but do not fall below 0.69 (0.94 ± 0.08). An increase in diatom flux between ~13.9 and 13.4 cal. kyr BP does not induce changes in community structure (SIMI value 0.98 ± 0.02). However, marked turnover occurs at ~13.4 cal. kyr BP whereupon SIMI values drop to ~0.1. Diatom communities stabilise thereafter until highly variable communities from ~8.2 cal. kyr BP to today (SIMI 0.55 ± 0.34). SIMI scores drop as low as ~0.05 between ~8.2 and 6.9 cal. kyr BP and lower still in the late Holocene (~0.01 at ~0.7 cal. kyr BP and ~0.05 at ~0.4 cal. kyr BP). Lake Pupuke diatom communities appear to be highly stable and composed of ~5 or fewer dominant taxa until the early-Holocene (~8.2 cal. kyr BP) whereupon highly variable and dynamic communities occur until today.
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.
5.3.3.1 Habitat Preference

Diatom percentage abundance has been combined with knowledge of taxonomic habitat preference (e.g., Pienitz et al., 1991) to reconstruct past changes in habitat (Figure 5.4). Diversity-related changes are evident in changes to habitat availability. The previously identified shift to reduced inter-sample similarity at ~26.2 cal. kyr BP is evident as a decline in the dominance of planktic/euplanktic taxa (prior to ~26.2 cal. kyr BP 83.14 ± 6.97 %) commensurate with an increase in abundance of tychoplanktic taxa until ~15.3 cal. kyr BP (from 11.91 % to 89.52 %). This period also records the greatest abundance of aerophilic taxa (3.96 ± 2.52 %) although the latter contribute minor proportions of the total diatom community throughout the entire series. Tychoplanktic diatom dominance continues from ~15.3 cal. kyr BP until ~8.2 cal. kyr BP (76.73 ± 8.51 %) whereupon an increasing proportion of diatoms are facultative planktic/meroplanktic taxa. Habitat preference during the interval ~8.2 cal. kyr BP to today is highly variable thereby contributing to the greater beta diversity observed within this interval. This period can be subdivided into an initial period of highly dissimilar but dominantly facultative planktic/meroplanktic taxa until ~6.9 cal. kyr BP prior to a decline in the latter and coeval increase in benthic taxa until ~4.6 cal. kyr BP. Thereafter, benthic proportions decline and diatoms are more evenly distributed between planktic/euplanktic, facultative planktic/meroplanktic and tychoplanktic taxa until today. Thus the Last Glacial is denoted by dominantly planktic/euplanktic taxa before a transitional community of increasingly tychoplanktic taxa beginning ~26.2 cal. kyr BP, whilst the Holocene is marked by substantial variability in habitat availability most notably from ~8.2 cal. kyr BP to today. Throughout however, planktic, meroplanktic and tychoplanktic taxa dominate indicating the continued presence of a deep lake water column.

5.3.3.2 Community Water Quality Indicators

Diatom percentage abundance data has been combined with autecological preferences (e.g., Van Dam et al., 1994) and weighted by relative abundance to yield community-scale changes to (1) pH; (2) dominant Nitrogen uptake mechanism; (3) Oxygen availability; (4) saprobity; (5) trophic state; and (6) moisture (Figure 5.5). Little change occurs to inferred salinity or moisture availability over the Pupuke composite sequence suggesting that the lake has remained circumneutral/alkaliphilous and fresh/brackish (<500 mg L Cl), and consistently deep (as per Van Dam et al., 1994). Changes to the dominant Nitrogen uptake mechanism, trophic status and saprobity also appear to be minor. However, trophic scores suggest a change from a eutrophic glacial community to a meso-eutrophic early Holocene community which is contradicted by quantitative diatom-inferred TP and DRP reconstructions (see below). This demonstrates a marked failure of the indicator scheme proposed by Van Dam et al (1994) to capture nutrient variability at Lake Pupuke, a possible result of the abundant presence of eurytopic species within the Pupuke composite sequence (e.g., Fragilariaceae [Cyclotella cf. planctonica, Staurosira microstriata]), poorly ascribed optima and more likely, the limitations of applying a dataset weighted to polluted catchments (see Van Dam et al., 1994). The only marked change to community indicators occurs to Oxygen availability which rises from moderate concentrations of DO (>50 % saturation) prior to ~26.2 cal. kyr BP, through continuously high levels (~100 %) during the transition to the Holocene, and more recently, a drop to fairly high levels (>75 % saturation) from ~3.3 cal. kyr BP until today.
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. Indicator scores are defined in Table 5.2.
5.3.4 Multivariate Paleoenvironmental Reconstruction

The following subchapter interprets diatom percentage abundance within a quantitative framework employing a suite of statistical approaches including hierarchical cluster analysis, ordination and multivariate linear regression.

5.3.4.1 Zonation

Diatom abundance estimates (% count) were zoned by agglomerative cluster analysis (e.g., constrained sum of squares [CONISS]) within R using the CHCLUST function within the Rioja package (Juggins, 2009). The resultant dendrogram and corresponding broken-stick model is presented in Figure 5.6. Only 4 or fewer groups explain sufficient variance to exceed that attributable to a random selection of zonal boundaries. A potential fifth zone could be defined within Zone 4 but this likely reflects a higher sampling frequency generating greater variability over the near recent (e.g., at ~2.7 cal. kyr BP). The 4 significant zones are defined as:

1. 44.0 ± 4.8 cal. kyr BP (95 % uncertainty) to 25.7 ± 2.0 cal. kyr BP (95 % uncertainty);
2. 22.5 ± 1.4 cal. kyr BP (95 % uncertainty) to 16.0 ± 1.2 cal. kyr BP (95 % uncertainty);
3. 15.4 ± 1.1 cal. kyr BP (95 % uncertainty) to 3.7 ± 0.6 cal. kyr BP (95 % uncertainty);
4. 3.3 ± 0.5 cal. kyr BP (95 % uncertainty) to today.

5.3.4.2 Zonal Taxonomic Change

Dominant (>30 %) and sub-dominant diatom taxa (>20 %) have been presented in Figure 5.7 and are summarised by CONISS-defined zones in Table 5.8. Zonal taxonomic changes are interpreted for variations in paleohydrology below. Zonal boundaries are also inspected to elicit likely rates of change as well as confidence in the timing of changes. Three taxa are classified as dominant throughout the composite series: *Aulacoseira granulata var. ambigua*, *Staurosira microstriata* and *Discotella stelligera*. Together they indicate circumneutral to weakly alkaline conditions persisted throughout precluding a need to discuss changes to pH (please refer to 5.3.4.3. Diatom Ordination Results to confirm the absence of pH in determining diatom community structure over the last ~44.0 cal. kyr BP at Lake Pupuke).

Table 5.8: Definition of diatom zones according to dominant taxa

<table>
<thead>
<tr>
<th>Zone</th>
<th>Cores</th>
<th>Composite (cm)</th>
<th>Depth</th>
<th>Age (cal. kyr BP)</th>
<th>Dominant Taxa</th>
<th>Subdominant Taxa</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1A1#1</td>
<td>2A1#4</td>
<td></td>
<td>3.3 to today</td>
<td><em>Aulacoseira granulata var. ambigua</em>, <em>Discotella stelligera</em></td>
<td><em>Staurosira microstriata</em>, <em>Stephanodiscus cf. alpinus</em></td>
</tr>
<tr>
<td></td>
<td>2A1#4</td>
<td>1C2#5</td>
<td></td>
<td>15.3-3.3</td>
<td><em>Staurosira microstriata</em></td>
<td><em>Aulacoseira granulata var. ambigua</em>, <em>Discotella stelligera</em>, <em>Stephanodiscus cf. alpinus</em></td>
</tr>
<tr>
<td></td>
<td>1B3#7</td>
<td>1D1#9</td>
<td></td>
<td>22.5-15.3</td>
<td><em>Discotella stelligera</em>, <em>Staurosira microstriata</em></td>
<td><em>Diatomella balfouriana</em>, <em>Staurosira pinnata</em></td>
</tr>
<tr>
<td>1</td>
<td>1D1#9</td>
<td>2C2#10</td>
<td></td>
<td>44.0-22.5</td>
<td><em>Discotella stelligera</em></td>
<td><em>Cyclotella cf. planktonica</em>, <em>Diatomella balfouriana</em>, <em>Staurosira microstriata</em>, <em>Staurosira pinnata</em></td>
</tr>
</tbody>
</table>
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.
5.3.4.2.1  Zone 1 (~44.0 to 22.5 cal. kyr BP)

Zone 1 is marked by the dominance of the planktic/euplanktic taxon, *D. stelligera* (73.05 ± 7.49 %). In addition, several subdominant diatom taxa occur including *Cyclotella* cf. *planctonica* whose abundance declines through Zone 1 and into Zone 2. Its decline is coeval with increased abundance of *S. microstriata* suggesting increased mixing and greater abundance of dissolved Oxygen into Zone 2. The shift from euplanktic/planktic to tychoplanktic taxa further confirms the likelihood of lake shallowing during increased abundance of aerophilous diatoms from ~29.1 to 18.4 cal. kyr BP. Nevertheless any shallowing of Lake Pupuke was not sufficient to significantly alter benthic or planktic diatom abundances or cause much diatom community change (SIMI score of 0.98 ± 0.02). Furthermore the dominance of *D. stelligera* implies a stable, deep water column existed throughout Zone 1.

5.3.4.2.2  Zone 2 (~22.5 to 15.3 cal. kyr BP)

Throughout Zone 2 diatom assemblages reflect a decreasing dominance of *D. stelligera* (43.24 ± 11.73 %) in favour of *S. microstriata* (15.24 ± 7.72 %) in line with increasing nutrient availability (Figure 5.7). As in Zones 4 and 3, Zone 2 records a period of species turnover and moderate-to-low inter-sample diversity (SIMI score 0.88 ± 0.10). However, unlike Zones 4 and 3, the entirety of Zone 2 is characterised by moderate species turnover denoting a lengthy period of environmental instability. Furthermore, the changes were less rapid throughout Zone 2 than during periods of turnover in the Holocene as recorded by a minimum similarity index score of 0.69.

Less abundant taxa are also of importance in Zone 2. Notably the increased abundance of the aerophilous taxon *Diatomella balfouriana* (4.01 ± 2.58 %) indicates lake shallowing with more of the greater catchment reverting to shallow ephemeral pools (e.g., Van Dam et al., 2001). *D. balfouriana* reaches higher abundance for a period of ~10,630 years beginning in Zone 1 at ~29.1 cal. kyr BP. By ~18.4 cal. kyr BP a decline in *D. balfouriana* and trend to increasing abundance of the post-glacial pioneer species, *S. microstriata*, implies the onset of post-glacial transitional conditions. Hence the diatom taxa record a change to glacial conditions favouring lake level decline between ~29.1 and ~18.4 cal. kyr BP.

The Zone 2 and 1 boundary is poorly constrained at ~25.7-22.5 cal. kyr BP due to the difficulty of extracting clean diatom samples and a consequent reduction in sampling frequency. Nevertheless limited beta diversity and the transitional nature of Zone 2 means that changes were likely gradational between Zones 2 and 1. This gradational change primarily involved an increase to nutrient availability and/or limited changes to lake level.

5.3.4.2.3  Zone 3 (~15.3 to 3.3 cal. kyr BP)

Zone 3 marks a period of dominance by *S. microstriata* (29.39 ± 9.03 %) and limited presence of *D. stelligera* (8.87± 6.99 %) (Figure 5.7). Several species occur briefly in high abundances including *A. granulata* var.
ambigua, Stephanodiscus cf. alpinus and Synedra capitata. For instance, a peak of S. capitata occurs between ~5.5 and 4.6 cal. kyr BP (22.25 ± 5.89 %). Similarly, S. cf. alpinus and A. granulata var. ambiguа occur in abundance just prior to S. capitata in a single sample (~6.9 cal. kyr BP: 28.40 % and 57.10 % respectively). During this interval S. microstriata undergoes a marked reduction in abundance suggesting an increase in nutrient loads during spikes in A. granulata var. ambiguа abundance followed by a brief period of oligotrophy and higher Si-availability favouring S. capitata. As noted earlier, the period of S. capitata abundance follows deposition of the Tahua tephra which forms a 20 mm thick horizon within Lake Pupuke. Prior to ~6.9 cal. kyr BP, diatom communities are consistently dominated by S. microstriata (31.67 ± 5.78 %) and to a lesser extent, D. stelligera (11.76 ± 6.03 %). The latter are tychoplanktic and planktic/euplanktic respectively, indicating little change to water column depth (e.g., limited availability of benthic habitat). Furthermore an affinity for lower nutrient status of D. stelligera implies changes to trophic state throughout the Last Glacial Interglacial Transition (LGIT) as the principle agent of change to diatom community structure. The zone is one of consistently moderate nutrient loads favouring S. microstriata and accordingly records a moderate inter-sample SIMI score (0.81 ± 0.31).

The boundary of Zones 3 and 2 is well constrained at ~16.0-15.3 cal. kyr BP, involving a shift from S. microstriata dominance to a mixed community with increasing D. stelligera dominance. Combined with its relatively high beta diversity, this implies Zone 3 to be a distinct period which grades smoothly into a transitional community dominated by D. stelligera and S. microstriata in Zone 2. As noted above, diatom assemblages from Zone 3 (~8.2-3.3 cal. kyr BP) possess greater inter-sample diversity suggesting changes induced by the shift from Zone 2 to 3 (see below) resulted in a stable diatom community for a period of ~7800 years prior to onset of marked early Holocene variability.

5.3.4.2.4 Zone 4 (~3.3 cal. kyr BP to today)

The uppermost diatom zone displays the most variable diatom abundances and fluxes. Average total fluxes are the highest of the entire composite sequence (11.0 ± 9.1 x 10^6 valves cm^2 yr) including the highest influx rate at ~0.3 cal. kyr BP (4.1 x 10^7 valves cm^2 yr). The zone is dominated by alternating periods dominated by Aulacoseira granulata var. ambiguа (29.78 ± 27.72 %) and Discotella stelligera (41.33 ± 31.31 %). Subdominance by Staurosira microstriata (13.42 ± 12.50 %) occurs in transitions between the latter two indicator species. An affinity for higher nutrient loads by A. granulata var. ambiguа, moderate loads by S. microstriata and restricted loads by D. stelligera suggests a period of higher but variable nutrient availability within the water column. A. granulata var. ambiguа is a facultative planktic/meroplanktic taxon indicating the presence of seasonal disturbance and eutrophication coupled to a more stable, meso/oligotrophic water column favoured by D. stelligera and S. microstriata. As noted earlier (5.3.3. Diversity), this interval is denoted by particularly high inter-sample diversity (SIMI score 0.58 ± 0.33) suggesting exchanges between dominant taxa occurred relatively quickly (refer to Figure 5.7). Similarly, whilst the boundary of Zones 4 and 3 is well constrained at ~3.7-3.3 cal. kyr BP, the boundary involves a shift from a younger, unstable diatom community dominated by A. granulata var.
ambigua to an unstable, older community dominated by S. microstriata, reflected in a SIMI score of ~0.35 (e.g., high inter-sample diversity). Thus the taxonomic changes coincident with the boundary of Zones 4 and 3 are similar to those expressed at ~6.9 cal. kyr BP.

5.3.4.3 Diatom Ordination Results

A DCA Axis 1 length in excess of >2 units of standard deviation confirmed the need to employ a detrending algorithm in ordination analyses (e.g., greater axis length reflects greater beta diversity and species turnover). DCA Axes 1 and 2 explain 15.83% and 5.82% of the total variance respectively amongst diatom samples. Species scores are presented in Figure 5.8 with taxa possessing >5% (by count) abundance in any single sample highlighted. Samples with high positive Axis 1 scores have high corresponding abundances of Stephanodiscus cf. alpinus and Aulacoseira granulata var ambigua ($\lambda_1 = +2.96$ and +2.36 respectively) whilst high negative Axis 1 scores denoted greater abundance of Cyclotella cf. planctonica, Discotella stelligera and Staurosira aff. venter ($\lambda_1 = -1.33$, -1.05 and -0.93 respectively). Similarly, high positive Axis 2 scores correspond to greater abundance of cf. Synedra capitata ($\lambda_2 = +4.48$) and high negative Axis 2 scores correspond to greater abundance of Cymbella microcephala ($\lambda_2 = -3.04$).

From earlier inspection of dominant species autecology, it is likely that Axis 1 reflects changes in trophic state with negative values corresponding to oligo/mesotrophy and positive to eutrophy (see Table 5.4). For instance, A. granulata var ambigua and S. cf. alpinus are associated with higher nutrient status and positive values along Axis 1, whilst D. stelligera and D. balfouriana are associated with oligo/mesotrophy and negative values along Axis 1. Certain taxa that occur less abundantly are even more informative of Axis 1 variation. For instance, Tabellaria fenestrata and Cymbella delicatula both receive high negative scores (-2.39 and -2.38 respectively) and are oligo/mesotrophic indicator taxa (Van Dam et al., 1994). Hence DCA Axis 1 is most likely a response of algal communities to changing levels of nutrient availability in Lake Pupuke over the last ~44.0 kyrs. However, DCA Axis 2 is more complex and likely reflects an interaction of trophic responses and saprobity. More positive values correspond to oligosaprobous species (e.g., cf. Synedra capitata) whilst more negative values correspond to mesosaprobous species (e.g., F. capucina var. capucina, C. bacillum and C. microcephala).

| 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]). |
|---|---|---|---|
| **DCA axis** | 1 | 2 | 3 |
| Eigenvalue ($\lambda$) | 0.3073 | 0.1127 | 0.0510 |
| Gradient length | 2.6246 | 1.9776 | 1.1706 |
| Percentage explained variance of the species data | 15.83 | 5.82 | 2.63 |
| Cumulative percentage explained variance of the species data | 15.83 | 21.65 | 24.28 |
| Total Inertia | 1.9405 |


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 fenestra, 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).
DCA ordinations of sample scores confirm earlier inferences regarding diatom community change and reveal 4 clusters of diatom samples that are similar in both species and relative abundances (Figure 5.9). The boundaries of each sample cluster are also largely in agreement with CONISS derived estimates: (1) ~44.0 to 22.5 cal. kyr BP; (2) ~22.5 to 15.3 cal. kyr BP; (3) ~15.3 to 6.9 cal. kyr BP; and (4) ~6.9 cal kyr BP to today. The boundary between clusters (4) and (3) is hard to resolve due to marked variation in both DCA Axes 1 and 2. This and the fact that rare species have been downweighted in ordination analyses, explain the discrepancy with earlier CONISS-based zonation.

As DCA uses units of standard deviation it is possible to assess variation in sample scores within each DCA cluster (e.g., beta diversity). Average DCA scores change most markedly along Axis 1 implying greatest species turnover through trophic change. Within each DCA cluster, variability in sample score ($\lambda_1$ and $\lambda_2$) is less than between-cluster variability with the exception of the most recent cluster (~6.9 cal. kyr BP to today). The latter possess highly dispersed sample scores implying marked variation in nutrient availability over the last ~6.9 kyrs (refer to Table 5.10).

### Table 5.10: Summary of DCA scores by diatom ordination cluster identified from Figure 5.9.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Sample Ages</th>
<th>Statistic</th>
<th>Axis 1</th>
<th>Axis 2</th>
<th>Axis 3</th>
<th>Axis 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6.9 cal. kyr BP to today</td>
<td>Average</td>
<td>0.71</td>
<td>-0.14</td>
<td>-0.11</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.51</td>
<td>0.45</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n = 22$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.3-6.9 cal. kyr BP</td>
<td>Average</td>
<td>0.15</td>
<td>0.34</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.09</td>
<td>0.15</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n = 13$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.5-15.3 cal. kyr BP</td>
<td>Average</td>
<td>-0.16</td>
<td>0.12</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.08</td>
<td>0.10</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n = 9$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>44.0-22.5 cal. kyr BP</td>
<td>Average</td>
<td>-0.63</td>
<td>-0.12</td>
<td>0.07</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.10</td>
<td>0.09</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n = 29$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.9 and Table 5.10 demonstrate that Lake Pupuke has moved along a gradient to higher nutrient availability from ~44.0 cal. kyr BP to 6.9 cal. kyr BP with a lesser shift to greater availability of dissolved Oxygen. This trend however, was abruptly halted at 6.9 cal. kyr BP whereupon nutrient availability increased more markedly whilst saprobity decreased though still to a state of fairly high dissolved Oxygen (>75 %). Considerable variation exists however, within the most recent cluster with several samples lying well beyond the cluster boundary and being more indicative of older assemblages. For instance, diatom algal communities shift markedly between eutrophic and mesotrophic dominated assemblages during the last ~6.9 kyrs (see Figure 5.9). Despite this variability, diatom communities of the last ~7.0 kyrs provide the greatest abundance of eutrophic indicators suggesting a marked recent increase in nutrient availability. Thus nutrient availability has increased markedly from the mid Holocene, albeit with greater variability about this eutrophic state.
5.3.4.4 Diatom Transfer Function Results

5.3.4.4.1 No Analogue

The Pupuke composite diatom sequence includes many species with no modern analogue within Reid’s (2005) diatom calibration dataset. However, these species contribute <3 % on average (2.92 ± 2.75 %) to the overall biomass with more recent samples prone to a greater abundance of no-analogue taxa. CONISS-defined zonation describes the presence of no-analogue taxa very well with a gradient of lesser to greater presence occurring from Zones 1 to 4 (Table 5.11).

Table 5.11: Presence of no analogue taxa within the Lake Pupuke composite diatom series.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Age (cal. kyr BP)</th>
<th>No analogue abundance (%) Average</th>
<th>Standard Deviation</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.3 to today</td>
<td>5.15</td>
<td>4.07</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>15.3-3.3</td>
<td>3.56</td>
<td>1.83</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>22.5-15.3</td>
<td>3.14</td>
<td>1.84</td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>44.0-22.5</td>
<td>1.19</td>
<td>0.86</td>
<td>29</td>
</tr>
</tbody>
</table>

5.3.4.4.2 DI-pH

Classical weighted averaging (WA) calibration and regression were applied to diatom percentage abundance (by count) to infer down-core changes in annual pH. Diatom-inferred pH (DI-pH) values lay within the gradient covered by Reid’s (2005) calibration dataset (DI-pH range = 7.64-7.82; calibration pH = 5.66-8.88) (Figure 5.10). DI-pH for the youngest sample (1946 AD) is 7.72 ± 0.12 units which compares favourably with a contemporary annual average pH of 7.84 ± 0.35 (~1976-2009).

DI-pH values offer limited variation, averaging 7.73 ± 0.04 pH units. Consequently, modelled uncertainty exceeds predicted change over the sedimentary record. Accordingly, little can be inferred with confidence from DI-pH. Ultimately the lack of DI-pH variation suggests its absence in driving community structural change as confirmed in earlier DCA of diatom assemblages.

5.3.4.4.3 DI-EC

Isothermal (e.g., at holomixis) and stratified diatom-inferred electrical conductivity (DI-EC) estimates calculated using a classical WA with tolerance downweighting (WA-tol) model consistently returned impossible negative EC values. The next best performing model for isothermal EC by classical WA was selected (e.g., EC_ISO [WA] $r^2_{\text{JACK}} = 0.75$, identical RMSEP of 0.17 μS cm [Reid, 2005:27]). This also yielded similar patterns in DI-EC to the isothermal model with the benefit of preventing reconstruction of impossible EC values. The isothermal DI-EC profile varies markedly over the last ~44 kyr with modelled values lying within the calibration dataset range (DI-EC range = 82-832 μS cm; calibration EC range = 20-1115 μS cm), and a reasonable estimate of contemporary EC (DI-EC of 1946 AD 479 ± 165 μS cm compared to modern 280 ± 3 μS cm (~1976-2009)).
Modelled DI-EC change conforms to CONISS-defined diatom zonation with a gradient of lesser to higher conductivity from ~44.0 cal. kyr BP to today (Figure 5.10). There is also marked variation in DI-EC within each zone, though with an absence of significant change prior to ~8.2 cal. kyr BP whereupon DI-EC rises to a peak of 774 μS cm before dropping again at ~5.5 cal. kyr BP. Similar behaviour is noted at ~4.1 cal. kyr BP with a DI-EC peak of 379 μS cm confined by lows at ~4.6 cal. kyr BP (156 μS cm) and ~3.7 cal. kyr BP (121 μS cm). The last ~2.7 cal. yrs are marked by an increasing trend to higher conductivity (419 ± 260 μS cm) composed of several peaks at ~2.0 cal. kyr BP (592 μS cm), ~1.0-0.8 cal. kyr BP (640 ± 27 μS cm) and ~0.5-0.4 cal. kyr BP (819 ± 19 μS cm).

DI-EC behaviour mirrors other diatom-inferred parameters, namely DRP, TP and Chl a suggesting that the mechanisms behind changes in conductivity have likely impacted on the availability of key limiting nutrients (see below). Changes to conductivity, DRP and TP appear to reflect the abundance of the facultative planktic/meroplanktic eutrophic taxon *A. granulata var. ambiguа* which increases in abundance at the expense of the tychoplanktic, mesotrophic taxon *S. microstriata*. Thus an oscillatory pattern of alternating more and less conductive conditions occurs throughout the Holocene, commencing ~6.9 cal. kyr BP.

### 5.3.4.4.4 DI-DRP and DI-TP

Isothermal DRP and annual TP were reconstructed from classical deshrinking WA-tol and WA models. Both are included here owing to their similarity, suggesting that DRP and TP are driven by similar mechanisms (Figure 5.10). Both DI-DRP and DI-TP demonstrate marked variation over the last ~44.0 cal. kyr BP with the values within the gradient covered by calibration sites (DI-DRP and DI-TP range 0.24-16.74 mg m⁻³ and 4.09-37.62 mg m⁻³; calibration range = 0.20-100.75 mg m⁻³ and 1.85-171.25 mg m⁻³ respectively). Inferred modern values correspond well to observed concentrations of DRP and TP (DI-DRP and DI-TP at 1946 AD are 5.8 ± 1.8 and 24.1 ± 3.4 mg m⁻³ compared to modern DI-DRP and DI-TP of 11.1 ± 1.8 and 27.8 ± 25.1 mg m⁻³ respectively [~1976-2009]). As noted, there are significant correlations between trends in DI-DRP and DI-TP and those of DI-EC (r_{DRP,EC} = 0.84, P < 0.005, n = 73; r_{TP,EC} = 0.97, P << 0.005, n = 73). DI-DRP and DI-TP present a trend of increasing values from ~44.0 cal. kyr BP to today (Table 5.12). DI-TP and DCA Axis 1 scores also demonstrate a significant correlation supporting the inference that changing nutrient availability is the principal cause of variation in diatom community structure over the last ~44.0 cal. kyr BP (r_{DCA1,TP} = 0.91, P < 0.005, n = 73).

The most notable features of DI-TP are those present in DI-EC, a broad peak in CONISS Zone 3 (~8.2 to ~5.5 cal. kyr BP, peak DI-TP = 35.42 mg m⁻³) followed by a relative decline and resumption of more elevated TP levels throughout much of CONISS Zone 4 (~2.7 cal. kyr BP to today, 21.51 ± 10.6 mg m⁻³). Inferred TP and EC values are however, far greater throughout CONISS Zones 4 and 3 than Zones 2 and 1 indicating that Lake Pupuke likely underwent eutrophication recently in which marked variability has occurred. The mid-Holocene period of reduced DI-TP (~5.5-4.1 cal. kyr BP, DI-TP = 12.68 ± 0.69 mg m⁻³) is coincident with an abundance of
oligotrophic taxa, particularly *Synedra capitata* (~20%). The latter, in particular, has higher Si-demands which further records reduced availability of TP. Inferred increases in TP and EC confirm inferences derived from increasing DCA Axis 1 scores of shift to a state of variable eutrophy coincident with increases in the abundance of eutrophic taxa particularly *Aulacoseira granulata var. ambigua* during the middle Holocene.

DRP represents a component of TP that is most readily available to algal producers (Wetzel, 2001). Consequently it represents a proxy for aquatic productivity rather than a complex of allochthonous and autochthonous components (e.g., TP) (Reid, 2005). The isothermal DI-DRP trend largely mirrors annual DI-TP although there are several marked differences (Figure 5.10). DI-DRP maintains slightly elevated values from ~44.0 cal. kyr BP to ~29.7 cal. kyr BP (1.40 ± 0.66 mg m^-3^) prior to reducing to negligible values throughout the interval ~29.0 cal. kyr BP to ~16.7 cal. kyr BP (0.43 ± 0.18 mg m^-3^) denoting a period of limited aquatic productivity. Thereafter from ~16.0 cal. kyr BP to today values are consistently higher (4.16 ± 4.03 mg m^-3^), although several peaks also occur between ~15.3 cal. kyr BP (5.39 mg m^-3^) and ~13.5 cal. kyr BP (5.40 mg m^-3^) prior to the increases in DI-TP and DI-EC from ~8.2 cal. kyr BP.

5.3.4.4.5 DI-Chl a

Isothermal changes to Chlorophyll *a* have been reconstructed by a classical WA model (DI-Chl a) and are presented in Figure 5.10. Reconstructed Chl *a* values lay within the gradient covered by calibration sites (calibration range = 0.28-22.63 mg m^-3^; model range = 1.21-12.01 mg m^-3^) and a reduced agreement to modern hydrology (DI-Chl a of 1946 AD is 7.6 ± 1.3 mg m^-3^ compared to modern 15.5 ± 40.8 mg m^-3^ [-1976-2009, *n* = 207]) can be explained by the fact that Lake Pupuke has undergone a recent reversal in nutrient availability limiting the availability of DRP on ~1940s levels (ARWB, 1990; Holmes, 1994). Moreover, the lake underwent CuSO_4_ treatment to remove noxious algal blooms in the 1930s which would have reduced Chl *a* abundance on present levels. Changes to DI-Chl *a* also reflect changes to DI-TP (*Pearson r*[^DCA1,TP] = 0.99, *P < 0.005, *n* = 73) imparting further confidence by demonstrating the crucial role played by Phosphate in effectively limiting algal biomass. Very little change to DI-Chl *a* occurs prior to ~8.2 cal. kyr BP (2.71 ± 0.82 mg m^-3^) although greater DI-Chl *a* occurs from ~44.0 cal. kyr BP to ~38.6 cal. kyr BP (2.86 ± 0.46 mg m^-3^) whereupon values decline to ~19.2 cal. kyr BP (2.07 ± 0.41 mg m^-3^). Over the interval ~18.4 cal. kyr BP to today, DI-Chl *a* values increase (5.07 ± 2.85 mg m^-3^) (refer to Figure 5.10). As before (e.g., DI-EC, DI-TP, DI-DRP) values of DI-Chl *a* increase markedly at ~8.2 cal. kyr BP (DI-Chl *a* max = 11.23 mg m^-3^), promptly decline and rise in an oscillatory fashion from ~6.9 cal. kyr BP to today. DI-Chl *a* thereby offers a complimentary window on the natural eutrophication of Lake Pupuke provided by DI-TP and DI-DRP.
Table 5.12: Diatom-inferred pH, EC, TP, DRP and Chl a with CONISS-defined zonation for the Lake Pupuke composite series.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Age (cal. kyr BP)</th>
<th>Statistic</th>
<th>Transfer Function</th>
<th>Di-pH (SI)</th>
<th>Di-EC (μS cm⁻¹)</th>
<th>Di-DRP (mg m⁻³)</th>
<th>Di-TP (mg m⁻³)</th>
<th>Di-Chl a (mg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.3 to today</td>
<td>Average</td>
<td>7.73</td>
<td>386</td>
<td>6.36</td>
<td>20.05</td>
<td>6.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.03</td>
<td>260</td>
<td>4.73</td>
<td>10.80</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.3-3.3</td>
<td>Average</td>
<td>7.77</td>
<td>177</td>
<td>2.20</td>
<td>13.40</td>
<td>4.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.04</td>
<td>162</td>
<td>1.80</td>
<td>6.03</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.5-15.3</td>
<td>Average</td>
<td>7.72</td>
<td>101</td>
<td>0.70</td>
<td>7.87</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.04</td>
<td>10</td>
<td>0.57</td>
<td>1.30</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>44.0-22.5</td>
<td>Average</td>
<td>7.70</td>
<td>92</td>
<td>1.18</td>
<td>6.45</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard deviation</td>
<td>0.02</td>
<td>6</td>
<td>0.74</td>
<td>1.03</td>
<td>0.55</td>
<td></td>
</tr>
</tbody>
</table>

n

158
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.
Chapter Five

5.4 Discussion

Diatom inferences are presented against a paleoclimate event stratigraphy based on geochemical proxy data as it has greater temporal resolution than diatom floristic change. The diatom-inferred paleolimnology of Lake Pupuke provides a complimentary record of environmental change to the bulk geochemical data by recording marked changes to habitat availability and lacustrine nutrient cycles over the last ~44 kyrs (refer to Table 5.13). For example, detrended correspondence analysis (DCA) demonstrated that nutrient availability is the principal factor governing floristic structure with high positive and negative $\lambda_1$ sample scores corresponding to greater abundance of *Aulacoseira granulata var. ambiguа* and *Discotella stelligera* respectively. CONISS-defined zones describe a progression to increased nutrient availability and mixing across 4 distinct diatom communities whose boundaries closely match earlier geochemical and physical proxy changes (Table 5.13). Knowledge of the seasonality exhibited in contemporary diatom assemblages and the autecologies of the dominant taxa is employed to link changes in nutrient availability to mixing and benthic REDOX, particularly an early onset and subsequent intensification of thermal stratification at ~5.5 cal. kyr BP and ~3.3 cal. kyr BP respectively. Similar ages for the initiation and subsequent intensification of thermal stratification have already been proposed by geochemical proxies for paleolimnology (~5.6 and ~3.2 cal. kyr BP) enabling coeval changes in diatom productivity and community structure to be linked to changes in mixing and benthic REDOX. Likewise, changes in catchment weathering and erosion altered the influx of essential nutrients at ~6.9 cal. kyr BP coincident with a rise in clastic influx between ~5.7 and 7.6 cal. kyr BP. However, the limited diversity of diatom assemblages restricts the likely significance of each quantitative diatom-inferred palaeolimnological gradient and offers a likely explanation for highly similar trends exhibited by DI-EC, DI-Chl a and DI-TP in the Pupuke composite sequence (e.g., $r_{EC,TP} = 0.97$, $r_{EC,Chl \ a} = 0.96$, $r_{TP,Chl \ a} = 0.99$; $P < 0.01$; $n = 73$). Nonetheless, as changes to EC, TP and Chl a are likely driven by the same process, changes in lake depth and circulation, they can offer a valid insight to paleolimnology at Lake Pupuke during the last 44.0 cal. kyr BP when combined.
Table 5.13: Diatom inferred paleoenvironment from the Pupuke composite sequence.

<table>
<thead>
<tr>
<th>CONISS Zones (cal. kyr BP)</th>
<th>DCA Axis 1 and Axis 2 Scores (μ ± 1σ)</th>
<th>Dominant Taxa (Subdominant Taxa)</th>
<th>Diatom Assemblage</th>
<th>Paleolimnology of Lake Pupuke</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 (~3.3 to today)</td>
<td>-0.62 ± 0.10 -0.12 ± 0.09</td>
<td>Aulacoseira granulata var. ambigua, Discocella stelligera (Staurosira microstria, Stephanodiscus cf. alpinus)</td>
<td>• High diatom influx • Relatively species rich • Low SIMI scores, high beta diversity, dynamic communities • Dominant shifts between euplankton, tychoplankton and meroplankton • Greatest but highly variable DI-EC, DI-TP, DI-DRP and DI-Chl a</td>
<td>Deep, productive lake</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Staurosira microstria (Aulacoseira granulata var. ambigua, Discocella stelligera, Stephanodiscus cf. alpinus)</td>
<td>• Low diatom influx with exception of brief, massive increase from ~13.9 and 13.0 cal. kyr BP • Relatively species rich • Moderate SIMI scores, high later beta diversity (~3-8.2 cal. kyr BP), low early beta diversity • Dominated by shifts between tychoplankton and meroplankton • Increasing DI-EC, DI-TP, DI-DRP and DI-Chl a with notable peak between ~8.2 and 5.5 cal. kyr BP</td>
<td>Deep (deepening), unproductive lake</td>
</tr>
<tr>
<td>3 (~15.3 to 3.3)</td>
<td>-0.16 ± 0.08 0.12 ± 0.10</td>
<td>Discocella stelligera, Staurosira microstria (Diatomella balfouriana, Staurosira pinnata)</td>
<td>• Low diatom influx • Relatively species poor • Moderate SIMI scores and beta diversity throughout entire period • Transitional zone of early euplankton and later tychoplankton dominance • Beginning of rise in DI-EC, DI-TP, DI-DRP and DI-Chl a</td>
<td>Shallow, unproductive lake</td>
</tr>
<tr>
<td>2 (~22.5 to 15.3)</td>
<td>0.31 ± 0.35 0.32 ± 0.29</td>
<td>Discocella stelligera, Staurosira microstria (Diatomella balfouriana, Staurosira pinnata)</td>
<td>• High diatom influx until ~31.3 cal. kyr BP • Relatively species poor • High SIMI scores and stable communities • Stable zone of euplankton dominance • Low DI-EC, DI-TP and DI-Chl a with notable decline in DI-DRP at ~29.0 cal. kyr BP</td>
<td>Deep (shallowing), moderately productive lake</td>
</tr>
<tr>
<td>1 (~44.0 to 22.5)</td>
<td>0.70 ± 0.54 -0.26 ± 0.35</td>
<td>Discocella stelligera (Cyclotella cf. planktonica, Diatomella balfouriana, Staurosira microstria, Staurosira pinnata)</td>
<td>• High diatom influx until ~31.3 cal. kyr BP • Relatively species poor • High SIMI scores and stable communities • Stable zone of euplankton dominance • Low DI-EC, DI-TP and DI-Chl a with notable decline in DI-DRP at ~29.0 cal. kyr BP</td>
<td>Deep (shallowing), moderately productive lake</td>
</tr>
</tbody>
</table>

• High diatom influx
• Relatively species rich
• Low SIMI scores, high beta diversity, dynamic communities
• Dominant shifts between euplankton, tychoplankton and meroplankton
• Greatest but highly variable DI-EC, DI-TP, DI-DRP and DI-Chl a

• Deep, intensely stratified lake with greater overall availability of nutrients and diatom productivity
• Diatom communities are unstable and exhibit high species turnover in response to variable strength of mixing at overturn
• Mixing controls the availability of nutrients and shifts in dominance between oligotrophic euplankton and eutrophic meroplankton.

• Deep lake exhibiting an early onset of less intense, but stable thermal stratification resulting in limited nutrient regeneration and circulation at overturn (~5.5 to 3.3 cal. kyr BP)
• An erosive event between ~7.6 and 5.7 cal. kyr BP corresponds to greater mixing and resuspension of denser, meroplankton at ~6.9 cal. kyr BP. A proposed mechanism of increased windspeed/duration offers an explanation for loss of terrestrial productivity (e.g., declining C/N atomic ratios of composite sediment) through more frequent destructive windstorms. Further sampling is needed to confirm diatom changes correspond to this wider erosional event although the latter supports the reported dates for Kauri (Agathis australis) expansion throughout the Northern North Island at ~7-8 cal. kyr BP in response to windstorms and possible drought (Ogden et al., 1992; Newnham et al., 1999)
• Early Holocene absent from diatom abundance or influx suggesting diatom productivity was limited throughout much of Zone 3 and prior to intense thermal stratification
• However, a peak in influx occurring between ~13.9 and 13.0 cal. kyr BP corresponds to greater mass accumulation of organic sediment suggesting a Late Glacial Interglacial Transition (LGIT) peak in productivity

• A transitional stage of lower lake level with limited mixing in the absence of thermal stratification
• A boundary at ~16.0-15.3 cal. kyr BP is marked by declining abundance of aerophilous diatom taxa and supports a delay in the aquatic response to improved paleoclimate from ~18.5 cal. kyr BP

• A period of variable lake level; relatively high until ~29.0 cal. kyr BP and lowered thereafter. Prior to ~29.0 cal. kyr BP greater diatom influx and euplankton followed by rise in aerophilous taxa thereafter through a decline in effective precipitation and lake level
5.4.1 Paleoerosion

Changes to the composite diatom sequence support the earlier paleoerosion event stratigraphy (Section 4.5.1. Paleoerosion). For instance, increased erosion was inferred from ~31.5 to 18.5 cal. kyr BP through increased clastic particle sizes. A coeval increase in the proportion of terrestrial organic matter (OM) and reduction in total Sulphur (TS) concentration record a reduction in aquatic productivity which coupled to increased erosion indicates a reduction in lake level and greater focussing of coarser particles to cored locations (Figure 5.11). The period ~29.0 to 18.4 cal. kyr BP corresponds to an increased abundance of aerophilous taxa, particularly Diatomella balfouriana (5.26 ± 1.74 %) whose abundance is markedly less both prior to (0.91 ± 0.88 %) and thereafter (1.20 ± 1.64 %). Aerophilous taxa inhabit shallow, ephemeral pools suggesting marked coeval shallowing to expose greater catchment area to intermittent inundation (Dam et al., 2001). Importantly, the abundance of D. balfouriana also increases to heightened values during a proposed intensification of erosion and allochthonous influx between ~15.5 cal. kyr BP and ~13.8 cal. kyr BP, before promptly declining from ~13.4 cal. kyr BP until today (Figure 5.11). This inferred lake shallowing event is closely bracketed by 8 diatom samples over an interval of ~2.3 kyrs stressing its significance. Combined, biological, geochemical and physical proxy data thereby imply similar mechanisms of lake level shallowing during the LGCP, and briefly during a reversal in the Last Glacial/Interglacial Transition (LGIT).

The closed hydrological status and absence of fluvial complexities within the site ensure that lake level responds directly to changes in the balance of precipitation and evaporation (e.g., effective precipitation). Accordingly, a shift to drier, zonal airflow during the LGCP has been proposed by numerous authors as driving a northern migration of dense podocarp-coniferous forest to refugia in the Northern North Island (NNI) during MIS 2 (e.g., Newnham, 1999; Shulmeister et al., 2001). A shift to strengthened westerly and southwesterly airflow resulting in a resurgence of zonal regimes and reduced effective precipitation over Lake Pupuke, could therefore offer an explanation for the inferred reductions in lake level and aquatic productivity during the LGCP (~28.5 to 18.5 cal.kyr BP) and briefly in the LGIT (~15.5 to 13.8 cal. kyr BP).

Geochemical and physical indicators of erosion also presented evidence of heightened erosion including a marked reduction in terrestrial productivity during the middle Holocene (~7.8 and 5.7 cal. kyr BP). A minor increase in D. balfouriana occurs earlier at ~8.2 cal. kyr BP (~4.0 %), and its subsequent rapid decline by ~6.9 cal. kyr BP (~0.6 %) offers little indication of lake level shallowing corresponding to greater clastic influx and reduced total organic Carbon (TOC) concentration within composite sediment. Diatom influx rises markedly during this interval (~7.8 to 5.7 cal. kyr BP) reaching a peak of 8.1 x 10⁶ valves cm⁻² yr at ~6.9 cal. kyr BP which is similar to the later eutrophication of Lake Pupuke (~3.3 cal. kyr BP to today). Consequently, reductions in total biomass do not correspond to declining diatom and potentially, microalgal communities.

The period ~7.8 to 5.7 cal. kyr BP may correspond to moderately high effective precipitation within the NNI as recorded by: greater abundance of aqueous diatom taxa at Crater Hill, Auckland (Lancashire et al., 2002); relatively depleted δ¹³C in the Waitomo master speleothem record (Williams et al., 2004); and increased
occurrence of aquatic plant macrofossils at Kopouatai Bog, Northland (Hazell, 2005). This period is highly unusual because it records a marked drop in terrestrial biomass and heightened catchment disturbance but with little change to lake level or aquatic productivity. Further evidence to support this can be gathered from diatom-inferred concentrations of dissolvable reactive Phosphate (DI-DRP). As the latter records the abundance of the Phosphate form most often limiting and readily accessible to aquatic producers, and as inferred values lay well within the range exhibited by calibration lakes, DI-DRP is a robust proxy for aquatic productivity within the Pupuke composite sequence. For instance, earlier inferred declines in aquatic productivity during the LGCP are mirrored by lesser DI-DRP between ~29.0 and 16.7 cal. kyr BP (0.43 ± 0.18 mg m$^{-3}$) than the LGIT and Holocene (4.16 ± 4.03 mg m$^{-3}$) and prior to the LGIT (1.40 ± 0.66 mg m$^{-3}$) (note: a decline in DI-DRP also occurs between ~15.1 and 13.4 cal. kyr BP in line with a proposed LGIT reversal from ~15.5 to 13.8 cal. kyr BP [see Chapter 4]). However, heightened erosional influx between ~7.6 and 5.7 cal. kyr BP corresponds to DI-DRP values typical of recent eutrophication (Figure 5.11). Corresponding nutrient availability between ~7.6 and 5.7 cal. kyr BP is high and unlikely to correspond to a reduction in lake level or autochthonous productivity. Instead, diatom-inferred water chemistry suggests an increase in leaching of terrestrial solutes accompanying the influx of clastic sediment amid greater catchment disturbance.

The deposition of the Tahua tephra (~7.0 cal. kyr BP) might complicate this inference as greater nutrient availability at ~6.9 cal. kyr BP might very well represent a corresponding diatom bloom following greater Si-availability. For instance, many older tephra possess a corresponding diatom influx peak (Section 5.4.2. Influx). Whilst closer sampling can elicit whether this was indeed a short- or longer-lived response, several factors suggest limited if any response to tephra deposition. The Tahua tephra is not particularly thick (~15 mm) and thicker ashfalls lack any noticeable effect on diatom abundance during the productive LGIT and Holocene including the Rotorua (~15.4 cal. kyr BP; 45 mm thickness) and Rotoma (~9.5 cal. kyr BP; 45 mm thickness) (Molloy et al., 2009). Secondly, depletion of δ$^{30}$Si in diatom silica suggests reduced competition for dissolved Si (DSi) between ~18.5 and 5.0 cal. kyr BP (see Chapter 6). Likewise, the Tahua tephra lacks other essential nutrients necessary to facilitate a diatom bloom; Phosphate and Nitrate concentrations are < 0.00 wt. % (Molloy et al., 2009). Thus it seems highly unlikely that ashfall can explain the presence of eutrophic taxa, notably *Stephanodiscus* cf. *alpinus* and *A. granulata* var. *ambigua* within Lake Pupuke at ~6.9 cal. kyr BP.

Although *A. granulata* var. *ambigua* is adapted to seasonal thermal stratification, geochemical proxies (e.g., TN contamination, Mn/Fe ratios, δ$^{15}$N) imply an onset for the latter no earlier than ~6.2 cal. kyr BP with greater intensity of thermal stratification much later (~3.2 cal. kyr BP [Section 4.5.4. Changes to Mixing and Benthic REDOX]). Having excluded the likelihood of lake level shallowing and intense thermal stratification, another mechanism capable of catchment disturbance is needed which can liberate greater nutrients and increase sample λ$\tau$ score, whilst simultaneously generating greater turbulence necessary to facilitate blooms of denser, heavily silicified meroplankton at ~6.9 cal. kyr BP. This in turn excludes a response to the nutrient-deficient Tahua tephra and instead necessitates better mixing of bottom waters through deeper wave bases and stronger windiness (e.g., Wetzel, 2001). An associated increase in landscape disturbance throughout the NNI has been proposed from ~7 cal. kyr BP in several palynological investigations (e.g., Newnham, 1992; Elliot et al., 1998;
Newnham et al., 1999; Newnham et al., 2007a). For instance, Kauri (*Agathis australis*) dominance of forest canopies within the NNI occurs from ~7 cal. kyr BP (Newnham, 1999). The cause of Kauri growth is keenly debated but a positive response to greater canopy exposure coincident with more frequent windstorm is likely (e.g., Ogden et al., 1992; Newnham, 1999; Newnham et al., 2007a). Thus catchment disturbance from ~7.6 to 5.7 cal. kyr BP might reflect heightened frequency of destructive cyclonic depressions.

Shulmeister et al (2001) proposed a relative warming of surface waters in the Oceanic South Pacific Gyre following stabilisation of sea levels at ~7 cal. kyr BP. An ensuing reduction in high altitude advection from the west to the east Pacific due to the reduced gradient in corresponding sea surface temperatures (SST) could have resulted in heightened northerly flows over Northern Australia and New Zealand (Shulmeister et al., 2001). Heightened northerly airflow originating in the tropics would be associated with increased frequency of extratropical cyclones and destructive windstorms (Lorrey et al., 2007). Thus heightened erosion between ~7.6 and 5.7 cal. kyr BP likely records the loss of some terrestrial vegetation through destructive windstorms which were associated with greater wave activity and turbulence within Lake Pupuke. Better mixing of deep waters thereby resulted in the observed increase in nutrient availability at ~6.9 cal. kyr BP. Although diatom-inferred paleolimnological change excludes a lake level decline associated with a corresponding decline in effective precipitation at ~6.9 cal. kyr BP (e.g., absence of aerophilous taxa, increased nutrient availability and dense, meroplankton blooms), without further sampling for diatom analysis, the precise date of a likely enhancement of greater mixing is not possible.

The coeval timing of increased catchment disturbance and greater mixing at ~6.9 cal. kyr BP at Lake Pupuke coupled with Kauri expansion to more southerly locations from ~7 cal. kyr BP (Newnham et al., 2007a) does imply more frequent destructive windstorms and therein increased northerly airflow were experienced at the site. An alternative hypothesis, the early onset of drier zonal airflow and corresponding reduction in effective precipitation leading to enhanced thermal stratification can be excluded as geochemical evidence suggests an onset of drier zonal airflow no earlier than ~6.2 cal. kyr BP which is itself noted by a marked change to diatom sample beta diversity at ~5.5 cal. kyr BP.

From ~0.6 cal. kyr BP until today, geochemical and physical proxies for paleoerosion indicate a substantial increase to clastic sediment influx (Figure 5.11). The latter also lacks a corresponding increase in aerophilous or benthic taxa, stressing the likelihood that a marked change in lake level did not occur. Instead, continued high aquatic productivity coincides with the increased leaching of terrestrial minerals that resulted in greater magnetic susceptibility (MS) as well as coarser clastic input (Section 4.5.1. Erosion). Accordingly diatom influx increases although this rise is more attuned to a proposed intensification of stratification at ~3.3 cal. kyr BP, making it hard to reliably distinguish any change in the allochthonous supply of nutrients. Nevertheless, sample SIMI scores drop to a minimum at ~0.7 cal. kyr BP (0.0076) suggesting marked coincident species turnover and structural change between ~0.7 and 0.5 cal. kyr BP. Thereafter and until today, samples exhibit marked beta diversity making the last ~700 yrs as a period of highly variable diatom community structure superimposed on greater natural variability attached to the onset of intense thermal stratification from ~3.3 cal. kyr BP.
Figure 5.11: Diatom paleoerosion event stratigraphy for the Pupuke composite sequence highlighting coeval changes to physical and geochemical indicators (water content \([W_c]\), dry bulk density \([DBD]\), particles >32 \(\mu m\) (>32 \(\mu m\)) and mass accumulation rate \((MAR)\). Shading denotes periods of increased erosion.

Laws in \(W_c\) and \(DBD\) record increased erosional influx to Lake Pupuke. Coeval increases to the abundance of amphipod taxa record declines in lake level, exposing more catchment area to intermittent inundation, which also resulted in greater species turnover and higher beta diversity.

A mid-LIG rise in erosional influx is recorded by the increased abundance of amphipod diatom taxa (>15.5 to 11.8 cal. kyr BP) and a reversal in \(DI\) to levels indicative of a shallower lake \(\sim 10\) m pelagic \(\sim 20-35\) m deep by 13.8 cal. kyr BP.

Increased catchment disturbance from \(\sim 7.8-5.7\) cal. kyr BP is coeval with increased diatom community turnover (beta diversity) but little change to amphipod taxa suggesting lake level remained high.
5.4.2 Paleoproductivity

Detrended correspondence analysis (DCA) of composite diatom samples stresses the principal role of changing nutrient availability driving diatom species turnover over the last ~44 kyrs. Pupuke composite samples shift from high negative to high positive $\lambda_1$ scores between ~44.0 cal. kyr BP and today with a corresponding shift in dominance from oligo/mesotrophic taxa (Discotella stelligera) to eutrophic taxa (A. granulata var. ambiguа). Consequently, $\lambda_1$ sample scores offer a proxy for nutrient availability which can explain ~15.78% of species variation downcore. In terms of deciphering major changes, taxonomic data thereby offer a complimentary record to geochemical and physical proxies for paleoproductivity, with the dominance of D. stelligera and Stauropsis microstriata indicative of glacial and interglacial paleoclimate respectively. CONISS-defined diatom zonal boundaries suggest a shift from oligotrophy to mesotrophy between ~16.0 and 15.4 cal. kyr BP indicated by marked declines in the abundance of D. stelligera from ~22.5 cal. kyr BP. This timing confirms a delayed response by aquatic producers to climatic improvement evident in increased terrestrial productivity from ~18.5 cal. kyr BP, that is not seen by proxies for aquatic productivity until ~16.5 cal. kyr BP (e.g., declining C/N atomic ratios of organic matter [OM] and increased total Sulphur [TS] concentration) (Figure 5.12). Subsequently, little substantive change occurs to diatom community structure until a shift to eutrophy at ~3.7 to 3.3 cal. kyr BP characterised by the eutrophic and stratification-adapted taxon, A. granulata var. ambiguа and which importantly, coincides with geochemical changes at ~3.2 cal. kyr BP that indicate enhanced seasonal thermal stratification and associated mixing during overturn (e.g., reduced C/N atomic ratios, increasing total organic Carbon [TOC] and total Nitrogen [TN] including increased inorganic Nitrogen concentration) (Section 4.5.2. Paleoproductivity).

Inspection of diatom fluxes offers further insight into paleoproductivity at Lake Pupuke over the last ~44 kyrs. For instance, a well-constrained increase in diatom productivity, particularly of the mesotrophic taxon S. microstriata, occurs between ~13.7 and 13.0 cal. kyr BP (refer to Figure 5.12). The latter taxon is associated with improved post-glacial climate in Scotland (Haworth, 1976). Increased abundance of S. microstriata therefore suggests markedly improved paleoclimate in the mid-to-late LGIT. Although diatom fluxes can incorporate changes to mass accumulation rate irrespective of any change in concentration (e.g., an MAR artefact), the magnitude of increased diatom influx is so substantial as to imply improved paleoclimate, greater nutrient availability and a consequent rise in productivity. Likewise, as the rise in MAR from ~14.8 to 12.7 cal. kyr BP corresponds to an increase in organic Carbon and Nitrogen concentration as well as declining clastic input, increased flux of mesotrophic diatoms lends further support for a proposed LGIT peak in productivity (Figure 5.12). A subsequent reduction in diatom influx until the clastic influx associated with heightened paleoerosion at ~6.9 cal. kyr BP, suggests a limitation on diatom abundance particularly as the later LGIT and early Holocene are particularly productive overall (i.e., greater TOC and TN concentration and flux between ~10.2 and 8.0 cal. kyr BP). Mixed C/N atomic ratios (i.e., >20) during the early Holocene demonstrate increased terrestrial productivity biomass. An associated decline in the supply of Si through reduced surface and subsurface flow might explain reduced diatom productivity although as noted, depletion of $\delta^{30}$Si in diatom silica suggests another mechanism of limited
diatom abundance (see Chapter 6). Instead, paleoclimate and hydrological changes related to mixing are more likely. For instance, heightened erosion from ~7.6 to 5.7 cal. kyr BP and a corresponding increase in more heavily silicified taxa suggest greater lake turbulence accompanied the large increase in diatom influx at ~6.9 cal. kyr BP. Similarly, increased diatom influx from ~3.3 cal. kyr BP until today corresponds to greater lake turbulence and eutrophication through greater seasonal overturn.

Although diatom influx, therefore, offers a somewhat limited proxy for paleoproductivity prior to the onset of thermal stratification, diatom-inferred water quality is not as limited because of its use of relative abundance estimates. Moreover, Reid’s (2005) DI-TF closely reconstructed near present (~2006-1976) estimates of isothermal conductivity (DI-EC) and Chlorophyll a (DI-Chl a), and annual mean total and dissolved reactive Phosphate (DI-TP and DI-DRP) from the uppermost diatom sample (~1940 AD). Furthermore, predicted values are also well within the range exhibited by calibration lakes lending further credence to downcore inferred change. The four profiles of DI-EC, DI-Chl a, DI-DRP and DI-TP demonstrate an increase in productivity and conductivity from ~16.5 cal. kyr BP, comprised of two peaks: (1) a poorly constrained increase in conductivity and the availability of TP and DRP resulting in greater productivity between ~8.2 and 5.5 cal. kyr BP; and (2) a better constrained rise in conductivity and increased availability of TP and DRP resulting in greater aquatic productivity from ~3.3 cal. kyr BP to today. These peaks in conductivity, nutrient availability and algal biomass exceed predicted (boot-strapped) error of preceding samples and therefore record significant changes in paleolimnology. Furthermore, a strong significant positive correlation between trends of DI-TP and DI-Chl a confers greater reliability to diatom inferred water chemistry trends as TP is an essential micronutrient to terrestrial and aquatic producers ($r_{TP,Chl~a} = 0.99, P < 0.001, n = 73$). A strong positive association between the two, therefore, records the likely limitation exerted upon productivity by nutrient availability. A strong correlation between DI-DRP and Chl a also emphasises the former’s limiting role in aquatic productivity ($r_{DRP,Chl~a} = 0.84, P < 0.001, n = 73$).

Trends in DI-DRP largely mirror earlier inferred changes to paleoproductivity (Section 4.5.2, Paleoproductivity): a notable decline in aquatic productivity during the LGCP (~29.0 to 16.7 cal. kyr BP; $0.43 \pm 0.18$ mg m$^{-3}$), preceded (~44.0 to 29.0 cal. kyr BP; $1.40 \pm 0.66$ mg m$^{-3}$) and followed by heightened values (~16.7 cal. kyr BP to today; $4.16 \pm 4.03$ mg m$^{-3}$). Increases in DI-DRP during the LGIT and Holocene also exceed those exhibited during the preceding ~27.3 kyrs in a similar fashion to TOC and TN concentration (Figure 5.12), and suggesting that DI-DRP offers an accurate record of autochthonous productivity. The onset of increased DI-DRP occurs between ~16.7 and 16.0 cal. kyr BP supporting geochemical evidence of a ~2-3 kyr delay by aquatic producers to ameliorating paleoclimate at the (last) Termination (~18.5 cal. kyr BP) in Lake Pupuke.

Due to the good agreement between DI-DRP and inferred paleoproductivity, several less marked events warrant further discussion. Notably, a decline in DI-DRP during an inferred peak of productivity during the Early Holocene Warm Period (~10.2 to 8.0 cal. kyr BP) and another decline following a likely early onset of thermal stratification at ~4.5 cal. kyr BP (e.g., greater accompanying Mn/Fe ratios and more enriched $\delta^{15}$N attached to...
composite sediment). The NNI experienced higher effective precipitation during the early Holocene in line with greater northerly airflow and wetter summers (Newnham, 1999). A corresponding increase in lake level might have restricted nutrient availability by reducing the capacity for wave-induced mixing to ventilate deeper waters. Likewise, the initial onset of thermal stratification at Lake Pupuke between ~5 and 6 cal. kyr BP could record a reduction in DI-DRP through the onset of stable stratification and weak overturn reducing ventilation of deeper waters and the availability of DRP. Importantly, these low magnitude changes in DI-DRP are poorly distinguished from predictive errors (Figure 5.12). Accordingly only the LGCP (~28.5 to 18.5 cal. kyr BP) offers robust proxy data for reduced aquatic productivity, in line with a drop in lake level, preceded and followed by higher aquatic productivity more recently from ~3.3 cal. kyr BP. During the LGIT and Holocene (~18.5 cal. kyr BP to today), the most marked events within diatom-inferred water chemistry include increased delivery of nutrients to surface waters and an associated increase in their conductivity and productivity during a proposed erosional event expressed at ~6.9 cal. kyr BP, and following intense stratification during the last ~3.3 kyrs.
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.

Low TS-concentration recorded an LGCP drop in lake level, marking the onset of a shift from deep to shallower water diatoms (i.e., *D. athleta* to *S. microcostata*), also linked to lower essential aquatic nutrients (e.g., DI-DRP and diatom influx from ~23.0 to 16.7 cal. kyr BP. Geochemical evidence suggests an LGOT onset at ~18.5 cal. kyr BP. Highlighting a ~1.9 kyr delay in recovery of aquatic biomass from the LGOP. A mid-LGT reversal to lower DI-DRP and aquatic biomass is evident from ~18.0 to 17.7 cal. kyr BP.

An early to mid-Holocene (~7.8 to 3.7 cal. kyr BP) reduction in biomass occurred amongst terrestrial producers as diatom influx decreases, as do essential aquatic nutrients and biomass (e.g., DI-DRP and DI-CN). Increased conductivity and abundance of heavy-stiochiolised monoprotic salt likely bering lake morning accompanied this rise in aquatic biomass.

A mid-to-late Holocene shift to higher biomass noted by increased TOC and TN is recorded by a distinct community shift to autrophic indicators from ~3.3 cal. kyr BP. Greater covest abundance of *A. granulata var. ambiguus* highlights an intensification of thermal stratification (noted earlier at ~5.2 cal. kyr BP) as the principal cause of this natural eutrophication.
5.4.3 Paleo-REDOX and Mixing

Whilst diatom responses to the transition from the Last Glacial Coldest Period include a positive response to rising effective precipitation and water-level, the greatest algal response is to increasing nutrient availability. Mixing via wave turbulence and breakdown of thermal stratification fundamentally limit the ability to redistribute nutrients within deep lakes (Wetzel, 2001). Intense thermal stratification occurring from ~3.3 cal. kyr BP to today has driven a corresponding increase in nutrient availability and diatom flux to lake sediment within Lake Pupuke. However, evidence for an earlier onset of less intense thermal stratification can be seen in altered diatom habitat preference occurring in the mid-to-late Holocene. An increase in benthic diatoms from ~5.5 to 4.1 cal. kyr BP necessitates a relatively high lake level to inundate the more expansive shallow shelves at ~5-15 m depth (see Chapter 2 [Section 2.3. Bathymetry and Morphometry]) and importantly, greater clarity in summer and spring to enable periphytic diatoms to bloom. An alternative hypothesis of greater littoral inwash supplying epiphytic taxa can be excluded as a corresponding increase to clastic influx does not occur (refer to Figure 5.11). Instead, a marked change to nutrient cycling at ~5-6 cal. kyr BP, restricting the availability of dissolved nutrients and phytoplankton growth would favour attached benthic species by permitting greater light transmission to deeper habitats. Coeval reductions in DI-DRP and DI-TP confirm reduced nutrient-availability (refer to Figure 5.12), as does a coeval increase in the abundance of the epiphyte, Synedra capitata. This taxon is oligo/mesotrophic, slow-growing and relatively large enabling it to compete well with other diatoms in a low-TP environment (Bradbury et al., 1994; Morley, 2005). The coeval overall decline in euplankton in favour of tychoplankton also supports a change in the seasonal nutrient cycle including reduced summer nutrient availability and increasing reliance on turbulence for resuspension (Figure 5.13). Tychoplankton are adapted to inhabit shallow, well-lit benthic habitats as well as open water (Gasse et al., 2002).

More restricted nutrient availability coupled to greater turbulence supports an early onset for thermal stratification between ~5 and 6 cal. kyr BP. Corresponding changes in geochemical indicators imply greater variation in benthic REDOX from ~5.6 cal. kyr BP (e.g., enrichment of bulk sedimentary $\delta^{15}$N and greater incorporation of Mn relative to Fe) (Figure 5.13). Reduced planktonic algae, enhanced water clarity and greater abundance of benthic diatoms from ~5.5 to 4.1 cal. kyr BP likely arose as a result of thermal stratification restricting the availability of nutrients in productive summer months and relatively weak overturn limiting regeneration/circulation of essential nutrients from deeper waters.

A shift to dominance of the meroplankton, A. granulata var. ambigua indicates a likely intensification of thermal stratification occurred within Lake Pupuke at ~3.3 cal. kyr BP (Figure 5.13). Meroplanktic diatoms typically possess very dense frustules and are adapted to survive for long periods in dark, anoxic conditions typical of a hypolimnion (Jewson, 1992). Similarly, meroplankton are R-strategists capable of rapid reproduction with a distinct competitive advantage over other taxa where increased turbulence accompanies increased nutrient flux during overturn (Kilham, 1990). Coeval increases in lake trophic status were observed in geochemical proxy data at ~3.2 cal. kyr BP (e.g., declining C/N ratios, greater TOC and TN concentration and flux) (Figure 5.13). Natural
eutrophication of the lake can be explained through greater accompanying seasonal variation in REDOX and mixing in response to a more intensely stratifying water column (Section 4.5.4. Change to Mixing and Benthic REDOX). For instance, greater regeneration of essential nutrients would occur in anoxic, more reduced sediments (e.g., release of phosphorus and ammonia that is subsequently nitrified at the oxycline). Through greater ventilation during overturn, this recycling of OM can explain fertilization of the water column during holomixis (Wetzel, 2001).

More intense stratification from ~3.3 cal. kyr BP would arise from enhanced westerly and southwesterly airflow as the latter cause drier, clearer summers (Lorrey et al., 2007). Clear, dry summers would favour a more stable thermocline (Wetzel, 2001). A mid-to-late Holocene strengthening of westerly and southwesterly circulation has been cited by regional palynological reconstructions of the Northern North Island (NNI) which indicate stronger zonal airflow associated with drier, clearer summers from ~3-4 cal. kyr BP (Newnham et al., 1999; Shulmeister et al., 2001; Newnham et al., 2007a). Increased summer insolation would permit development of a stronger thermocline under which more reducing conditions would favour greater denitrification.

Shifts in habitat preference amongst composite diatoms samples can shed further light on the mid-to-late Holocene pattern of mixing and thermal stratification within Lake Pupuke. Tychoplanktic and facultative planktic taxa prefer increased turbulence whilst euplanktic taxa prefer stable, less turbulent conditions (Round et al., 1990; Jones, 2007). Shifts in the dominance of tychoplanktic and facultative planktic taxa compared to euplanktic taxa thereby offer a proxy for the relative stability of thermal stratification (e.g., Panizzo et al., 2008b). For instance, turbulent conditions are associated with breakdown of the thermocline which presently occurs under increasing windiness and cooling in winter/spring months (Section 2.5. Hydrology). Particularly mild winters with limited increase to windspeed or duration and precipitation would result in limited wave generation and reduced breakdown of the thermocline. Thus during the period of intense thermal stratification from ~3.3 cal. kyr BP until today, increased planktic dominance between ~3.3 and 2.0 cal. kyr BP represents particularly stable thermal stratification and reduced breakdown of the thermocline to keep phytoplankton continuously suspended within the epilimnion. The absence of marked changes in erosional proxies over the same period makes any change in lake level favouring planktic taxa unlikely. Furthermore, the lower nutrient tolerance of planktic diatoms occurring between ~3.3 and 2.0 cal. kyr BP (e.g., Cymbella microcephala, D. stelligera) would support a mechanism of more intense and stable thermal stratification associated with limited overturn and recirculation of essential nutrients from the hypolimnion. Panizzo et al (2008b) proposed similar changes in stratification and associated mixing to explain changing abundance of A. granulata in a dimictic Norwegian lake during the early Holocene whereby greater lake turnover was essential to generate sufficient turbulence to recirculate nutrients and resuspend the heavily silicified alga.

Consequently, changes in the degree of thermal stratification and seasonal breakdown offer a possible mechanism to explain the lesser SIMI scores and greater beta diversity between diatom communities in the late Holocene and characterised by oscillating abundances of A. granulata var. ambiguа, S. microstriata and D.
stelligera (in order of higher to lesser nutrient tolerance and greater to lesser seasonal overturn). For instance, sample DCA $\lambda_1$ and $\lambda_2$ scores identified several late Holocene samples whose diatom assemblies were more indicative of restricted nutrient abundance in the LGCP (Figure 5.14). Despite differences in sampling resolution, the Pupuke composite sediments exhibit a clear trend to lower $\lambda_1$ scores corresponding to more enriched bulk organic $\delta^{13}C$ signatures. This underscores the likelihood that peaks in composite $\delta^{13}C$ offer a complimentary, and importantly, high-resolution record of thermal stratification and its seasonal breakdown throughout the last ~6 cal. kyr BP. Given dependence of thermal stratification on zonal airflow, a proposed mechanism of more restricted nutrient availability arising from lesser breakdown of the thermocline, enables the composite $\delta^{13}C$ to be applied as a proxy for the dominance of zonal airflow; greater zonal dominance in winter/spring months limiting breakdown of the thermocline and resupply of DIC from the hypolimnion and vice versa under lesser zonal airflow (see Chapter 7).
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 $\delta^{15}$N) 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 $^{13}$C 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 $^{12}$C through productivity and sedimentation, whilst other dissolved nutrients would also become more limited favouring dominance of oligotrophic diatom taxa producing $^{13}$C-enriched organic sediment.
5.5 Summary

Diatom microfossil assemblages have been analysed at high resolution throughout the Pupuke composite sequence revealing marked paleolimnological change over the last ~44 kyrs. The transition to heightened glacial conditions characterised by lesser effective precipitation during the LGCP (~28.5 to 18.5 cal. kyr BP [Alloway et al., 2007]) is recorded by a decline in lake level and increased abundance of aerophilous taxa. Overall dominance of diatom communities by euplanktic, tychoplanktic and meroplanktic taxa confirm that a relatively deep lake has existed at the site from ~44 cal. kyr BP until today. Whilst absolute diatom abundances offer a clear response to the LGCP through reduced influx at ~28.5 cal. kyr BP, they fail to record the onset of the LGIT at ~18.5 cal. kyr BP. Relative diatom abundance however, demonstrates a marked shift in dominance from the oligotrophic euplankton *D. stelligera* to the mesotrophic meroplankton *S. microstriata* at ~16.0 cal. kyr BP which supports a delay in the response of aquatic producers to climatic amelioration (noted in greater terrestrial productivity commencing ~18.5 cal. kyr BP). CONISS-defined zonal boundaries mark the onset of increased nutrient availability between ~25.7 and 22.5 cal. kyr BP, and again between ~16.0 and 15.3 cal. kyr BP. Further changes are harder to define and implying nutrient availability has varied markedly throughout the Holocene. For instance, the EHWP does not form a distinguished feature of diatom taxonomies but an increase in erosional influx noted from ~7.6 to 5.7 cal. kyr BP, corresponds to greater abundance of the heavily silicified meroplankton, *A. granulata var. ambiguа* at ~6.9 cal. kyr BP.

A lack of corresponding changes to geochemical indicators of REDOX state until ~5.6 cal. kyr BP, supports an inference of increased catchment disturbance through destructive windstorms whose deeper wave bases would generate increased turbulence at greater depth. Reliable evidence for the onset of thermal stratification includes a shift to reduced nutrient abundance during a relatively high lake stand from ~5.5 cal. kyr BP. During the latter, an influx of oligotrophic plankton and periphyton records increased summer stratification through the isolation of surface nutrients in poorly mixed deeper waters. However, the intensification of thermal stratification and greater overturn only occurs from ~3.3 cal. kyr BP, in line with a shift to greater dominance of *A. granulata var. ambiguа*. This period also corresponds to greater beta diversity and rapid species turnover suggesting marked changes in the intensity of seasonal overturn. A proposed climatic control includes lesser and greater zonal airflow in winter months associated with more and less intense overturn.
CHAPTER SIX

The Paleolimnology of Lake Pupuke Inferred from Diatom Stable Isotopes

6.1 Introduction

Oxygen and Silicon each possess three distinct stable isotopes (e.g., non-radioactive): $^{16}$O (99.7630 %), $^{17}$O (0.0375 %), and $^{18}$O (0.1995 %); and $^{28}$Si (92.23 %), $^{29}$Si (4.67 %) and $^{30}$Si (3.10 %) (Garlick, 1974; Barnes et al., 1975). Stable isotopes possess minor mass differences through the addition of extra neutrons which result in different activation energies and consequently altered biological, physical and chemical reaction rates (Leng and Barker, 2006). Through inclusion of these stable isotopes within biological or geological precipitates, information on past hydrology, ecology and climate can be reconstructed within lacustrine systems (Leng and Barker, 2006). For instance, in Chapter 1 the basis for reconstruction of temperature by application of a fractionation coefficient for temperature of rainfall was outlined ($\sim$0.2-0.7‰/°C [Dansgaard, 1964]). Similarly the O-isotopic signature of biological microfossils can offer a proxy for past temperature but more often like the Si-isotopic signature, a record of the complicated interactions of several environmental factors (Leng and Marshall, 2004).

As a consequence of their abundance and ubiquity in many aquatic and marine environments, diatoms are ideal proxies for stable isotope paleohydrology as they incorporate Oxygen and Silicon isotopes within the silica tetrahedrons (Si-O-Si) of their opaline frustules (Figure 6.1) (Leng and Barker, 2006). As diatoms bloom within a water body they consume dissolved nutrients. Fractionation of dissolved Oxygen (DO) occurs through Rayleigh distillation as hydroxyl functional groups (OH) are assimilated with orthosilicic acid (DSi; $\text{H}_4\text{SiO}_4$) to condense firstly into Si-OH and then into covalently bonded Si-O-Si (Leng et al., 2009). Where fractionation occurs in equilibrium with ambient DO, changes in the O-isotopic composition of diatom silica are driven largely by temperature (Leng et al., 2009). Even where kinetic fractionation occurs, diatom isotopic signatures can yield information on paleohydrology at the time of formation (Leng and Barker, 2006). Hence diatoms and other siliceous microfossils (e.g., radiolaria, plant phytoliths, sponge spicules) offer proxies for paleolimnology and climatology via past changes to dissolved Si and O pools (Leng and Barker, 2006). For instance, changes in diatom O-isotopes record changes in source water composition, seasonality and amount of precipitation, whilst the links between the global Carbon and Silicon cycles permit identification of past changes to weathering and biological productivity from diatom Si-isotopes (e.g., Treguer et al., 1995; Dugdale et al., 2004; Street-Perrott et al., 2008).
Figure 6.1: The distribution of an inner tetrahedrally bonded internal silica node (Si-O-Si) with an outer, hydrous layer (Si-OH) where \( Q_4 \) and \( Q_n \) are Si-O-Si and Si-OH species respectively (Source: Leng et al., 2009: 69).

An essential requirement of any paleoenvironmental proxy is an absence of post-depositional alteration (Smol et al., 2001). However, within diatom silica, condensation processes operate along a gradient from outer to inner microfossil surfaces whereby the hydroxyl groups of outermost silica (-Si-OH) are readily exchangeable, whilst central regions form an isotopically homogenous, increasingly condensed silica skeleton (Si-O-Si) (Swann, 2007). This outer silica is subject to post-depositional fractionation (e.g., with reagent and atmospheric Oxygen and/or Silicon) whereas O and Si condensed into these central siliceous tetrahedrons is assumed to reflect the \( \delta^{18}O \) and \( \delta^{30}Si \) of the surrounding media at the time of formation (Leng and Barker, 2006). To accurately reconstruct past O- and Si-isotopic ratios and recover this condensed fraction, isolation and removal of the exchangeable outer fraction is required (~7 - 30 wt. % of total Oxygen [Lewin, 1961]). Given the increased application of diatoms to stable isotope paleolimnology, contaminant removal has become a significant research area (e.g., Brewer et al., 2008).

In this thesis traditional techniques for the removal of this outer, less dense siliceous layer are explored including the precise physical separation of silicate contaminants and application of a contaminant mixture model to account for those inclusions impossible to physically separate. Finally, the effect of changing silica maturity on sedimentary \( \delta^{18}O \) and \( \delta^{30}Si \) diatom signatures is explored in a novel approach employing Fourier-Transform Infra-Red Spectroscopy (FTIR). This thesis applies all three approaches to the Pupuke composite sequence, and is the first to reconstruct a \( \delta^{18}O \) and \( \delta^{30}Si \) series for a lake from Australasia.
6.1.1 Diatom Oxygen Isotopes in Paleolimnology

The use of diatom Oxygen isotope signatures has increased dramatically since the discovery of a relationship between O-isotope fractionation and ambient temperature at the moment of atmospheric precipitation (Dansgaard, 1964; Swann and Leng, 2009). Attempts to elucidate a $\delta^{18}$O$_{\text{Diatom}}$-temperature calibration curve have their origins in marine research where Labeyrie (1974), Juillet-Leclerc and Labeyrie (1987), Matheney and Knauth (1989) and Shemesh et al (1992) produced a $\delta^{18}$O$_{\text{Diatom}}$-temperature calibration relationship equivalent to $\sim$-0.3 ‰/ºC, between oceanic water $\delta^{18}$O ($\delta^{18}$O$_{\text{Marine}}$) and $\delta^{18}$O$_{\text{Diatom}}$. This relationship has been shown to be inaccurate for polar and high-latitude regions of upwelling and Shemesh et al (1992) proposed a sea-surface temperature (SST) calibration of $\sim$-0.5 ‰/ºC. Following these marine diatom investigations during the 1990s, limnologists have revealed lacustrine $\delta^{18}$O$_{\text{Diatom}}$-temperature calibration coefficients of $\sim$-0.2 ‰/ºC between 5 and 25 ºC (Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010). Moschen et al (2005) also demonstrated that temperature coefficients for freshwater planktonic diatoms are independent of diatom cell size as mixed taxonomy diatom opal from 5-10 µm, 10-20 µm and 20-80 µm size classes revealed a linear relation between water temperature and fractionation (Figure 6.2). Temperature coefficients ($\tau$) varied -0.216‰/ºC to -0.194‰/ºC supporting a physical, temperature controlled fractionation of Oxygen in lacustrine diatom silica.

![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 1σ. Centre lines are regression lines; neighbouring curves express 95% confidence intervals. Regression coefficients are identical at P<0.05 (Source: Moschen et al 2005, 32, L07708).](image)

Whilst variation between marine and lacustrine $\delta^{18}$O$_{\text{Diatom}}$-temperature coefficients could be the result of improved analytical procedures (the marine investigations were conducted over 17 years ago), it remains highly likely that a systematic vital effect exists between freshwater and marine environments (Swann and Leng, 2009; Crespin et al., 2010). Further experimentation with diatom communities under simulated conditions and within the natural realm, indicate further imprecision of the temperature coefficients (Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010). Hence any application of $\delta^{18}$O as a paleothermometer is hindered by the need to exclude changes to $\delta^{18}$O$_{\text{Diatom}}$ introduced by changes in source water composition. The latter is highly likely
within lacustrine systems whose volume makes them more susceptible to changes to input $\delta^{18}$O (e.g., changes in isotopic composition and proportion of inflows) as well as hydrological balance (e.g., equilibrium and kinetic evaporation of surface waters) (Leng and Marshall, 2004). Consequently, biogenic silica (BSi) $\delta^{18}$O values are more often employed to indirectly reconstruct changes to source water $\delta^{18}$O composition rather than direct temperature change.

Processes which alter $\delta^{18}$O$_{\text{Lake}}$ can be distinguished as either lacustrine or non-lacustrine in origin (Figure 6.3). Non-lacustrine shifts in $\delta^{18}$O of meteoric precipitation naturally become expressed within $\delta^{18}$O$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Diatom}}$ through couplings to surface water bodies within the global hydrologic cycle. Accordingly each is discussed below with the focus on changes induced by glacial/interglacial climatic variation as well as the prominent effects of thermal stratification, a process which has been demonstrated to control water quality and diatom productivity within Lake Pupuke (Section 5.4.3. Paleo-REDOX and Mixing). The major controls on $\delta^{18}$O$_{\text{Diatom}}$ have been reviewed extensively (e.g., Leng and Marshall, 2004; Leng and Barker, 2006; Swann and Leng, 2009) such that each mechanism is only briefly examined here.

**Figure 6.3:** Schematic diagram explaining the principal controls on lacustrine $\delta^{18}$O$_{\text{Diatom}}$: Changes in $\delta^{18}$O$_{\text{Diatom}}$ incorporate variation in $\delta^{18}$O$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Precipitation}}$. 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 $\delta^{18}$O (e.g., through changes in oceanic $\delta^{18}$O) as well as changes to airmass $\delta^{18}$O 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).
6.1.1.1 Non-lacustrine controls on δ¹⁸O<sub>Diatom</sub>

Lacustrine DO reservoirs are ultimately dependent upon oceanic and atmospheric DO reservoirs for recharge (Leng and Barker, 2006). The global hydrological cycle ensures lake sensitivity to oceanic and cryospheric change via evaporation and precipitation (Clark and Fritz, 1997). Whilst it is beyond the scope of this thesis to discuss every control on δ¹⁸O signatures in precipitation δ¹⁸O<sub>P</sub> it is necessary to discuss several major determinants of oceanic δ¹⁸O (δ¹⁸O<sub>Marine</sub>) that have varied during the Quaternary and which could alter δ¹⁸O<sub>Lake</sub> within Lake Pupuke including global ice volume, oceanic mixing and biological productivity. With the onset of cyclical ice-sheet growth and retreat ~34 Myr ago, oceanic DO reservoirs became successively enriched and depleted by ~1-2 ‰ respectively as ice-sheets captured isotopically depleted moisture (Lisiecki and Raymo, 2005). These changes are highly variable through time and space due to variable ice volume as well as oceanic mixing during the Quaternary, making it difficult to identify their effects on sedimentary δ¹⁸O values (Swann and Leng, 2009). Oceanic mixing is also of importance to changes in marine δ¹⁸O (Swann et al., 2010). Throughout the Quaternary, deep ocean ventilation has varied as evidenced by changes in atmospheric pCO₂ (e.g., Leuenberger et al., 1992). Importantly, these and other processes have resulted in spatiotemporal changes to δ¹⁸O<sub>Marine</sub> (Swann and Leng, 2009).

As precipitation is largely derived from marine sources, changes in local source region(s) or the relative proportion of different sources have the potential to alter lacustrine δ¹⁸O values without a change in site limnology (Leng and Marshall, 2004). Similarly, changes in airmass trajectory alter the amount and composition of precipitation delivered to a catchment (Clark and Fritz, 1997). Heavier isotopes preferentially rainout of airmasses because the vapour pressure of D₂¹⁸O is lower than H₂¹⁸O (Clark and Fritz, 1997). Consequently, precipitation nearer the source water will be ¹⁸O-enriched relative to more distal sites (~ 0.0002 ‰ per km travelled inland [Sonntag et al., 1978]). Preferential rainout of isotopically enriched moisture also occurs in response to airmass temperature with cooler temperatures favouring greater fractionation of suspended moisture (Clark and Fritz, 1997). For instance, the modern isotopic composition of mean annual precipitation (δ<sub>P</sub>) varies systematically with mean annual temperature resulting in the so-called Dansgaard relationship of δ<sub>P</sub> with latitude (Δδ<sub>P</sub>/ΔT = ~+0.2 to +0.7 ‰/°C [Dansgaard, 1964]).

A similar relationship exists for altitude (e.g., a thermodynamic response of ~2 ‰ per km increased elevation [Clark and Fritz, 1997]) meaning paleoceanic changes to sea level can alter δ¹⁸O<sub>Lake</sub> through the combined effects of altered moisture source, airmass trajectory, temperature and site altitude (Leng and Marshall, 2004). Finally, even the intensity or amount of rainfall govern δ<sub>P</sub> (Clark and Fritz, 1997). The greater the amount of rainfall, the more depleted δ<sub>P</sub> in a so-called ‘amount’ effect reflecting lesser recycling of atmospheric moisture (Siegenthaler and Oeschger, 1980). Tropical regions receive greater amounts of rainfall than temperate and often demonstrate an “amount effect” on δ<sub>P</sub> whereby rainy months are relatively depleted whilst drier months yield enriched δ<sub>P</sub> (Ricketts and Anderson, 1998). This myriad of forcing factors influencing δ<sub>P</sub> make any reconstruction of δ<sub>P</sub> or paleotemperature via δ¹⁸O<sub>Diatom</sub> difficult (Leng and Marshall, 2004). Hence those
researching diatom isotopes often focus instead on reconstructing trends to $\delta^{18}O_{\text{Lake}}$ alone (Leng and Barker, 2006).

6.1.1.2 Lacustrine controls on $\delta^{18}O_{\text{Diatom}}$

As diatom opal precipitates within a water column, values of $\delta^{18}O_{\text{Diatom}}$ can be altered through changes to $\delta^{18}O_{\text{Lake}}$ (Leng and Marshall, 2004). Thus whilst $\delta^{18}O_{\text{Diatom}}$ offers a proxy for paleotemperature, it is important to isolate and exclude changes in $\delta^{18}O_{\text{Diatom}}$ caused by altered catchment or water column hydrology (Anderson et al., 2001).

The Global Meteoric Water Line (GMWL) is an empirically determined relationship of $\delta D$ and $\delta^{18}O$ derived from the global variation between meteoric ratios (Gat, 1971). Lake water isotope values plotting nearer the GMWL have undergone little isotopic fractionation and represent hydrologically open systems, whilst those that deviate from the GMWL along a Local Evaporation Line (LEL), have undergone marked fractionation (Leng and Marshall, 2004). Evaporative fractionation of $\delta D$ exceeds $\delta^{18}O$ resulting in a shallower LEL gradient than the GMWL (Gat, 1971). Importantly, evaporative effects are variable through time and cannot be corrected easily within $\delta^{18}O_{\text{Diatom}}$ without additional proxy information regarding effective precipitation (e.g., balance of precipitation and evaporation) (Leng and Marshall, 2004). Consequently, changes to $\delta^{18}O_{\text{Diatom}}$ incorporate changes in water balance (Leng and Marshall, 2004).

As before, $\delta P$ undergoes seasonal variation (~2-8‰ in temperate regions with seasonal ranges increasing with continentality [Leng and Marshall, 2004]). Even on shorter time scales, $\delta P$ can undergo marked isotopic variability (Darling, 2004). For instance, temperate winter rainfall is significantly depleted in $^{18}O$ relative to summer rainfall signatures (Clark and Fritz, 1997). However, the impact of variable $\delta P$ upon $\delta^{18}O_{\text{Lake}}$ is mediated by lake volume and residence time. Within smaller and/or shorter residence time lakes, $\delta^{18}O_{\text{Lake}}$ will undergo greater short term variation (e.g., storm, meltwater pulse) (Benson, 1994). Likewise, whether a lake is groundwater or precipitation fed is important as greater residence time attached to groundwater ensures spring-fed lakes are not as subject to seasonal $\delta P$ variation (Leng and Marshall, 2004). Hence changes to lake volume and residence time can alter $\delta^{18}O_{\text{Lake}}$ (e.g., Schleser et al., 1999).

Even hydrologically-closed and/or larger lakes with longer residence times can suffer from seasonal variability in $\delta^{18}O_{\text{Lake}}$ if they exhibit stratification (Leng and Marshall, 2004). Stratification prevents mixing leading to distinct isotopic signatures within a lake, a so-called ‘vital habitat’ effect (Swann, 2007). For instance, thermal stratification leads to greater evaporative enrichment of $\delta^{18}O_{\text{Lake}}$ within the epilimnion (Leng and Marshall, 2004). Diatom production is limited to the photic zone and hence seasonal changes in surface water $\delta^{18}O_{\text{Lake}}$ are particularly important to $\delta^{18}O_{\text{Diatom}}$. For instance, summer blooming taxa might exhibit a marked enrichment artefact absent at overturn. This further underscores the need to monitor spatial and seasonal trends in $\delta^{18}O_{\text{Lake}}$ by stressing changes in the latter can arise through altered mixing, hydrologic residence time, and most
importantly, effective precipitation (P/E balance) (Leng and Marshall, 2004). In turn, these are imprinted on \( \delta^{18}O_{\text{Diatom}} \) values, obscuring any temperature-related effect (Table 6.1).

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

<table>
<thead>
<tr>
<th>Lake-water volume</th>
<th>Very small</th>
<th>Small-medium lakes</th>
<th>Large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time</td>
<td>&lt;1 year ('open' lake)</td>
<td>≥ 1 year (10’s years)</td>
<td>100’s years ('closed' lake)</td>
</tr>
<tr>
<td>Predominant forcing</td>
<td>S, T, ( \delta_P )</td>
<td>( \delta_P )</td>
<td>P/E</td>
</tr>
<tr>
<td>( \delta^{18}O ) ranges through the Holocene</td>
<td>Often -ve values, small range of 1-2 %( \delta ), possibly large range in %( \delta ) for materials precipitated in different seasons e.g., Lake Chuma (Kola Peninsula)(^a), Lake Abisko (Sweden)(^b)</td>
<td>Often -ve values, large swings (5 to &gt;10 %( \delta )) e.g., Greenland lakes(^e), Lake Tilo (Ethiopia)(^d), Lake Golhisar (Turkey)(^g)</td>
<td>+ve values, subdued signal homogenised by buffering of large lake volume e.g., Lake Malawi(^h), Lake Turkana (Kenya)(^i)</td>
</tr>
</tbody>
</table>

\( S = \) seasonality, \( T = \) temperature, \( \delta_P = \) isotope composition of precipitation, \( P/E = \) amount of precipitation relative to evaporation. References: (a) Jones et al., 2004; (b) Shemesh et al (2001); (c) Marshall et al (2002); (d) von Grafenstein et al., 1999a,b; (e) Anderson and Leng, 2004; (f) Lamb et al (2000); (g) Eastwood et al (in press); (h) Ricketts and Johnson (1996); (i) Ricketts and Anderson (1998).

### 6.1.3 Summary

Lacustrine \( \delta^{18}O_{\text{Diatom}} \) is subject to changes mediated by marine, atmospheric and terrestrial processes (Leng and Barker, 2006). To reliably employ a \( \delta^{18}O_{\text{Diatom}} \)-temperature relationship changes other than thermodynamic fractionation must be excluded. Changes to precipitation source, amount and pathway can each alter \( \delta^{18}O_{\text{Lake}} \), whilst changes to catchment hydrology (sources, mixing, and P/E balance) are also capable of imparting changes to \( \delta^{18}O_{\text{Diatom}} \). Consequently, many isotope investigations simply infer paleolimnological change from \( \delta^{18}O_{\text{Lake}} \).

### 6.1.2 Diatom Silicon Isotopes in Paleolimnology

Silicon is weathered by carbonic acid within meteoric rainfall, altering atmospheric \( \rhoCO_2 \) by drawdown and producing orthosilicate (\( H_2SiO_3 \)) as the major source of dissolved silica (DSi) (De La Rocha, 2006). Delivery of orthosilicate to the oceans fertilizes silicate primary producers including diatoms that comprise ~50% of marine producer biomass (De La Rocha, 2006). Changes in diatom abundance and geochemistry can therefore offer an important proxy for changes to weathering and paleoclimate (Tréguer and Pondaven, 2000). For instance, experimental studies have demonstrated a positive relationship between \( \rhoCO_2 \) and silicate weathering (e.g., Andrews and Schlesinger, 2001), paleoceanic reconstructions have also established a link between the Si-isotopic composition of diatom frustules and paleoproductivity (De La Rocha et al., 1998; Brzezinski et al., 2002). Recent application of Silicon stable isotopes to continental waters also points to \( \delta^{30}Si \) being a proxy for weathering/\( \rhoCO_2 \) and paleoproductivity (De La Rocha et al., 2000; Ding et al., 2004; Street-Perrott et al; 2008; Swann et al., 2010). Production of a diatom frustule results in a \( \delta^{30}Si_{\text{Diatom}} \) value ~1.1 %\( \delta \) more depleted than the
DSi source (De La Rocha et al., 1997; Reynolds et al., 2006; Demarest et al., 2009). Several laboratory investigations have demonstrated the capacity for $\delta^{30}\text{Si}_{\text{Diatom}}$ to reflect its source water composition over a wide variety of environments likely to have been experienced during glacial/interglacial transitions including temperature ranges of 12-22 °C (De La Rocha et al., 1997) and variable dissolved CO$_2$ levels (Milligan et al., 2004) in fresh and marine diatoms (Alleman et al., 2005).

The fundamental role of diatoms in global productivity, sensitivity to variations in orthosilicate availability and the latter's dependence upon weathering intensity/erosional flux, permit $\delta^{30}\text{Si}$ of diatom silica to offer an exciting proxy for paleoclimate (Demarest et al., 2009; Leng et al., 2009; Swann et al., 2010). Furthermore, the absence of a vital diatom taxonomic effect enables $\delta^{30}\text{Si}_{\text{Diatom}}$ to better record changes in Si-availability within lakes ($\delta^{30}\text{Si}_{\text{Lake}}$) (Street-Perrott et al., 2008; Leng et al., 2009). As biological organisms preferentially take up lighter isotopes, biogenic records of $\delta^{30}\text{Si}$ can yield important information on DSi availability and demand within lacustrine systems (Barker et al., 2001, 2007; Leng et al., 2009). Until recently however, analytical limitations have prevented the accurate measurement of $^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$ (Leng et al., 2009). Improvements to IR-MS procedures and equipment now enable the simultaneous analysis of changes to Si and O stable isotopes from biogenic silica (BSi) (Leng and Sloane, 2008).

6.1.2.1 Controls on $\delta^{30}\text{Si}_{\text{Diatom}}$

Application of $\delta^{30}\text{Si}_{\text{Diatom}}$ to lacustrine archives requires an understanding of the controls on Si-availability within lakes (Figure 6.4). These include: (1) weathering and subsequent release of soluble Si; (2) resupply of DSi by mixing (overturn and/or wave-induced); and (3) biological uptake to inorganic silicate precipitates (Sommer et al., 2006; Leng et al., 2009). Further dry and wet Si-deposition through aeolian processes is minor outside of arid/semi-arid climates (Sommer et al., 2006).

Changes to weathering and erosional regimes alter the supply and isotopic composition of soil water and lacustrine DSi ($\delta^{30}\text{Si}_{\text{Lake}}$) (Leng et al., 2009). Three factors affect DSi supply and uptake to lakes, climate, $p\text{CO}_2$ and vegetation cover (Sommer et al., 2006). Increased precipitation can result in greater denudation and weathering, whilst reductions in precipitation reduce the overall supply of DSi to a lake. Carbonic acid readily forms from atmospheric CO$_2$ within water droplets, which upon reaching a mineral surface, results in dissolution and leaching of aluminosilicates via surface or subsurface flow (Sommer et al., 2006). Accordingly, increased runoff results in greater catchment-derived DSi, whilst increased temperature has a similar effect by increasing dissolution rate (White and Blum, 1995; Turner et al., 2003). A more complex relationship exists between DSi and catchment productivity. Increased terrestrial biomass reduces runoff and DSi supply through greater evapotranspiration and interception, but can also increase DSi concentration within soil waters via leaching of aluminosilicates through the diagenetic release of organic acids (e.g., humic and fulvic acid) and increased soil water $p\text{CO}_2$ via root-tissue and detrital respiration (Sommer et al., 2006).
Figure 6.4: Schematic diagram explaining the principal controls on lacustrine $\delta^{30}\text{Si}_{\text{Diatom}}$: Changes to $\delta^{30}\text{Si}_{\text{Diatom}}$ 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 phytogenic Si (phytoliths) (enriching DSi); (4) dissolution or desilication of soils (depletion of DSi) (Modified from Leng et al., 2009: 67).

Fractionation of DSi occurs during weathering through the preferential incorporation of lighter isotopes into solution and expulsion of heavier isotopes into secondary precipitated phases (e.g., clays or adsorption onto metal oxides) (Leng et al., 2009). For instance, Ziegler et al (2005) recorded depletion of soil water $\delta^{30}\text{Si}$ through weathering of juvenile basalts, whilst Oplergelt et al (2008, 2009) have demonstrated enriched $\delta^{30}\text{Si}$ values in secondary crystalline clays associated with enhanced soil weathering and depleted soil water $\delta^{30}\text{Si}$. Consequently, increasing soil weathering results in higher $\delta^{30}\text{Si}$ values of soil water (Cardinal et al., 2010). Further changes to soil water $\delta^{32}\text{Si}$ occur through changes to catchment vegetation whereby soil waters of organic rich sediments can become depleted in $\delta^{30}\text{Si}$ when organic acids released by decaying OM react with aluminosilicates, preferentially leaching lighter $^{28}\text{Si}$ and $^{29}\text{Si}$ into soil water (e.g., Bluth and Kump, 1994). Thus ‘weathering intensity’ (the balance of aluminosilicate precipitation and dissolution [Lugolobi et al., 2010]) is a fundamental control on $\delta^{30}\text{Si}$ values of soil and lake water, enriching and depleting DSi $\delta^{30}\text{Si}$ by greater secondary precipitation and leaching respectively. Whilst a change in the overall supply of DSi might not alter $\delta^{30}\text{Si}$ values, a change in weathering intensity and/or terrestrial biomass can result in altered $\delta^{30}\text{Si}$ signatures of DSi influxes, and consequently $\delta^{30}\text{Si}_{\text{Lake}}$ (Leng et al., 2009).
Catchment vegetation exerts a further control on $\delta^{30}\text{Si}_{\text{lake}}$ via the selective uptake of lighter Si-isotopes during the formation of opaline phytoliths (Street-Perrott et al., 2008). Changes in terrestrial biomass alter weathering intensity and uptake of DSI with consequent changes in the $\delta^{30}\text{Si}$ of soil moisture (Street-Perrott et al., 2008). In addition to abundance of biomass, changes in floristic composition can also result in changes to the $\delta^{30}\text{Si}$ of soil moisture: greater/reduced abundance of Si-accumulator plants (e.g., grasses, sedges, palms) will result in enhanced/reduced enrichment of soil and lake water $\delta^{30}\text{Si}$ (Hodson et al., 2005). Whilst Si can return to soil via throughfall, stemflow and/or litterfall, often this phytogenic component is lost to DSI unless subject to sedimentary dissolution whereupon lighter $^{28}\text{Si}$ and $^{29}\text{Si}$ will preferentially be lost in a process of desilication (Sommer et al., 2006). Unless total redissolution of phytogenic Si occurs, DSI will suffer selective enrichment through terrestrial filtering (Sommer et al., 2006). Thus changes to weathering intensity, and catchment floristic biomass as well as composition, can alter soil water DSI availability and isotopic composition (Cardinal et al., 2010).

A change in the isotopic composition of inflowing DSI will alter source water $\delta^{30}\text{Si}$ ($\delta^{30}\text{Si}_{\text{lake}}$) (Leng et al., 2009). Any consequent change in $\delta^{30}\text{Si}_{\text{diatom}}$ however, will be limited by trends in diatom abundance because aquatic siliceous organisms like terrestrial Si-accumulators, selectively assimilate lighter isotopes (Leng et al., 2009). Changes to diatom biomass can therefore result in changes to the availability of DSI and lead to altered values of $\delta^{30}\text{Si}_{\text{lake}}$ (Swann and Leng, 2009). In lakes where orthosilicates are limiting (e.g., deep, closed and stratifying) changes to source water $\delta^{30}\text{Si}$ are subject to greater aquatic productivity-driven changes in $\delta^{30}\text{Si}_{\text{diatom}}$ (Swann and Leng, 2009). Nevertheless, even in open or well DSI-supplied lakes, productivity-related changes in $\delta^{30}\text{Si}_{\text{diatom}}$ offers the ability to reconstruct paleolimnology through knowledge of controls on diatom productivity (e.g., nutrient availability, temperature, water clarity) (Leng et al., 2009). The, using additional proxies for diatom productivity (see Chapter 5) it is possible to reliably identify changes in $\delta^{30}\text{Si}_{\text{diatom}}$ due to variations in source water $\delta^{30}\text{Si}$ (e.g., weathering intensity, runoff [e.g., Street-Perrott et al., 2008]).

Whilst chemical weathering offers a link to the global Carbon cycle it also means global DSI fluxes (i.e., fluvial, soil moisture, lacustrine) have varied on glacial-interglacial cycles, in line with changes to the marine biological pump and $p\text{CO}_2$ (Street-Perrott et al., 2008). During the last glacial $p\text{CO}_2$ levels fell by ~80-100 p.p.m.v. (Leuenberger et al., 1992) leading several authors to propose a corresponding decrease in the concentration of carbonic acid within precipitation, and reduction in effective weathering (Street-Perrott et al., 2008; Leng et al., 2009; Swann et al., 2010). Any such change would however, be subject to variation through catchment-based mechanisms (e.g., changes in vegetation cover, runoff and sub-surface flow). For instance, any reduction in $\text{H}_2\text{CO}_3$ concentration might be remediated by increased overall precipitation leading to increased overall weathering and supply of DSI. Knowledge of the catchment and atmospheric controls on $\delta^{30}\text{Si}$ is too limited to rank their relative importance although it is likely both interact in a paleolimnological series. Systems which are Si-limited will better record these catchment-derived changes to DSI as reduced DSI results in less selective uptake of lighter isotopic forms and less depletion of $\delta^{30}\text{Si}_{\text{diatom}}$ relative to source water $\delta^{30}\text{Si}$. Thus it is important to assess whether a system is Si-limited prior to interpretation of a paleolimnological $\delta^{30}\text{Si}_{\text{diatom}}$ series.
Lake Pupuke is hydrologically closed and has no significant runoff or groundwater inflow (see Chapter 2). The absence of fluvial inputs precludes changes to δ^{30}Si_{lake} through changes to the intensity of ‘fluvial filtering’ (the selective uptake of lighter Si-isotopes within fluvial systems [Alleman et al., 2005]). Instead DSi sources are limited to catchment rocks (e.g., basaltic rock, basement sandstone) and tephra deposition. Complication of DSi source might therefore arise through assimilation of tephra which is thought to possess variable δ^{30}Si signatures (Leng et al., 2009). Chapter 5 demonstrated diatom blooms coincident with tephra deposition within the Pupuke composite series. Thus BSi stable isotope samples were chosen to exclude tephra and the effects of changing δ^{30}Si through altered DSi source. Likewise catchment extent is limited (0.85 km² compared to 1.1 km² of lake surface) reducing the effects of changes to weathering intensity. Instead, as with other hydrologically closed or stratifying lakes the dominant effects on δ^{30}Si_{diatom} are likely to result primarily from changes in the availability of DSi through erosional input and Si-recycling (via sediment mixing and resuspension) (e.g., Alleman et al., 2005; Street-Perrott et al., 2008). A limited groundwater input means runoff will offer the fundamental control on DSi input to Lake Pupuke whilst internal mixing will determine sediment recycling via resuspension of DSi locked in deeper waters. In addition, changes in uptake and productivity will compete with these to become expressed in the composite δ^{30}Si_{diatom} series.

6.1.2.2 Data Assessment: Relationship of δ^{29}Si to δ^{30}Si

An empirical relationship of ~2:1 between δ^{29}Si and δ^{30}Si has been demonstrated for a range of silicate compounds (biogenic and non-biogenic) by De La Rocha (2002) (Figure 6.5). Whilst this relationship was used to extrapolate δ^{30}Si from δ^{29}Si it can also be used as a sample quality indicator. For instance, provided samples have undergone mass-dependent fractionation alone, δ^{30}Si and δ^{29}Si values will be related by the following equation:

\[ \delta^{30}\text{Si} = \delta^{29}\text{Si} \times (29/30) \times ([30-28] / [29-28]) = \delta^{29}\text{Si} \times 1.93 \]

(Relationship between δ^{30}Si and δ^{29}Si in reagent grade silica, SiF₄ gas, natural quartz and biogenic silica. Note this implies a fractionation coefficient of 1.93 between δ^{29}Si and δ^{28}Si [Source: De La Rocha, 2002: 7])

Any deviation from this relationship can highlight mass-independent fractionation (De La Rocha, 2002). Most equilibrium and kinetic fractionation (e.g., evaporation, condensation, diffusion, biological uptake) is mass-dependent (Young et al., 2002). De La Rocha’s (2002) analyses of ~600 samples across a gradient of habitat and precipitate type (e.g., fluvial, marine, hydrothermal), and subsequent investigations (Street-Perrott et al., 2008; Swann et al., 2010) stress the dominance of mass-dependent fractionation in biogenic silica (Figure 6.5). Hence any deviation from a ~2:1 δ^{29}Si to δ^{30}Si relationship highlights the presence of some mass-independent fractionation or analytical error, and can be used to assess sample quality.
6.1.3. Uncertainty and Error in Diatom Stable Isotope Paleolimnology

Whilst $\delta^{18}O_{Diatom}$ or $\delta^{30}Si_{Diatom}$ signatures can record marked climatic or environmental change, there are several sources of uncertainty affecting their interpretation. For instance, the process of silica formation could vary on a taxonomic or size-related gradient (Leng and Barker, 2006). Such processes result in what are broadly described as ‘vital’ effects and could be introduced by life-cycle variations, seasonality and/or taxonomic or ontogenetic variation between samples (Leng and Marshall, 2004). In addition, secondary isotopic exchange has the potential to alter diatom isotope series through changes to silica maturity, dissolution and/or reprecipitation. Each is discussed in Appendix D and represents a post-depositional or taphonomic process, which, in light of the limited variation often expressed in $\delta^{18}O_{Diatom}$, and moreover $\delta^{30}Si_{Diatom}$ series, represents a significant source of variation beyond changing temperature or source water isotopic composition (Moschen et al., 2005). If significant, changes in isotope offset attributable to vital effects (taxonomic and habitat), silica maturation and silica dissolution will result in marked, and importantly, dynamic changes to downcore isotopic signatures, thereby removing the dominant effect of changing source water composition and/or temperature (Leng and Barker, 2006; Swann and Leng, 2009).
Despite recent advances in sedimentary diatom purification (e.g., SPLITT fractionation, density flotation), samples often contain mixed taxa and sizes due to a limited range of densities exhibited by diatom silica as well as limited range in grain sizes (e.g., through similarity and breakdown of larger frustules) (Leng et al., 2009). Any diatom assemblage of mixed taxa or size could potentially include changes to sample isotope values attributed to species-specific or ontogenetic changes (Leng et al., 2009). For instance, variable fractionation factors might exist between and within diatom taxa (e.g., by species or growth phase) (Leng and Barker, 2006). Similarly, taxa grow and incorporate DSi from different habitats within a lake (e.g., benthic vs. planktic taxa) and during different seasons (e.g., spring or summer blooms) (Leng and Marshall, 2004). Microenvironmental change within a lacustrine system (e.g., through weak mixing, evaporative enrichment and/or variable input signatures coupled to seasonal variability) can thereby accentuate changes in downcore $\delta^{18}O_{\text{Diatom}}$ or $\delta^{30}Si_{\text{Diatom}}$ where shifts in dominant taxa or habitat/seasonal preference occur (Leng and Marshall, 2004). Marked contemporary hydrological variation is expressed within Lake Pupuke by depth and season in line with changes to thermal stratification (Section 2.4.1.2. Temperature and Thermal Stratification). Marked evaporative enrichment of $\delta^{18}O_{\text{Lake}}$ occurs through surface-water isolation resulting in marked variation in $\delta^{18}O_{\text{Lake}}$ by depth and season through onset and breakdown of stratification in September and July respectively. Changes in the extent of stratification and P/E over the last ~50000 yrs are likely to result in changes to microenvironmental variation in $\delta^{18}O_{\text{Lake}}$ or $\delta^{30}Si_{\text{Lake}}$. Changes to stratification might also result in a further vital effect through its effect on rates of diatom growth. Schmidt et al (2001) suggest a possible growth rate effect in diatom stable isotope signatures (quicker growth equating to lesser fractionation of source waters). As noted in Chapter 5, diatom taxonomic variation within the Pupuke composite series stresses marked beta diversity involving variable dominance of rapidly blooming Fragilariaceae from ~5.0 to 6.0 cal. kyr BP to today in response to changing stratification intensity (e.g., restricted seasonal nutrient availability). If verified at Lake Pupuke, Schmidt et al’s (2001) findings imply that any changes to $\delta^{18}O_{\text{Diatom}}$ and possibly $\delta^{30}Si_{\text{Diatom}}$ with stratification, will include a vital effect attached to changing growth rate.

Silica maturation is associated with a diagenetic enrichment of diatom frustules (up to 10 ‰ [Schmidt et al., 2001]). Whilst analytical procedures might negate much of this affect (e.g., through removal of the outer, exchangeable layer [e.g., Leng and Sloane, 2008]) changes in the degree of frustule maturity can introduce variation to $\delta^{18}O_{\text{Diatom}}$ and presumably $\delta^{30}Si_{\text{Diatom}}$. The extent of silica maturation can be inferred from the ratio of Si-OH/Si-O which increases with dehydroxylation (Schmidt et al., 2001). IR-spectroscopy offers a rapid means of assessing maturity ratios through corresponding changes in the absorbance of IR-radiation at ~950 cm$^{-1}$ and ~800 cm$^{-1}$ respectively (Farmer, 1974). Accordingly Fourier-Transform IR (FTIR) spectroscopy is employed to estimate changes in $\delta^{18}O_{\text{Diatom}}$ sample maturity down core in this thesis.

Dissolution of biogenic silica occurs in terrestrial and oceanic aquatic environments under-saturated with DSi, resulting in the enrichment of remnant diatom silica (Demarest et al., 2009; Leng et al., 2009). Alleman et al (2005) recognised the effects of opal dissolution in deep water (~200 m) within Lake Tanganyika resulting in higher bottom water DSi through higher pH. However, intense silica dissolution within Lake Pupuke is highly
unlikely for three reasons: (1) limited contemporary seasonal hypolimnetic variation around neutral pH (1976-2009); (2) rapid movement through a relatively shallow water column (max. ~57 m); and (3) strong annual mixing (Section 2.4.1. Hydrology). Diatom transfer function (DI-TF) reconstructions also suggest limited temporal variability in surface water pH beyond neutral over the last ~44000 yrs (DI-pH 7.73 ± 0.04 [μ ± σ, n = 73]) (Section 5.3.4.4.2. DI-pH) such that if surface waters continued to exhibit a trend of higher than benthic pH, bottom-water pH over the composite sediment series has not exceeded pH 7.82 (e.g., maximum DI-pH estimate). Hence it is likely that limited isotopic fractionation will have occurred as Moschen et al (2006) noted limited dissolution and fractionation in diatom silica exposed to water of neutral pH. Similarly, rapid burial of sedimenting diatoms limits dissolution further as sedimenting diatoms will contain greater remnant organic coating – the latter effectively prevents dissolution (Bidle et al., 2003; Moschen et al., 2006). Nevertheless, as hydrologic conditions have varied over the Lake Pupuke sedimentary record, rates of secondary dissolution (and reprecipitation) may have varied and warrant examination. Accordingly samples are examined by light and SEM to identify and exclude any affected samples from interpretation (Section 6.3. Methods).

6.2 Modern Stable Isotope Systematics of Lake Pupuke: Evaporation-dominated Basin

Changes to source-water isotope composition are translated to variations in diatom stable isotope composition (Leng and Marshall, 2004). Hence prior to interpreting down core δ18O_Diatom or δ30Si_Diatom it is essential to study the modern controls and seasonality upon δ18O_Lake and δ30Si_Lake within Lake Pupuke. However, the expense of δ30Si analyses confine this to a modern calibration exercise of O-isotopes in precipitation, surface waters and diatom silica at Lake Pupuke (05/2008-01/2010). From this data it is possible to establish whether δ18O_Lake is driven by precipitation composition, or changes in effective precipitation (P/E), and whether local precipitation observes a thermal or amount relationship.

6.2.1 Methods

6.2.1.1 Precipitation and Lake Water Sampling

Precipitation δD and δ18O analyses were carried out by Geological and Nuclear Sciences, Wellington (GNS) courtesy of Dr. Russell Frew (University of Otago) for the period 05/2008 to 01/2010 at monthly intervals across 59 independent locations in the North and South Islands. Sampling was conducted as part of the International Atomic Energy Agency (IAEA) Global Network of Isotopes in Precipitation (GNIP) mapping programme. Representative precipitation data have been collected for the nearest meteorological station (Agent Number A64775; 36º78.60’S, 174º74.00’E). Analytical methodology and uncertainties are as for lake water samples.

Water column samples (n = 54) were collected monthly, over the interval 05/2008 to 01/2010 at 3 depths (surface, 15 m and 28 m) to monitor stable isotope composition (δD_Lake and δ18O_Lake). Sterile 1 L Nalgene™ plastic vials were rinsed in the field, filled and returned to the School of Environment, University of Auckland
where water samples were filtered through 0.45 μm Whatman™ GFC ashless filter paper to isolate microorganisms and limit post-collection fractionation. Filtered water samples were transferred to sterile 50 ml Nalgene™ bottles and wrapped with Parafilm™ tape before delivery to GNS for stable isotope analyses.

6.2.1.2 Modern Diatom Sampling

Modern diatom samples were collected as part of the lake monitoring exercise described in Chapter 4. Sediment traps were deployed at ~40 m depth across four seasonal envelopes (03/2008-06/2008; 06/2008-10/2008; 10/2008-02/2009; 02/2009-07/2009). Diatom silica was isolated following standard protocols described in Section 5.3.1. Methods. Sediment was acid-washed to eliminate carbonate (1N HCl, 5% v/v) and oxidised with hydrogen peroxide (27% H₂O₂, ~75 ml). A final acid-leaching stage was necessary to eliminate remnant iron and manganese precipitates (1N HNO₃, 5% v/v). Samples were rinsed with ultra-pure water (X3), Vortex mixed and centrifuged (X3500, 15 minutes) between and after each treatment. Light microscope examination of remaining silicates demonstrated near-total diatom provenance (>95% by count).

6.2.1.3 Lake Water and Diatom Stable Isotope Analyses

Lake water δD and δ¹⁸O analyses were performed at the Stable Isotope Laboratory (Geological and Nuclear Science, Wellington, NZ) (Marsden Subcontract No. UOA0517). The Oxygen isotope composition of water samples (δ¹⁸OLake) was calculated using an on-line water-gas equilibration system (AquaPrep) coupled to a GVI Isoprime mass spectrometer (GV Isoprime, Manchester, UK). The Deuterium composition of water samples (δDLake) was calculated using a PyrOH equilibration system coupled to a GVI Isoprime mass spectrometer (GV Isoprime, Manchester, UK). Oxygen and Deuterium isotope ratios of water are reported as per mille (‰) deviations from V-SMOW and calibrated against international water standards. Precision for δ¹⁸OLake and δDLake analyses at GNS is rated at ± 0.1 ‰ and 1.0 ‰ (1σ) respectively (http://www.gns.cri.nz/nic/stableisotopes/oxygen and http://www.gns.cri.nz/nic/stableisotopes/deuterium/html [last accessed 20/01/2010]).

Diatom silica was analysed for δ¹⁸O and δ³⁰Si at the National Isotopes Geosciences Laboratory (NERC, UK) using a step-wise fluorination technique (Leng and Sloane, 2008). For each sample ~10 mg of silica was placed into a Ni vacuum reaction vessel and outgassed for 2 hours at 250 °C prior to stepwise pre-fluorination with BrF₅: (1) initial removal of the outer-exchangeable Si-OH layer at 250 °C for 6 minutes; and (2) dissociation of Si and O in remaining condensed silica in excess reagent at 550 °C for 12 hours. An interval of ~6 minutes has been demonstrated as sufficient to remove the majority of exchangeable O and for δ¹⁸O values to stabilise (Leng and Sloane, 2008). Liberated O passed along a sealed line through several liquid-N traps (trapping SiF₄) and was converted to CO₂ over a graphite rod as per Clayton and Mayeda (1963) prior to calculation of yield using a capacitance manometer. SiF₄ by-products were collected by replacing liquid-N traps with a dry ice/acetone slush...
(trapping BrF$_3$ and excess BrF$_5$). SiF$_4$ gas is then frozen in a collection vessel and liquid-N bath. As before a capacitance manometer is used to estimate yield.

CO$_2$ and SiF$_4$ gases were analysed offline using a gas-source IRMS (Finnegan Matt 253 fitted with a MEMCO [Multi Element Multi Collector] system to allow simultaneous measurement of $\delta^{29}$Si and $\delta^{30}$Si). O and Si stable isotopes in biogenic silica were calibrated against the international reference standard V-SMOW and NBS28 respectively via an intermediary internal laboratory standard (BFC$_{mod}$). Isotope ratios are presented as per mil (‰) deviations from V-SMOW and NBS28. Replicate analysis of random sedimentary samples indicate sample reproducibility of ± 0.28 and ± 0.07 ‰ (1σ, n = 8 and 4 [$\delta^{18}$O$_{biatom}$ and $\delta^{30}$Si$_{biatom}$ respectively]). Analytical precision is ± 0.45 ‰ and ± 0.07 ‰ (1σ, n = 20 and 6 [$\delta^{18}$O and $\delta^{30}$Si respectively]).

6.2.2 Results and Interpretations

6.2.2.1 Modern Isotope Hydrology (Precipitation and Lake Water Composition)

Stable isotopes of local precipitation and surface waters plot along trajectories of δD and δ$^{18}$O defined by a Local Meteoric Water Line (LMWL) and Local Evaporation Line (LEL) respectively (Gat, 2000). The LMWL is formed by regression of H and O stable isotope data of monthly average precipitation (Gat, 2005). Similarly, the LEL is formed through a corresponding regression of H and O stable isotope data for mean annual lake water (δD$_{Lake}$ = 1.95 ‰; δ$^{18}$O$_{Lake}$ = 0.75 ‰) and the amount-weighted mean for annual precipitation (δD$_P$ = -26.10 ‰; δ$^{18}$O$_P$ = -5.40 ‰). The LMWL and LEL for Lake Pupuke are presented in Figure 6.6 and equations below:

$$\delta D = 5.5734 \times \delta^{18}O + 4.0759 \quad (R^2 = 0.83, \ P < 0.01, \ n = 12)$$

(Calculation of the LMWL for Lake Pupuke)

$$\delta D = 4.5595 \times \delta^{18}O - 1.4689$$

(Calculation of the LEL for Lake Pupuke)

An LMWL slope of ~8 would closely match the global pattern of precipitation (e.g., GMWL of δD = 8 * δ$^{18}$O + 10 [Craig, 1961]). The LMWL slope for Auckland is less than 8 which implies marked fractionation of precipitation from source composition through advection. Stronger kinetic effects exist in δ$^{18}$O compared to δD causing greater relative enrichment of δ$^{18}$O (Gibson et al., 2008). Similarly, LEL can possess a lower slope due to evaporative enrichment of δ$^{18}$O within surface waters (Brock et al., 2007). Thus a LEL of 4.56 for Lake Pupuke is typical of its mid-latitude, seasonal climate in which local surface waters have undergone marked subsequent evaporation (e.g., Brock et al., 2007).
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 E. Briefly, δ_P is the amount-weighted annual precipitation, δ_SS is the steady state isotopic composition of a terminal basin, δ* is the limiting isotopic composition and δ_Lake is the modern isotopic composition of Lake Pupuke. Diamonds mark monthly precipitation δD and δ¹⁸O samples.

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 E.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Abbreviation</th>
<th>Value (δD, δ¹⁸O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity normalised to surface temperature</td>
<td>h (%)</td>
<td>72</td>
</tr>
<tr>
<td>Evaporative surface temperature</td>
<td>T (C, K)</td>
<td>17.67, 290.82</td>
</tr>
<tr>
<td>Equilibrium liquid-vapour fractionation factor</td>
<td>α</td>
<td>1.0856, 1.099</td>
</tr>
<tr>
<td>Equilibrium isotopic separation (liquid-vapour)</td>
<td>ε+ (‰)</td>
<td>85.60, 9.87</td>
</tr>
<tr>
<td>Kinetic isotopic separation (liquid-vapour)</td>
<td>Δε (‰)</td>
<td>3.6773, 4.2068</td>
</tr>
<tr>
<td>Amount-weighted annual precipitation signature</td>
<td>δ_P (‰)</td>
<td>-26.10, -5.40</td>
</tr>
<tr>
<td>Evaporation-flux weighted annual evaporation signature</td>
<td>δ_A (‰)</td>
<td>-98.46, -14.32</td>
</tr>
<tr>
<td>Steady-state isotopic composition</td>
<td>δ_SS (‰)</td>
<td>5.64, 1.06</td>
</tr>
<tr>
<td>Limiting isotopic composition</td>
<td>δ* (‰)</td>
<td>28.97, 5.31</td>
</tr>
<tr>
<td>Annual lake isotopic composition</td>
<td>δ_Lake (‰)</td>
<td>1.95, 0.75</td>
</tr>
<tr>
<td>Slope of predicted LEL</td>
<td>S</td>
<td>5.11</td>
</tr>
<tr>
<td>Intercept of predicted LEL</td>
<td>D</td>
<td>1.37</td>
</tr>
</tbody>
</table>
To examine the representivity of stable isotope data collected between 2008 and 2010, the LEL can be predicted using local isotopic and hydroclimatic information in the linear resistance model of Craig and Gordon (1965). The latter has been applied successfully to a range of freshwater systems across latitudinal and hydrological gradients (tropical, temperate and polar; open vs. closed basins) (Gibson, 2002; Benson and Paillet, 2002; Kebede et al., 2009; St. Amour et al., 2010). This also helps assess data veracity and identify the hydrological status of Lake Pupuke (see below). Key model parameters include the respective annual δD and δ\(^{18}\)O values of amount-weighted precipitation (δ\(P\); -26.10 ‰, -5.40 ‰), evaporation-flux weighted ambient atmospheric moisture (δ\(A\); -98.46 ‰, -14.32 ‰) and relative humidity (\(h = 72\) %) (Table 6.2). Annual values were employed over summer alone because the lake undergoes marked evaporation year-round. The slope of the LEL (S\(_{LEL}\)) can then be predicted from:

\[
S_{LEL} = \frac{\frac{h(\delta_A - \delta_P) + (1 + \delta_P)(\Delta \varepsilon + \varepsilon^+ / \alpha)}{h - \Delta \varepsilon - \varepsilon^+ / \alpha} \delta D - \delta A}{\frac{h(\delta_A - \delta_P) + (1 + \delta_P)(\Delta \varepsilon + \varepsilon^+ / \alpha)}{h - \Delta \varepsilon - \varepsilon^+ / \alpha} \delta^{18}O}
\]

(Prediction of LEL for an evaporating water body in isotopic and hydrological steady state [Gibson et al., 2008: 3])

where \(\varepsilon^+\) and \(\Delta \varepsilon\) are the equilibrium (\(\varepsilon^+; 85.60 \%e; 9.87 \%\)) and kinetic separation factors for δD and δ\(^{18}\)O (\(\Delta \varepsilon = 3.68 \%e; 4.21 \%\)), and \(\alpha\) is the liquid-vapour equilibrium fractionation factor for δD and δ\(^{18}\)O (1.0856, 1.099) derived empirically from Horita and Wesolowski (1994). Calculation of \(\varepsilon^+, \Delta \varepsilon\) and \(\alpha\) terms is included in Appendix E. The resultant isotopic framework for Lake Pupuke is shown in Figure 6.6 with parameter estimates listed in Table 6.2. A key reference point along the predicted LEL is the steady-state isotopic composition of a terminal lake (δ\(SS\) = 5.64 ‰, 1.06 ‰ [δD, δ\(^{18}\)O]) predicted for hydrological and isotopic steady state as follows:

\[
\delta_{SS} = \frac{\delta_P + m x \delta^*}{1 + m x}
\]

(Prediction of δ\(SS\) for hydrological and isotopic steady state [Source: Kebede et al., 2009: 178])

where \(x\) is evaporation to inflow ratio (annual E/P ~ 0.61 [707 mm / 1161 mm]), \(\delta_P\) is the amount-weighted annual isotopic composition of precipitation, \(\delta^*\) is the limiting isotopic composition - a theoretical maximum in δD and δ\(^{18}\)O attained by a basin as it approaches complete desiccation (\(\delta^* = 28.97 \%e, 5.31 \%\) [δD, δ\(^{18}\)O]) and the parameter \(m\), calculated as follows:

\[
m = \frac{h - \varepsilon / 1000}{1 - h - \Delta \varepsilon / 1000}
\]

\[
\delta^* = (h \delta_A + \varepsilon) / (h - 10^{-3} \varepsilon)
\]

(Calculation of the \(m\) parameter employed to calculate δ\(SS\) [Source: Kebede et al., 2009: 178])
where $\varepsilon$ represents the sum of kinetic and equilibrium fractionation (e.g., sum of $\varepsilon_+ + \Delta\varepsilon$). The $\delta^*$ value is the end-point of the predicted LEL, and accordingly, Lake Pupuke possesses isotopic values less enriched than $\delta^*$. $\delta^D_{\text{Lake}}$ and $\delta^{18}O_{\text{Lake}}$ values are very close to those of $\delta^{SS}$ suggesting the system is nearing a state of hydrologic and isotopic steady state (e.g., total evaporation approaching total precipitation) and confirming the hydrologically closed status of the basin (Gibson et al., 2008). Nevertheless, whilst the predicted LEL correctly models isotopic enrichment in the basin, differences in observed and predicted gradients (4.56 and 5.11 respectively) suggest that the model has failed to sufficiently account for total evaporative fractionation of the lacustrine isotopic reservoir (e.g., through greater relative evaporation over the last $\sim$30 years [residence time] than over 2006-2009 [meteorological survey period]). Kebede et al. (2009) modelled crater lake isotope hydrology in Ethiopia which exhibit similar LEL values to this study (~4 to 6). Therefore as $\delta_p - \delta_a < \varepsilon_+$ the lake possesses isotopically-enriched vapour during periods of peak evaporation (a response to thermal stratification and isolation of isotopically-enriched surface water).

Empirical and modelled isotopic responses within Lake Pupuke are very similar giving confidence in the climatic as well as isotopic precipitation and lake water data, and the estimated responses of lake or precipitation isotopes to changing climate (see Dansgaard relationship below). A critical point to reiterate however, is that marked enrichment of Lake Pupuke water occurs presently driving it towards the $\delta^{SS}$ isotope composition. Consequently, the site does not closely approximate changes in the isotopic composition of precipitation, and instead responds largely to changes in effective moisture (P/E). Under present boundary conditions, any application of $\delta^{18}O_{\text{Diatom}}$ to the Lake Pupuke composite series will have to interpret changes to $\delta^{18}O_{\text{Lake}}$ as responses to altered residence time and P/E balance (i.e., more or less kinetic fractionation through greater or lesser evaporation) in addition to a thermodynamic response to past temperature.

### 6.2.2.2 Temporal Variability in $\delta^{18}O_{\text{Precipitation}}$

Seasonality in air temperature, precipitation and evaporation affects the hydrology of Lake Pupuke (Section 2.4. Climatology). For instance, between January 2006 and January 2010, mean monthly air temperature ranges from 10.97 to 19.80 °C (July to January) with an annual average of 15.06 °C. Monthly precipitation ranged from 49 to 152 mm (November to July) with a monthly average of 97 mm. A corresponding seasonal pattern is exhibited in $\delta^D_p$ and $\delta^{18}O_p$ (Figure 6.7). Precipitation samples have a range of -40.27 to -12.19 ‰ in $\delta^D$ and -7.82 to -2.99 ‰ in $\delta^{18}O$. Mean $\delta^D_{\text{Precipitation}}$ and $\delta^{18}O_{\text{Precipitation}}$ values are -24.21 and -5.08 ‰ respectively. Isotope means differ little when weighted with precipitation amount (-26.10 and -5.40 ‰ [$\delta^D_{\text{Precipitation}}$ and $\delta^{18}O_{\text{Precipitation}}$]). This pattern of seasonality is characteristic of a mid-latitude Southern Hemisphere site with enrichment of precipitation occurring in the austral summer (December to February) and depletion in the austral winter (June to August) (Clark and Fritz, 1997). This thereby suggests a strong thermal or amount relationship in the isotope composition of precipitation (Clark and Fritz, 1997).
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.
Precipitation samples scatter along a regression in δD and δ¹⁸O space, the LMWL (δD = 5.57 * δ¹⁸O + 4). Although the local gradient in precipitation δD and δ¹⁸O is ~6 the global equivalent is ~8 (GMWL; δD = 8 * δ¹⁸O + 10 [Craig, 1961]). The intercept of the GMWL represents that of deuterium excess (d-), a value dependent on oceanic or other sources of atmospheric vapour and which changes in response to marked re-evaporation (advection) of precipitation back into the atmosphere (Gat, 2005). Deuterium excess is calculated from:

\[ d- = \delta D - 8 * \delta^{18}O \]

(Calculation of Deuterium excess [Source: Dansgaard, 1964])

where d- is the intercept for a δD and δ¹⁸O relationship of identical gradient to the GMWL (Dansgaard, 1964). Examination of d- can thereby reveal marked changes to precipitation source and/or advection in transit to Lake Pupuke.

Deuterium-excess values ranged from 5.29 to 23.58 with an annual average of 16.39. This seasonal profile is typical for a Southern Hemisphere location (e.g., enrichment in winter months and depletion in summer months; Figure 6.7) (Gat, 2005). Changes to d- reflect changes in relative humidity and wind speed at source as well as changes in source area (Gat and Gonfiantini, 1981). Reduced d- in January and March likely reflects a brief influx of warm, moist sub-tropical air with a lower fractionation factor resulting in less kinetic fractionation at source (and possibly limited advective fractionation) (Gat and Gonfiantini, 1981). Enriched d- in winter precipitation implies a cooler more southerly source of lower relative humidity enabling greater fractionation and enrichment of deuterium relative to ¹⁸O in evaporation from source water. This occurs as at lower relative humidity less equilibrium exchange occurs meaning that the higher molecular diffusivity of ²H¹H¹⁶O relative to H₂¹⁸O or ¹H²H¹⁸O leads to greater kinetic enrichment of atmospheric moisture (Gat and Gonfiantini, 1981). Thus d- values at Pupuke suggest the dominance of a single southerly source of precipitation (d- enriched), interrupted by a northerly source in summer months (d- depleted).

**6.2.2.3 Thermal (‘Dansgaard’) and Amount Relationships in δ¹⁸O<sub>Precipitation</sub>**

The capacity for δ¹⁸O<sub>Diatom</sub> to record changes to temperature through the combined isotopic effects of ambient water temperature at silica precipitation and air temperature of meteoric rainfall has already been discussed. Empirical data suggests an ambient water-column thermal coefficient of ~-0.2 ‰/°C in freshwater diatoms (Moschen et al., 2005). This must be applied in conjunction with the thermal coefficient for atmospheric precipitation to yield a combined thermal effect in δ¹⁸O<sub>Diatom</sub> (Leng and Marshall, 2004).

Dansgaard (1964) published the first estimate of the atmospheric thermal coefficient for δ<sub>p</sub> through a linear regression of δ¹⁸O<sub>Precipitation</sub> and air temperature (~+0.69 ‰/°C, 0-20 °C). Application of climatic data gathered for Lake Pupuke over the interval 05/2008-01/2010 yields a coefficient of +0.41 ‰/°C (R² = 0.65, \( P < 0.01 \ n = 11 \)) (Figure 6.8) which compares favourably with an estimate of ~+0.58 ‰/°C in the Global Network of Isotopes in Precipitation (GNIP) data (Rozanski et al., 1993). However, despite the strong thermal dependency of
\[ \delta^{18}O_{\text{Precipitation}} = 0.4063 \times T - 11.027 \quad (R^2 = 0.65, \ n = 11) \]

(Thermal or 'Dansgaard' relationship for precipitation collected in Auckland [05/2008-01/2010] where \( \delta^{18}O_{\text{Precipitation}} \) is the monthly \( \delta^{18}O \) signature of meteoric rainfall [‰] and \( T \) is monthly mean air temperature [Celsius])

\[ \delta^{18}O_{\text{Precipitation}} = -0.0317 \times A - 1.9023 \quad (R^2 = 0.52, \ n = 11) \]

(Amount relationship for precipitation collected in Auckland [05/2008-01/2010] where \( \delta^{18}O_{\text{Precipitation}} \) is the monthly \( \delta^{18}O \) signature of meteoric rainfall [‰] and \( A \) is the monthly mean rainfall amount [mm])

Figure 6.8: Thermal or 'Dansgaard' relationship for precipitation collected in Auckland (05/2008-01/2010).
6.2.2.4 Spatial and temporal variability in $\delta^{18}$O$_{\text{Lake}}$

Combined lake water isotope composition ($\delta$D$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Lake}}$; 1.95 and 0.75 ‰ respectively) demonstrates marked seasonality characterised by summer enrichment (January = 3.60 and 0.87 ‰ [$\delta$D and $\delta^{18}$O]) and winter depletion (August = 1.30 and 0.59 ‰ [$\delta$D and $\delta^{18}$O]) (Figure 6.10). Marked enrichment of annual lake composition from $\delta$P is far greater than this seasonal variation (monthly range in $\delta$D$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Lake}}$ is 3.67 and 0.28 ‰ respectively, compared to +28.05 and +6.15 ‰ enrichment of annual average $\delta$D$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Lake}}$ from $\delta$P [minimum $\delta$D$_{\text{Lake}}$ occurs in May, -0.07 ‰]). Lake water composition never approaches $\delta$P suggesting contemporary isotopic signatures include accumulated evaporative effects over the lake’s residence time (~30 years). This also offers an explanation for weak relationships between climatic/hydrologic factors and isotopic composition (Table 6.3). Of these, P/E balance and water temperature appear to most influence $\delta$D$_{\text{Lake}}$ and $\delta^{18}$O$_{\text{Lake}}$ (Table 6.3). Only a very weak correlation exists between lake and precipitation isotopic composition ($r_{\delta D} = 0.25$, $r_{\delta^{18}O} = 0.23$, $n = 11$). This underscores the observation that changes in the isotopic composition of rainfall are not readily expressed in changes to lake water isotopic composition.
Figure 6.10: Monthly stable isotopic composition of Lake Pupuke by depth (05/2008-01/2010).
In addition to seasonality, \( \delta D_{\text{Lake}} \) and \( \delta^{18}O_{\text{Lake}} \) exhibit distinct variation with depth (Figure 6.10). Annual average lake water composition varies markedly between the epilimnion \( \langle \delta D, \delta^{18}O_{\text{Surface}} \rangle \) \( 2.11 \pm 1.17 \%o, 0.81 \pm 0.15 \%o \), thermocline \( \langle \delta D, \delta^{18}O_{15m} \rangle \) \( 2.09 \pm 1.22 \%o, 0.76 \pm 0.14 \%o \) and hypolimnion \( \langle \delta D, \delta^{18}O_{28m} \rangle \) \( 1.65 \pm 0.85 \%o, 0.68 \pm 0.07 \% \) (Table 6.4). Seasonality is also evident with depth as greater and lesser variability is present in surface waters and hypolimnetic waters respectively. For instance, annual ranges in \( \delta D \) and \( \delta^{18}O \) by 0, 15 and 28 m depth are 4.4 and 0.4 \%o, 4.2 and 0.39 \%o and 3.3 and 0.22 \%o respectively (Figure 6.10). This reflects isolation of a deep, voluminous isotope reservoir in the hypolimnion by thermal stratification from September until June. Variation in \( \delta D \) and \( \delta^{18}O \) between depths decreases markedly during overturn (July and September) when the whole lake readily mixes (Figure 6.10). Evaporative enrichment and a strong thermocline enable a greater gradient of change in \( \delta D \) and \( \delta^{18}O \) to develop between surface and hypolimnetic waters from October until May. In particular, greatest variation in \( \delta D \) and \( \delta^{18}O \) exists between epilimnetic and hypolimnetic water between January and March (1.80 and 0.37 \%o respectively between 0 and 28 m depth).

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).

<table>
<thead>
<tr>
<th>Depth</th>
<th>Stable Isotope</th>
<th>2008 May</th>
<th>Jun</th>
<th>Aug</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>2009 Mar</th>
<th>Apr</th>
<th>Jun</th>
<th>Jul</th>
<th>Sep</th>
<th>2010 Jan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>( \delta D ) (%)</td>
<td>0.1</td>
<td>1.3</td>
<td>0.9</td>
<td>1.4</td>
<td>1.5</td>
<td>2.8</td>
<td>2.7</td>
<td>2.7</td>
<td>1.3</td>
<td>2.3</td>
<td>2.9</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>( \delta^{18}O ) (%)</td>
<td>0.86</td>
<td>0.84</td>
<td>0.62</td>
<td>0.59</td>
<td>0.78</td>
<td>0.86</td>
<td>0.98</td>
<td>0.98</td>
<td>0.7</td>
<td>0.75</td>
<td>0.66</td>
<td>0.99</td>
</tr>
<tr>
<td>15 m</td>
<td>( \delta D ) (%)</td>
<td>0.0</td>
<td>0.7</td>
<td>0.8</td>
<td>0.3</td>
<td>2.2</td>
<td>2.1</td>
<td>3.2</td>
<td>3.2</td>
<td>2.3</td>
<td>2.9</td>
<td>2.6</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>( \delta^{18}O ) (%)</td>
<td>0.91</td>
<td>0.84</td>
<td>0.59</td>
<td>0.59</td>
<td>0.65</td>
<td>0.73</td>
<td>0.94</td>
<td>0.99</td>
<td>0.75</td>
<td>0.7</td>
<td>0.63</td>
<td>0.98</td>
</tr>
<tr>
<td>28 m</td>
<td>( \delta D ) (%)</td>
<td>-0.3</td>
<td>0.3</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.2</td>
<td>3.2</td>
<td>2.7</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>( \delta^{18}O ) (%)</td>
<td>0.68</td>
<td>0.71</td>
<td>0.57</td>
<td>0.73</td>
<td>0.63</td>
<td>0.67</td>
<td>0.58</td>
<td>0.84</td>
<td>0.83</td>
<td>0.79</td>
<td>0.70</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Variation in isotopic composition suggests thermal stratification effectively prevents hypolimnetic and epilimnetic oxygen isotope reservoirs from mixing. Consequently, surface waters reflect changes to direct evaporation from the lake surface, estimated at 707 mm per year (61% of precipitation), ranging from 27.5 mm (July) to 94.1 mm (January) (Section 2.4. Climatology). Thus changes to seasonality and the extent of stratification will affect evaporative enrichment of Lake Pupuke, particularly the productive epilimnion. Nevertheless, mixing and the large volume of Lake Pupuke buffer any annual effects. Instead the ~30 year residence time has enabled evaporative effects to accumulate. For instance, seasonal variation in \( \delta^{18}O_{\text{Lake}} \) (~0.40 \%) is far less than the difference in annual \( \delta^{18}O \) of lake water and precipitation (~6.15 \%). Consequently, rapid climate events including ENSO variability are likely to be prevented from becoming expressed in records of \( \delta^{18}O_{\text{Lake}} \) within Lake Pupuke.
6.2.2.5 Diatom Isotope Seasonality

Modern diatom samples had a mean silica yield of 64.6% suggesting that 35.4% of total mass was loosely bound hydroxyl groups, water (OH⁻ and H₂O) and/or other contaminants. Variation between the four seasonal envelopes was 1.67 and 0.31‰ (δ¹⁸O and δ³⁰Si respectively). Up to 1.67 and 0.31‰ of variation can therefore be introduced as a vital seasonal effect within the Pupuke δ¹⁸O_Diatom and δ³⁰Si_Diatom composite sequence. δ¹⁸O_Diatom shows greatest enrichment between June and October (2008; 27.28‰) and greatest depletion between February and July (2009; 25.61‰). Greatest enrichment in δ³⁰Si_Diatom occurs between March and June (2008; 0.38‰) and greatest depletion between June and October (2008; 0.07‰).

The large seasonal window between deployment and collection of each sediment sample restricts comparison of diatom isotope composition to lake water chemistry for 3 reasons: (1) poorly defined period of sedimentation, particularly given the propensity for particulate matter to remain suspended in the epilimnion until breakdown of stratification (Wetzel, 2001); (2) resuspension of surface sediment at overturn, contributing older silica to sediment samples; and (3) failure to capture short-term variability in water chemistry associated with rapid diatom blooms. For instance, comparison of the isotopic offset between diatom silica and lake water (∆δ¹⁸O_Diatom-Lake) to changes in water temperature over each seasonal window, yielded a highly variable thermal coefficient in δ¹⁸O_Diatom of -0.26 to +0.30‰/°C. As noted, an accurate estimate for the thermal coefficient of precipitation in freshwater diatoms is -0.20‰/°C (Moschen et al., 2006). Indeed δ¹⁸O_Diatom is only strongly correlated with total Sulphur content (TS, r = 0.99, P < 0.01 n = 4) (Table 6.5). As the latter and former were recorded in the same sample, these relationships are robust. This therefore records a strong relationship between aquatic productivity and diatom O-isotope signatures (R² = 0.98, P < 0.001 n = 4) with peak biological productivity associated with greater TS-concentration and enrichment of δ¹⁸O_Diatom, and vice-versa.

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

<table>
<thead>
<tr>
<th>Correlation Matrix</th>
<th>δ¹⁸O_Diatom</th>
<th>δ³⁰Si_Diatom</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (wt. %)</td>
<td>0.49</td>
<td>-0.94</td>
</tr>
<tr>
<td>TN (wt. %)</td>
<td>0.38</td>
<td>-0.95</td>
</tr>
<tr>
<td>C/N (Atomic ratio)</td>
<td>0.80</td>
<td>-0.72</td>
</tr>
<tr>
<td>TS (wt. %)</td>
<td>0.99</td>
<td>-0.32</td>
</tr>
<tr>
<td>δ¹⁸O</td>
<td>-0.00</td>
<td>0.73</td>
</tr>
<tr>
<td>Silica Maturity</td>
<td>-0.25</td>
<td>-0.66</td>
</tr>
<tr>
<td>Water Temperature (°C)</td>
<td>-0.15</td>
<td>0.85</td>
</tr>
<tr>
<td>δ¹⁸O_Lake</td>
<td>-0.81</td>
<td>0.89</td>
</tr>
<tr>
<td>Air Temperature (°C)</td>
<td>-0.45</td>
<td>0.91</td>
</tr>
<tr>
<td>Chl a</td>
<td>0.53</td>
<td>-0.05</td>
</tr>
<tr>
<td>Evaporation (mm)</td>
<td>0.14</td>
<td>0.62</td>
</tr>
<tr>
<td>Effective Precipitation</td>
<td>-0.29</td>
<td>-0.42</td>
</tr>
</tbody>
</table>

Correlation analyses also demonstrate a strong positive relationship between δ³⁰Si_Diatom and organic δ¹³C of trapped sediment (r = 0.73, P > 0.1, n = 4). In Chapter 4 (Section 4.2. The Modern Geochemical Framework of Lake Pupuke) it was noted that enrichment of organic δ¹³C within Lake Pupuke occurs in response to stratification whereby isolation of the epilimnetic dissolved inorganic Carbon (DIC) reservoir causes δ¹³C-enrichment of organic matter. A strong positive correlation between modern sediment sample δ¹³C and...
\( \delta^{30}\text{Si}_{\text{Diatom}} \) suggests that stratification also controls the availability of dissolved Silica (DSi), with isolation of the epilimnion resulting in enrichment of \( \delta^{30}\text{Si}_{\text{Diatom}} \). The strength of thermal stratification is dependent upon water temperature, explaining a strong positive correlation between \( \delta^{30}\text{Si}_{\text{Diatom}} \) and water temperature \((r = 0.85, P < 0.025, n = 4)\). Hence the process of thermal stratification effectively links Carbon and Silicon cycles in Lake Pupuke.

### 6.2.3 Summary of Modern Stable Isotope Systematics

Seasonal air temperature variation results in changes to the isotopic composition of precipitation typical of mid-latitude austral seasonality (summer enrichment and winter depletion) \((\text{Gat, 2005})\). For instance, peak enrichment and depletion of precipitation isotopic composition occurred in January \((-12.51 \text{ and } -2.98 \% \text{[}\delta D \text{ and } \delta^{18}\text{O}\text{]}) \) and July respectively \((-40.27 \text{ and } -7.82 \% \text{[}\delta D \text{ and } \delta^{18}\text{O}\text{]}) \). This results in a thermal coefficient of fractionation of \(+0.41 \% / ^\circ\text{C} \) in \( \delta^{18}\text{O}_{\text{Precipitation}} \) \((R^2 = 0.65, n = 11)\). Inspection of deuterium excess \((\delta d)\) also revealed the likelihood of a dominant southerly water source of precipitation, with a \( \delta \)-enriched northerly source in late summer \((\text{January to March})\). Changes in the proportions of each source might thereby complicate paleoclimatic inferences from \( \delta^{18}\text{O}_{\text{Diatom}} \) by introducing changes in \( \delta^{18}\text{O}_{\text{Precipitation}} \) in addition to paleotemperature. Similarly, the weak amount effect present in \( \delta^{18}\text{O}_{\text{Precipitation}} \) \((R^2 = 0.52, n = 11)\) has the potential to further distort \( \delta^{18}\text{O}_{\text{Diatom}} \) by changes in intensity of paleoprecipitation.

Seasonality in air temperature and windiness results in strong thermal stratification of Lake Pupuke \((\text{Section 2.4.1.2. Temperature and thermal stratification})\). This trend is expressed in surface water \( \delta D_{\text{Lake}} \) and \( \delta^{18}\text{O}_{\text{Lake}} \) values which become progressively more enriched with the onset of thermal stratification \((\text{September})\) until breakdown and dilution by relatively \( ^{18}\text{O} \)-depleted deeper waters \((\text{July})\). Application of the Craig and Gordon \((1965)\) steady-state lacustrine isotope model, and interpretation of seasonal \( \delta D_{\text{Lake}} \) and \( \delta^{18}\text{O}_{\text{Lake}} \) demonstrated very limited capacity for Lake Pupuke to record subtle changes in precipitation composition \((\text{e.g., in line with thermal or amount effects})\). Changes to paleohydrology might have resulted in less evaporative enrichment and approximation of annual precipitation \((\delta p)\) by lake isotopic composition. Hence, subtle changes in source water could become incorporated in \( \delta^{18}\text{O}_{\text{Diatom}} \). Presently however, evaporative enrichment overwhelms any affect of altered source in \( \delta^{18}\text{O}_{\text{Lake}} \). A residence time of \(~30\text{ years} \) and high annual evaporation \(~61 \% \) of precipitation) effectively enrich H- and O-isotope reservoirs within Lake Pupuke to a composition similar to that of a terminal, steady-state lake \((\text{e.g., one in which evaporation effectively equals precipitation})\) \((\text{Yi et al., 2008})\). The modern \( \delta D \) and \( \delta^{18}\text{O} \) isotopic composition of Lake Pupuke is \( 3.69 \) and \( 0.31 \% \) more depleted than the latter \((\delta_{\text{Lake}} = 1.95 \) and \( 0.75 \% \text{[}\delta D \text{ and } \delta^{18}\text{O}\text{]}; \delta_{\text{SS}} = 5.64 \text{ and } 1.06 \% \text{[}\delta D \text{ and } \delta^{18}\text{O}\text{]) but 28.05 \text{ and } 6.15 \% \) more enriched than its annual amount-weighted source water composition \((\delta p = -26.10 \text{ and } -5.40 \% \text{[}\delta D \text{ and } \delta^{18}\text{O}\text{])}. Consequently, records of \( \delta^{18}\text{O}_{\text{Lake}} \) held by diatom silica are likely to reflect dominant changes to P/E rather than temperature at precipitation; drier climates and/or greater residence time causing enrichment; and wetter climate and/or lesser residence time causing depletion in \( \delta^{18}\text{O}_{\text{Diatom}} \) \((\text{Froelich et al., 2005})\).
6.3 Paleolimnologic Methods

6.3.1 Sample Selection

A total of 146 sediment samples were prepared for isolation of diatom silica in two research exercises with the University of Lancaster (UK) and the National Isotope Geosciences Laboratory (NERC, UK) (04/05/2008 to 04/08/2008 and 25/02/2009 to 21/06/2009). Depths for sample analyses are recorded in Appendix B. To ensure diatom isotope data would capture hydrological and ecological conditions of the past at centurial to millennial time-scales, samples were initially spaced at ~300 yr (~10 cm) intervals ($n = 93$). Following chemical treatments and physical separation (see below), only 35 were of sufficient cleanliness (>90 % diatom) for stable isotope analysis; resolution was limited to ~900 yr (~30 cm). Over the second research exercise samples were selected to enhance resolution. A total of 53 further samples were prepared of which 34 were sufficiently clean to permit isotope analysis. Combined sample resolution improved to ~680 yr (~23 cm) ($n = 69$).

6.3.2 Chemical and Physical Separation

Diatom silica samples were prepared for O and Si isotope analysis following a 6–stage methodology (Figure 6.11) (modified from Juillet-Leclerc, 1986; Shemesh et al., 1995; Morley et al., 2004; Swann, 2007). Sediment samples were prepared over 1 cm intervals, vacuum dried and immersed in 30% v/v H$_2$O$_2$ at 60 ºC for 48 hours or until cessation of reaction. Following removal of organic matter present in the sediment matrix and attached to diatom frustules, samples have been repeatedly (x3) Vortex mixed, centrifuged (x3500 rpm/15 minutes) and rinsed with deionised water. Following centrifuge washing, inorganic carbonates were removed by exposure to a weak acid overnight (5% v/v HCl per 20 ml solution). Samples were centrifuge washed again until pH reached that of deionised water.

Subsequent treatment for split-flow lateral-transport thin (SPLITT) separation necessitates the near-complete removal of organic tissue; remnant algal compounds negate separation properties of microfossils (Rings et al., 2004). To ensure oxidation of remnant organic matter an additional 30-40 ml of strong nitric acid (2N HNO$_3$) was added to each sample, immersing the latter in a 60 ºC water bath and topping up the acid solution over a period of 24 hrs. Samples were wet-sieved for size-specific fractions; >125 µm, 125-63 µm, 63-38 µm, 38-20 µm and <20 µm. Following visual light microscopical inspection (x600-1000) of microfossil separates, the <20 µm fraction was chosen as it provided the least proportion of contaminants. While the range of sample sizes would ideally reflect particular taxon boundaries (e.g., isolate single species classes [Swann, 2009]) thereby circumventing the debate regarding kinetic vital effects amongst and between taxa), this was not possible owing to the inclusion of sponge spicules in all fractions larger than 10 µm (foremost in 38-63 µm) and the increasing dominance of larger fractions by volcanic glass. There are also size limitations inherent in SPLITT-separation procedures whereby microfossils larger than 20 µm cause blockage of peristaltic tubing in- and outlets (Barker, pers.comm., 2008). The <20 µm fraction included largely intact diatom frustules (e.g., *Aulacoseira* spp., *Discotella* spp., *Staurosira* spp.,) and also fractured, disaggregated larger taxa (e.g., *Epithemia* spp., *Nitzschia* spp.), and several sponge spicules (having passed through the sieve along their shorter axis).
Figure 6.11: The 6-stage methodology employed to extract purified biogenic silica stable isotopic ($\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$) signatures from the Lake Pupuke composite sequence.
Whereas in previous studies diatom frustules have been further isolated from impurities along density gradients (e.g., Shemesh et al., 1995; Morley et al., 2005) preliminary examination of classes isolated by immersion in 40 ml Sodium Polytyngstate Solution across a gradient of specific gravity (1.9-2.2 g/ml), Vortex mixed and centrifuged (x4000 rpm/15 minutes) revealed no noticeable improvement in diatom purity. Brewer et al (2008) modelled density separation and concentration criteria (CC [Wills, 1992]) for a range of contaminants mixed with diatom frustules. With the exception of pumice, a range of inorganic mineral contaminants (e.g., feldspars, micas, clays) were demonstrated to be below the necessary concentration criterion for opaline silica to effectively separate the latter. Coupled to evidence of SPT contaminating Oxygen isotope analyses through adherence to diatom frustules (Tyler et al., 2007; Leng, pers. comm., 2008), a density flotation stage has been omitted to ensure samples were not further contaminated prior to laminar-flow SPLITT separation.

6.3.3 SPLITT Separation

The application of diatom silica to Oxygen isotope paleolimnology hinges on the purity of recovered diatom samples (Leng and Marshall, 2004). Failure of other traditional approaches (e.g., density flotation, sieving, acid-digestion) necessitated another approach to physically separate O and Si-yielding contaminants. Several researchers have demonstrated the capacity for diatoms to behave hydrodynamically, permitting isolation of size specific fractions along a density and diametrical gradient in a laminar carrier fluid (Keil et al., 1994; Zhang et al., 1994; Fuh and Giddings, 1995, 1997; Fuh and Chen, 1998; Fuh, 2000; Gustafsson et al., 2000). Split-flow lateral-transport thin separation (SPLITT) is a novel technique for diatom purification (Rings et al., 2004). A continuous stream of particles mixed in suspension is introduced through the upper inlet a′ with a carrier liquid (deionised water) introduced via inlet b′ (Figure 6.12). Both flows are laminar across the SPLITT plane and particles settle from the upper carrier fluid according to their density, shape and size, leading to capture in one of two outlets (a and b). Given a uniform density and field strength, diameter becomes the criterion for separation leading to a cut-off diameter (dC) below or above which particles are collected by outlet a and b (Giddings, 1985). Further details of SPLITT-fractionation are provided in Appendix F.

This study utilised the University of Lancaster Geography Department’s SPLITT cell (dimensions: 200 x 40 x 0.371 mm) aligned along a 40° inclination. Sample concentrations were kept to ~0.1% (w/v) to aid microfossil separation, restrict particle-particle interactions and ensure high throughput under continuous flow (Gupta et al., 1997; Jiang et al., 1997). Flow rates in all necessary SPLITT fractionations employed on each sample are listed in Table 6.6. For the majority of samples a 3-step SPLITT fractionation approach was adopted: (1) 5 by 15 ml/min; (2) 5 by 10 ml/min; and (3) 5 by 7.5 ml/min (a’ and b’ respectively) (with the exception of sponge spicule rich samples in which flow rates were inverted to 25 by 15 ml/min [a’ and b’ respectively]). Flows were controlled by peristaltic pumps, calibrated using volumetric measuring flasks. A bubble trap was fitted to the carrier fluid inlet to remove air bubbles that could form and alter flow conditions in the channel. Air bubbles that entered the SPLITT cell were removed by increased flow velocity and/or passing several millilitres of pure ethanol through the cell, followed by rinsing with 1L deionised water.
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).

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.

<table>
<thead>
<tr>
<th>Diatom Outlet</th>
<th>Sieve Fraction</th>
<th>Step Number</th>
<th>Flow Rate (ml/min)</th>
<th>Sample Volume (ml)</th>
<th>Operation Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a and b</td>
<td>&lt;20µm</td>
<td>1</td>
<td>5</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>b</td>
<td>&lt;20µm</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>a and b</td>
<td>&lt;20µm</td>
<td>3</td>
<td>5</td>
<td>7.5</td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>&lt;20µm</td>
<td>3</td>
<td>6.5</td>
<td>8.5</td>
<td>200</td>
</tr>
<tr>
<td>a, b</td>
<td>&lt;20µm</td>
<td>2, 3</td>
<td>7.5</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>&lt;20µm</td>
<td>3</td>
<td>10</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>&lt;20µm</td>
<td>3</td>
<td>15</td>
<td>7.5</td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>&lt;20µm</td>
<td>3</td>
<td>20</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>a, b</td>
<td>&lt;20µm</td>
<td>2, 3</td>
<td>25</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>&lt;20µm</td>
<td>3</td>
<td>30</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>a and b</td>
<td>&lt;20µm</td>
<td>4</td>
<td>5</td>
<td>6.5</td>
<td>200</td>
</tr>
</tbody>
</table>
Before and after SPLITT fractionation sub-samples of cleaned biogenic silica samples were mounted onto glass slides (final step solutions with Naphrax® mounting media) prior to examination for contamination and enumeration of diatom microfossil dominance at x100 magnification using a light microscope. Those samples with >10% by count non-biogenic silicate present were excluded from further analysis (this figure is higher than others [e.g., Swann, 2009] but owing to the inclusion of volcanic glasses in nearly all samples, this figure was chosen to ensure sufficient samples for analysis, and is within the capacity of mass balance corrections).

6.3.4 Stable Isotope Analysis

Diatom silica was analysed for δ¹⁸O and δ³⁰Si at the National Isotopes Geosciences Laboratory (NERC, UK) using the step-wise fluorination technique described previously (Section 6.2.1.3. Lake Water and Diatom Stable Isotope Analyses). A combined method was applied for determination of δ¹⁸O and δ³⁰Si. Dual isotope analysis of δ¹⁸O and δ³⁰Si by IRMS has been possible since the 1960s (e.g., Taylor and Epstein, 1962) but suffered from limited uptake until support from the working group, Isotopes in Biogenic Silica (IBiS; www.bgs.ac.uk/ibis). For further details of the combined method for IRMS analysis please refer to Leng and Sloane (2008). Isotope ratios are presented in the usual δ form, as per mil (‰) deviations from V-SMOW and NBS28. A random selection of samples were analysed in duplicate to give estimates of sample reproducibility (± 0.28 and 0.07 ‰, 1σ, n = 8 and 4 [δ¹⁸O and δ³⁰Si respectively]). Analytical precision is reported by reproducibility of the laboratory standard is ± 0.45 ‰ and 0.07 ‰ (1σ, n = 20 and 6 [δ¹⁸O and δ³⁰Si respectively]).

6.3.5 Contaminant Analysis

Owing to the relatively minor changes observed in sedimentary O- and Si-isotope series (e.g., per mil variation), the presence of even minor traces of O- or Si-yielding contaminants can substantially alter corresponding δ¹⁸O or δ³⁰Si values (Leng and Barker, 2006). In this thesis novel physical and mathematical techniques were explored to limit error in δ¹⁸O_Diatom or δ³⁰Si_Diatom due to contamination (e.g., split-flow lateral transport thin fractionation [SPLITT] and micro-XRF mixture modelled contributions of volcanic glass).

Standard diatom preparation approaches involve stages targeting individual components: weak acids (e.g., HCl) to remove inorganic carbonate; strong oxidisers (e.g., H₂O₂, HNO₃) to remove organic matter; and size/density separation to remove clays and volcanic glasses (e.g., SPLITT-separation). Despite the time-consuming nature of cleaning by physical and chemical methods, contamination can still occur by adherence of finer clays, reprecipitation of volcanic/weathered silicates in frustule cavities, and limited “corresponding density and size” for laminar flow separation (Swann and Leng, 2009). For instance, Morley et al. (2004, 2005) reported the inclusion of fine clays within small (<10 µm) frustules for which a "meniscus effect" protects contaminants and organic tissue from digestion. Therefore, to reduce uncertainty in O and Si isotope estimates it is essential to provide a quantitative estimate of the latter’s contribution to cleaned diatom δ¹⁸O and δ³⁰Si signatures.
Morley et al. (2004) provided the first semi-quantitative approach in which a density separation cleaning stage (Sodium Polytungstate [SPT] ~1.9-2.2 sg) is coupled to light microscopical assessment of contamination. Lamb et al. (2007) produced the first truly quantitative approach to assessing contamination in $\delta^{18}O_{\text{Diatom}}$ by major and trace element geochemistry. This mass balance approach was subsequently modified in Brewer et al. (2008) and Swann and Leng (2010). This modified micro-XRF and mass balance approach is employed here to estimate and remove the contaminant effects in 63 SPLITT-fractionated diatom silica samples.

6.3.5.1 Light and Electron Microscopical Analyses

Purified diatom samples have been analysed by light microscopy (mounted with Naphrax$^\text{TM}$ agent) at X600-1000 (Leica DMLB) and scanning electron microscopy (SEM; Philips XL30S FEG equipped with a Polaron SC 7640 Pt sputter coating unit [5-10 mA, 1.1 kV]) for signs of weathering/dissolution/reprecipitation and to identify contaminant types present. A series of random transects were taken across each prepared slide recording the presence of whole diatom frustules (x2 valves), tephra and sponge spicules (whole or fragmented) until 100 frustules had been counted. Results indicated an absence of clays but an abundance of volcanic glass shards. Accordingly, the focus was on modelling and removing the effect of volcanic glass on sample $\delta^{18}O$ and $\delta^{30}Si$ values.

6.3.5.2 Geochemical Mass-Balance Modelling

Provided contaminants possess geochemistry that is distinct from diatom opal, its contribution to sample mass can be analysed by micro-XRF (Lamb et al., 2007). When coupled with corresponding stable isotope signatures, this enables the contribution to $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ to be modelled and removed (Brewer et al., 2008). Fortunately, volcanic glass has characteristically distinct major and trace element chemistry from biogenic opal (Lamb et al., 2007). However, volcanic glass has a characteristically depleted isotopic signature relative to that of diatoms, meaning that even minor contributions can generate significant noise in a diatom series (e.g., Lamb et al., 2007; Brewer et al., 2008; and Table 6.7). It was therefore essential to model and remove glass shard contamination from the Pupuke composite isotope sequence with a geochemical mass balance approach consisting of two stages: (1) micro-XRF assessment of contaminant and sample geochemistry; and (2) use of contaminant and clean diatom geochemistry as end-members in a linear mass-balance mixture model. As before, the product of contaminant abundance by stable isotopic signature is removed from sample composition to yield a downcore record of tephra-free isotope composition.

A detailed methodology for XRF geochemical analysis and mass-balance modelling is available in Brewer et al (2008) and what follows is a brief summary. Prior to XRF geochemical analyses diatom samples were oven dried overnight at 105 °C to remove moisture, weighed into a pre-combusted Pt micro-crucible and combusted at 950 °C. Samples were reweighed for loss-on-ignition (LOI; CO$_2$ and/or H$_2$O content). XRF fusion beads were cast on a Pt-Au disc from 0.1 g of combusted powder and 3.0 g of Li-tetraborate flux in a Pt-Au crucible heated to
1050°C on a blast burner and cooled prior to analysis for major oxides and trace elemental abundance at the University of Leicester (Panalytical Axios advanced X-ray spectrometer). In total, 63 purified samples were analysed for geochemistry (12 trace elements and 11 major oxides). To model volcanic glass contributions, 2 purified basaltic (Rangitoto and AVF8), 2 rhyolitic (Rotoma and Rotoehu) and 1 andesitic tephra (Eg10) recovered from the Pupuke composite sequence were also analysed (e.g., Molloy et al., 2009). The same tephras have been analysed for O-isotope composition although only the Rangitoto, AVF8 and Rotoehu tephra were analysed for Si-isotope composition (Section 6.3.4. Stable Isotope Analysis), necessitating the following assumptions:

(1). Geochemistry of the 5 analysed tephra is indicative of their broader type (e.g., Rangitoto and AVF8 are indicative of the AVF basaltic glass present in Lake Pupuke);

(2). Stable isotope ratios of the analysed tephra are indicative of their broad type.

Differences in the geochemistry of pure diatom and tephra silica enable their abundance to be estimated from a linear relationship between diatom and tephra end members (Brewer et al., 2008). The recommendations of Brewer et al (2008) were followed; the geochemistry of several very clean samples (>98% by light microscopy) offers a clean diatom end member. Those samples whose trace element abundances were in the lower quartile for at least 9 of the 12 elements examined (Rb, Sr, Zr, Nb, Pb, Ga, Zn, Ni, Co, Cr, V and Ba) (n = 3) were selected to represent the uncontaminated diatom end member (sample codes: LF31364, LF 31372 and LF31376). Their corresponding geochemical signatures were averaged across the 12 trace elements and 11 major oxides to yield averaged geochemistry of pure diatom silica (e.g., diatom end member) (Table 6.7).

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; nRhyolite = 2).

<table>
<thead>
<tr>
<th>Indicator</th>
<th>TiO₂ (wt. %)</th>
<th>Fe₂O₃ (wt. %)</th>
<th>MgO (wt. %)</th>
<th>K₂O (wt. %)</th>
<th>Ba (ppm)</th>
<th>Rb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatom End Member</td>
<td>0.38 (0.10)</td>
<td>1.13 (0.18)</td>
<td>0.25 (0.15)</td>
<td>0.05 (0.02)</td>
<td>45.91 (2.89)</td>
<td>36.89 (4.79)</td>
</tr>
<tr>
<td>Basalt End Member</td>
<td>3.12 (0.17)</td>
<td>11.75 (0.48)</td>
<td>3.93 (0.55)</td>
<td>2.14 (0.73)</td>
<td>214.94 (28.42)</td>
<td>14.13 (2.62)</td>
</tr>
<tr>
<td>Rhyolite End Member</td>
<td>0.33 (0.07)</td>
<td>1.84 (0.09)</td>
<td>0.47 (0.08)</td>
<td>2.73 (0.09)</td>
<td>961.36</td>
<td>124.07 (20.14)</td>
</tr>
</tbody>
</table>

Basalt and rhyolite tephra are markedly different in terms of geochemistry, particularly major oxide abundance in which MgO, TiO₂ and Fe₂O₃ are indicative of local basaltic tephra, whereas Al₂O₃, Na₂O and K₂O are indicative of rhyolitic tephra (Table 6.7). To improve contaminant modelling, each has been modelled independently to yield a basaltic and rhyolitic contribution. Note that andesitic tephra possesses a geochemistry intermediate to that of basalt and rhyolite preventing its accurate modelling without significant overlap and duplication of rhyolitic and basaltic contributions. Estimation of contamination is then performed by comparing the abundance of indicator elements – MgO, TiO₂ and Fe₂O₃ (basalt); and K₂O, Ba and Rb (rhyolite) – against the diatom end member geochemical profile. Tephra proportions were calculated as follows:

\[ \% \text{Tephra} = \left( \frac{\text{Sample}_C - \text{Clean}_C}{\text{Tephra}_C} \right) \times 100 \]

(Calculation of relative tephra abundance from sample and end-member geochemistry [Source: Brewer et al., 2008: 325])
where Sample$_C$ is the analysed sample element/oxide abundance, Clean$_C$ is the corresponding element/oxide abundance in the diatom end member and Tephra$_C$ is the element/oxide abundance in basalt or rhyolite end-members (Table 6.7). Percentage contributions are calculated for each of the indicator elements/oxides and averaged (e.g., basalt contribution calculated from average of MgO, TiO$_2$ and Fe$_2$O$_3$ estimates). The estimate of the sample mass contributed by tephra is not an estimate of total sample Oxygen or Silicon contributed by that tephra. For instance, of the basaltic tephra analysed, 43.81% is Oxygen. In rhyolite this rises to 49.02% whilst in pure diatom this is 52.56%. The corresponding values for Silicon are 21.67%, 34.52% and 44.39% in basalt, rhyolite and diatom silica respectively. Therefore, to correct for variable Oxygen and Silicon concentration between contaminant tephras and diatom silica, estimates of basaltic and rhyolitic abundance have been multiplied by a correction factor to account for greater proportion of O and Si in diatom silica: 0.83 and 0.93 for Oxygen contribution (basalt and rhyolite); and 0.49 and 0.77 for Silicon contribution (basalt and rhyolite) (e.g., %O in tephra / %O in diatom; %Si in tephra / %Si in diatom). Corrected estimates of sample Oxygen and Silicon contamination by tephra (rather than mass contamination) are employed to calculate tephra-free $\delta^{18}$O$_{\text{Diatom}}$ and $\delta^{30}$Si$_{\text{Diatom}}$ as follows:

$$
\delta^{18}\text{O}_{\text{Corrected}} = \left( \delta^{18}\text{O}_{\text{Sample}} - (\%\text{Tephra}/100) \times \delta^{18}\text{O}_{\text{Tephra}} \right) / (\%\text{Purity}/100)
$$
$$
\delta^{30}\text{Si}_{\text{Corrected}} = \left( \delta^{30}\text{Si}_{\text{Sample}} - (\%\text{Tephra}/100) \times \delta^{30}\text{Si}_{\text{Tephra}} \right) / (\%\text{Purity}/100)
$$

(Calculation of tephra-free sample isotope signature [Source: Swann and Leng, 2009: 389])

where the base ‘corrected’, ‘sample’ and ‘tephra’ refer to isotopic composition of corrected samples, raw samples and tephra respectively, %Tephra refers to corrected abundance of tephra (%), and %Purity refers to abundance of sample less tephra.

### 6.3.6 Silica Maturity Analysis

Variation in the relative maturity of diatom silica has the capacity to alter downcore isotopic profiles. Thus to exclude changes in maturity from the Pupuke composite sequence, infrared (IR) spectra were determined for Si-O-Si and Si-OH vibration bands at 800 and 950 cm$^{-1}$ respectively with a Siemens FTIR-spectrometer at the University of Auckland. Pupuke core and sediment trap silica samples were mixed with 250 mg KBr in a ratio of 1:250, ground using an agate pestle and mortar to homogenise sample distribution, pressed to a tablet using a stainless steel dye (8 metric tons; 3 minutes) and kept in a dry vacuum chamber to reduce contamination by atmospheric moisture. Spectra were referenced to pure matrix spectra every 10 samples, prior to conversion to absorption spectra. Acquisition times were 10 seconds with 6 repetitions per sample across the 4000-370 cm$^{-1}$ range. Peak areas of IR absorption at 800 and 950 cm$^{-1}$ were calculated by best-fit mixed Gaussian-Lorenz curves in the spectrographic software GRAMS/32. Ratios of 800:950 cm$^{-1}$ absorption were generated in Excel whereby higher values indicate increased silica maturity and lower ratios vice-versa. Importantly, as FTIR analyses have been performed upon non-fluorinated extract, uncertainty also surrounds the impact of prefluorination and removal of the outer exchangeable, least mature silica.
6.4 Results and Interpretation

6.4.1 Diatom Preservation

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 \( \mu m \) from top to bottom rows.
Light and scanning electron microscopy (SEM) revealed the 63 purified sample extracts to be composed largely of intact centric and fractured pennate frustules (Figure 6.13). Importantly, each sample contains varying proportions of different species with the potential for a taxonomic vital effect. In each sample, diatom silica appeared unweathered with little evidence of silica dissolution (e.g., loss of ornate surface architecture) or reprecipitation (e.g., structureless precipitates). SEM analysis also revealed the presence of other sources of biogenic silica, particularly sponge spicules and chrysophyte cysts. Each might possess a varying fractionation factor thereby introducing a vital effect.

SEM analysis also revealed little if any presence of clays in the purified extracts (Figure 6.13). Clays possess a distinct plate-like appearance and are often readily identified (e.g., Morley et al., 2005; Swann and Leng, 2009). Importantly, the absence of clays removes a potentially severe contaminant of diatom isotope series (Brewer et al., 2008). However, SEM analyses revealed the presence of glass shards in nearly all purified samples.

### 6.4.2 Silica Contaminant Profile

Modelled abundance of basaltic glass amongst purified diatom extracts varied from 0-19.87 wt. % with an average abundance of 4.87 ± 3.71 wt. % (μ ± 1σ, n = 63). Modelled rhyolitic abundance varied from 0-28.02 wt. % with an average of 5.03 ± 5.40 wt. % (μ ± 1σ, n = 63). Combined XRF-inferred estimates of tephra abundance varied from 0-30.60 wt. % with an average of 9.71 ± 7.38 wt. % (μ ± 1σ, n = 63). Despite several periods of simultaneous contamination, basalt and rhyolite abundance exhibit dissimilar profiles (r = 0.29, P < 0.01, n = 63) (Figure 6.14). Peaks in basaltic contamination occur at ~7.8 cal. kyr BP (12.03 wt. %) and ~13.5 cal. kyr BP (19.87 wt. %) (Figure 6.14) whilst peak abundance of rhyolite occurs at ~7.8 cal. kyr BP (11.46 wt. %), ~13.0 cal. kyr BP (16.93 wt. %), between ~23.4-24.8 cal. kyr BP (28.02-14.27 wt. %) and at ~27.9 cal. kyr BP (13.45 wt. %). The period ~13-33 cal. kyr BP records a distinct rise in the overall abundance of tephra whilst older and younger sediments display less contamination (Figure 6.14).

Application of O- and Si-correction factors to XRF-inferred tephra abundance yields the same trends in O and Si contamination as above although the overall magnitude of contamination is reduced as basalt and rhyolite contain less O and Si relative to pure diatom silica. Average basaltic O and Si contamination is therefore reduced to ~4.23 and ~2.38 % whilst average rhyolitic O and Si contamination is reduced to ~4.89 and ~3.91 % respectively.

Light microscope counts of tephra are also plotted in Figure 6.14. Comparison of XRF-modelled and light microscope estimates of tephra abundance demonstrate strong correlation (r = 0.42, P < 0.01, n = 63) (Figure 6.14). Sample extracts possessed an average counted diatom content of ~94.1 ± 5.3 % (μ ± 1σ) and tephra abundance of 3.3 ± 3.6 % tephra (μ ± 1σ). Light microscope estimates of tephra are therefore on average ~6.4 % lower than corresponding XRF-estimates. Light microscopy also revealed the presence of sponge spicules whose abundance varies markedly down core from 0-13.3 % with an average of ~2.7 ± 2.8 % (μ ± 1σ).
IRMS-analysis also demonstrated marked variation in basaltic and rhyolitic O- and Si-isotope composition. Basaltic δ^{18}O and δ^{30}Si analysed on Rangitoto and AVF8 averaged 10.81 ± 3.07 ‰ and -0.04 ± 0.10 ‰ respectively (μ ± 1σ). Rhyolitic δ^{18}O and δ^{30}Si analysed on a single tephra (Rotokohu) is more depleted at 8.86 ± 0.95 ‰ and -0.26 ± 0.11 ‰ respectively (μ ± 1σ). The product of corrected O- and Si-contamination and corresponding isotopic signatures yields a basaltic and rhyolitic δ^{18}O and δ^{30}Si contaminant effect. The average basaltic effect is thus -0.46 and -0.002 ‰ whilst the average rhyolitic effect is -0.43 and -0.010 ‰ (δ^{18}O and δ^{30}Si respectively). The actual effect on samples is greater due to the need to correct sample mass to 100% (following removal of tephra mass). Consequently average tephra-free δ^{18}O_{Diatom} and δ^{30}Si_{Diatom} sample values are enriched by 2.84 ‰ and 0.04 ‰ respectively relative to their raw values (see below).

6.4.3 Silica Maturity Profile

Prior to application of the FTIR maturity index to purified sedimentary samples, it was applied to sediment trap samples. Higher and lower index scores record greater and lesser maturity respectively (e.g., greater and lesser condensation of Si-OH to Si-O-Si). Over the period March 2008 until May 2009, silica maturity varied from 0.40 to 0.59 with an average of 0.51 (Table 6.8). Highest values (greatest maturity) were recorded by overturn samples, whilst lower values (lesser maturity) were recorded before and after overturn. Corresponding δ^{18}O_{Diatom} values revealed no significant relationship to maturity (r = -0.25, P > 0.10, n = 4) although a strong negative correlation exists between δ^{30}Si_{Diatom} and maturity index scores (r = -0.66, P < 0.1, n = 4). However, the small number of samples limits the significance of the relationship.

Table 6.8: Sediment trap biogenic silica maturity and stable isotope composition (δ^{18}O_{Diatom} and δ^{30}Si_{Diatom}).

<table>
<thead>
<tr>
<th>Sediment Trap</th>
<th>Silica Maturity</th>
<th>δ^{18}O_{Diatom} (% VSMOW)</th>
<th>δ^{30}Si_{Diatom} (% NBS28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deployment</td>
<td>Collection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15/03/2008</td>
<td>19/06/2008</td>
<td>0.40</td>
<td>26.52</td>
</tr>
<tr>
<td>20/06/2008</td>
<td>08/10/2008</td>
<td>0.56</td>
<td>27.27</td>
</tr>
<tr>
<td>09/10/2008</td>
<td>21/02/2009</td>
<td>0.49</td>
<td>26.79</td>
</tr>
<tr>
<td>22/02/2009</td>
<td>22/07/2009</td>
<td>0.59</td>
<td>25.61</td>
</tr>
</tbody>
</table>

58 purified diatom silica samples yielded sufficient mass for analysis by FTIR to generate maturity index scores (Figure 6.14). Sample maturity scores exhibited a range of 0.84 (minimum = 0.24; maximum = 1.08) with an average of 0.64 ± 0.15 (± 1σ). A trend to decreasing maturity from oldest to youngest samples (~48.2 to 0.1 cal. kyr BP) is apparent although marked variation is also present. For instance, older samples between 43.0 and 48.2 cal. kyr BP were relatively mature (0.97 ± 0.10, n = 4) after which and until ~14.0 cal. kyr BP, maturity index scores decline and remain low (0.63 ± 0.12 [μ ± 1σ, n = 31]). At ~13.6 cal. kyr BP, silica maturity reaches a minimum of 0.24 before rising to 0.47 shortly thereafter (~13.5 cal. kyr BP). Maturity continues to increase until ~11.6 cal. kyr BP (0.99) before declining until ~0.1 cal. kyr BP (0.60 ± 0.08 [μ ± 1σ, n = 19]). Trends in silica maturity do not appear to be driven by abundance of volcanic tephra although a weak correlation exists between XRF-inferred tephra abundance and FTIR maturity scores (r = -0.28, P < 0.025, n = 55).
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 ($r = 0.42$, $R^2 = 0.18$, $P < 0.01$, $n = 63$), 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).
6.4.4 Diatom Oxygen Isotope Profile

63 purified diatom samples were analysed for $\delta^{18}O$ (Figure 6.15). Diatom O-isotopic composition was then corrected for the depletion effect of rhyolitic and basaltic tephra (Figure 6.15). Correcting for the presence of tephra in samples has not substantially altered the trend in $\delta^{18}O_{\text{Diatom}}$ values (Figure 6.15). Three broad periods of change are expressed in uncorrected and tephra-free $\delta^{18}O_{\text{Diatom}}$ series:

1. ~30.5 to 48.2 cal. kyr BP: enriched uncorrected $\delta^{18}O_{\text{Diatom}}$ (36.90 ± 1.26 ‰ [μ ± 1σ, n = 18]) and tephra-free $\delta^{18}O_{\text{Diatom}}$ (39.15 ± 2.06 ‰ [μ ± 1σ, n = 18]).
2. ~19.1 to 28.6 cal. kyr BP: depleted uncorrected $\delta^{18}O_{\text{Diatom}}$ (29.29 ± 2.99 ‰ [μ ± 1σ, n = 14]) and tephra-free $\delta^{18}O_{\text{Diatom}}$ (33.53 ± 4.47 ‰ [μ ± 1σ, n = 14]);
3. ~0.5 to 18.5 cal. kyr BP: enriched uncorrected $\delta^{18}O_{\text{Diatom}}$ (33.94 ± 1.42 ‰ [μ ± 1σ, n = 31]) and tephra-free $\delta^{18}O_{\text{Diatom}}$ (36.50 ± 2.78 ‰ [μ ± 1σ, n = 31]).

Correcting for tephra has however, substantially increased overall variability in $\delta^{18}O_{\text{Diatom}}$. For instance, the uncorrected $\delta^{18}O_{\text{Diatom}}$ series exhibits a range of 15.06 ‰ (maximum = 39.15 ‰ and minimum = 24.09 ‰) whilst the tephra-free $\delta^{18}O_{\text{Diatom}}$ series demonstrated a greater range of 18.79 ‰ (maximum = 45.55 ‰ and minimum = 26.75 ‰). Both uncorrected and tephra-free $\delta^{18}O_{\text{Diatom}}$ series also demonstrate a marked enrichment during Zone 2, between ~23.4 and ~24.3 cal. kyr BP. Thereafter diatom silica is markedly $^{18}O$-depleted between ~24.9 and ~27.1 cal. kyr BP (uncorrected and tephra-free $\delta^{18}O_{\text{Diatom}}$ reaching a series minimum of 24.09 and 26.75 ‰ respectively at ~26.0 cal. kyr BP). Peak tephra-free $\delta^{18}O_{\text{Diatom}}$ enrichment occurs more recently at ~13.5 cal. kyr BP (45.55 ‰). The latter is particularly notable as 6 samples record this isotope excursion over a very narrow temporal envelope (~13.0 to ~14.0 cal. kyr BP). Another older isotope excursion is present in Zone 2 between ~28.6 and 27.1 cal. kyr BP with $\delta^{18}O_{\text{Diatom}}$ values reaching 37.04 ‰ and also bracketed by 6 samples.

Whilst more recent samples (~0.5 to 2.9 cal. kyr BP) do not demonstrate as marked a variation in $\delta^{18}O_{\text{Diatom}}$ as those events at ~13.5 and ~27.6 cal. kyr BP, they capture short-term variability in $\delta^{18}O_{\text{Diatom}}$. A trend to more depleted $\delta^{18}O_{\text{Diatom}}$ is apparent with the most recent sample approaching values expressed in sediment trap diatom silica (~0.5 cal. kyr BP uncorrected and tephra-free $\delta^{18}O_{\text{Diatom}}$ = 30.14 and 31.13 ‰; average sediment trap $\delta^{18}O_{\text{Diatom}}$ = 26.55 ‰). Comparison of the Pupuke composite $\delta^{18}O_{\text{Diatom}}$ series with contemporary $\delta^{18}O_{\text{Diatom}}$ reveals an even greater average enrichment of 7.20 ‰ and 10.05 ‰ expressed in the raw and tephra-free $\delta^{18}O_{\text{Diatom}}$ sedimentary record. Even the most depleted tephra-free $\delta^{18}O_{\text{Diatom}}$ value (26.75 ‰) is more enriched than contemporary diatom silica suggesting the presence of a marked post-depositional taphonomic effect or recent substantial change in basin isotope hydrology.
Figure 6.15: Raw and modelled tephra-free $\delta^{18}$O$_{Diatom}$ 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 $\delta^{18}$O$_{Diatom}$ signatures (~30.5 to 48.2 cal. kyr BP). Basalt and rhyolitic tephra is depleted in $\delta^{18}$O hence modelled tephra-free signatures are relatively enriched over uncorrected $\delta^{18}$O$_{Diatom}$. 
6.4.5 Diatom Silicon Isotope Profile

23 purified diatom samples were analysed for $\delta^{30}$Si$_{\text{Diatom}}$. $^{30}$Si/$^{29}$Si ratios ranged from 1.49 to 3.15 with an average of 2.02 ± 0.34 (μ ± 1σ, n = 23). Two samples record particularly high isotope ratios (~1.7 cal. kyr BP: 2.71; ~14.0 cal. kyr BP: 3.15). Kinetic fractionation can vary in response to changing species bonded to the isotopes of interest (e.g., in response to different sources of silica) (Young et al., 2002). The presence of tephra can therefore significantly alter the $^{30}$Si/$^{29}$Si ratio. Although both samples are in proximity to macroscopic tephra (Taupo, ~1.7 cal. kyr BP; Waiohau, ~13.6 cal. kyr BP), XRF-inferred tephra abundances (0 and 20.7 % respectively) suggest only the latter sample could have attained an unusual $^{30}$Si/$^{29}$Si ratio through inclusion of tephra. As tephra $^{30}$Si effects have been modelled and removed we have included this sample within the composite $^{30}$Si$_{\text{Diatom}}$ series. The uncontaminated younger sample is, however, likely to be highly erroneous because the deviation from a 2:1 ratio of $^{30}$Si/$^{29}$Si ratio has not been driven by tephra inclusion and has therefore been excluded from further interpretation.

The 22 $^{30}$Si$_{\text{Diatom}}$ samples are plotted in Figure 6.16. Uncorrected sample $^{30}$Si$_{\text{Diatom}}$ signatures ranged 0.73 ‰ (minimum = -0.08 ‰ and maximum = +0.65 ‰) and averaged +0.40 ± 0.17 ‰ (μ ± 1σ, n = 22). Combined XRF-inferred tephra abundance offers little correlation to raw $^{30}$Si$_{\text{Diatom}}$ scores (r = 0.09, P > 0.1, n = 22) and removal of the modelled tephra effect led to an average enrichment of sample $^{30}$Si$_{\text{Diatom}}$ by 0.04 ± 0.05 ‰ (μ ± 1σ, n = 22). Tephra-free modelled $^{30}$Si$_{\text{Diatom}}$ signatures varied 0.81 ‰ (minimum = -0.05 ‰ and maximum = 0.76 ‰) with an average of 0.44 ± 0.20 ‰ (μ ± 1σ, n = 22). Modelling for tephra-contamination has not altered the overall trends in $^{30}$Si$_{\text{Diatom}}$ (Figure 6.16). Three broad periods of change apparent:

1. ~18.5 to 48.2 cal. kyr BP: enriched uncorrected $^{30}$Si$_{\text{Diatom}}$ (0.48 ± 0.08 ‰ [μ ± 1σ, n = 11]) and tephra-free $^{30}$Si$_{\text{Diatom}}$ (0.54 ± 0.10 ‰ [μ ± 1σ, n = 11])
2. ~9.4 to 14.0 cal. kyr BP: depleted uncorrected $^{30}$Si$_{\text{Diatom}}$ (0.16 ± 0.26 ‰ [μ ± 1σ, n = 4]) and tephra-free $^{30}$Si$_{\text{Diatom}}$ (0.19 ± 0.26 ‰ [μ ± 1σ, n = 4])
3. ~0.6 to 5.0 cal. kyr BP: enriched uncorrected $^{30}$Si$_{\text{Diatom}}$ (0.39 ± 0.15 ‰ [μ ± 1σ, n = 7]) and tephra-free $^{30}$Si$_{\text{Diatom}}$ (0.41 ± 0.15 ‰ [μ ± 1σ, n = 7])

A notable feature of Figure 6.16 is a brief period of $^{30}$Si$_{\text{Diatom}}$ enrichment at ~13.6 cal. kyr BP coincident with enrichment of $^{18}$O$_{\text{Diatom}}$. However, comparison of $^{30}$Si$_{\text{Diatom}}$ and $^{18}$O$_{\text{Diatom}}$ reveals little correlation ($r_{^{18}O^{30}Si} = 0.07$, P >0.1, n = 22) suggesting different drivers of change in lake water $^{18}$O and $^{30}$Si composition. Accordingly, zonal boundaries in $^{30}$Si$_{\text{Diatom}}$ are markedly different to $^{18}$O$_{\text{Diatom}}$ (refer to Figures 6.15 and 6.16). Unlike for $^{18}$O$_{\text{Diatom}}$, the $^{30}$Si signatures of contemporary diatom silica (0.27 ± 0.14 ‰ [μ ± 1σ, n = 4]) approach those of the raw and tephra-free downcore $^{30}$Si$_{\text{Diatom}}$ series ($^{30}$Si$_{\text{Diatom}}$ ~0.6 cal. kyr BP = 0.24 and 0.27 ‰ [uncorrected and tephra-free]). However, like $^{18}$O$_{\text{Diatom}}$, a trend is also evident to more depleted modern values (refer to Figure 6.16).
Figure 6.16: Uncorrected (raw) and tephra-free (corrected) $\delta^{30}$Si$_{Diatom}$ 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 $\delta^{30}$Si$_{Diatom}$ signatures (~18.5 to 48.2 cal. kyr BP). Downcore $^{30}$Si/$^{29}$Si ratio scores are also presented for 23 samples analysed for $\delta^{30}$Si$_{Diatom}$ and $\delta^{29}$Si$_{Diatom}$ (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 $^{30}$Si/$^{29}$Si ratio, whilst another at ~14.0 cal. kyr BP has been included because the tephra-contaminant effect has been modelled and removed from $\delta^{30}$Si$_{Diatom}$. 

Chapter Six
6.5 Discussion

Diatom stable isotope paleolimnology is increasingly focussed on improving methodological approaches because of the often minor changes in isotopic composition recorded by a paleolimnological series (Swann and Leng, 2009). Four factors can introduce variation in diatom stable isotopic composition beyond changing environment: (1) contamination; (2) diatom dissolution; (3) non-vital contaminant effects (e.g., temporal variation in silica maturity); and (4) vital contaminant effects (e.g., temporal variations in diatom community structure) (Leng and Barker, 2006). Contamination by O- and Si-containing particulates has been carefully minimised by application of chemical and physical separation procedures (e.g., oxidising reagents, sieving and SPLITT fractionation). The moderate but significant correlation between visual estimates of tephra abundance and total XRF-inferred tephra abundance is reassuring because tephra and diatoms occupied a similar range of sizes (<20 μm) and densities (e.g., failure to separate tephra by density flotation) thereby reducing the potential for changing size or density of tephra to obscure any link between counts (which lack estimates of volume and density) and XRF-inferred mass contamination (rXRF,Light = 0.42, P < 0.01, n = 63). Nevertheless, the XRF modelling approach is liable to error in two ways: (1) failure to remove the outer exchangeable hydroxyl layer prior to analysis (an artefact of the technical difficulty of removing this microscopic boundary layer); and (2) the minor abundance of trace and major oxide indicators of rhyolite within basaltic end-members, and vice versa thereby incorporating some duplication of tephra abundance when modelling rhyolite and basalt contributions separately. The mass balanced, purely biogenic isotope sequence is thus likely to be a conservative estimate of the true tephra-free sample isotopic composition. Accordingly, uncorrected and tephra-free δ18ODiatom and δ30SiDiatom are used to more accurately infer changes to paleohydrology and mixing in Lake Pupuke during the last ~48 kyrs.

Although the present rate of diatom dissolution is unknown at Lake Pupuke, it is a significant process within lake and marine water columns which continues even in sediment pore waters (e.g., Carter and Colman, 1994; Ryves et al., 2003). However, laboratory experimentation with dissolution of diatom silica under varying pH demonstrated no significant enrichment of δ18ODiatom in waters <9.0 pH. Diatom-inferred pH (DI-pH) reconstructions suggest limited variation in pH at Pupuke above 7.82 (~44.0 cal. kyr BP to today) whilst present limnology suggests that benthic pH is typically lower than that of surface water (Section 5.3.4.4. Diatom Transfer Function Results). Support for a weakly acidic to alkaline pH characterising benthic conditions during the last ~44 kyrs can be gathered from the absence of marked dissolution in SEM sample micrographs (Figure 6.13). It is therefore highly unlikely that core samples have been subject to marked dissolution of diatom silica. Furthermore, the magnitude of down core variation in δ18ODiatom (15.06 and 18.79 ‰ [uncorrected and tephra-free]) limits error attributable to dissolution of BSi. The poor understanding of the effects of dissolution on δ30SiDiatom requires further research and stresses the need for caution when inferring paleolimnological changes from this proxy.
6.5.1 Error and Uncertainty in Contaminant Mixture Models

Assessment of the contaminant model performance is difficult between samples because each has been prepared through a unique methodology (e.g., varying stages of SPLITT-fractionation, varying flow rates). Likewise, grain size, solubility and density of each tephra as well as disturbance (e.g., mixing, current scour, wave activity) experienced in the composite sequence ensure no two tephra are identical in terms of their physical characteristics or post-depositional environment. For instance, there is no apparent relationship between tephra thickness or distance from a sample, and the corresponding estimate of sample contamination (Figure 6.17). Hence other depositional mechanisms must be important in determining the tephra content of any single sediment sample including the potential for sub-macroscopic (<1 mm) cryptotephra to exist throughout the composite sequence (Geer, PhD thesis, in prep.). Accordingly, it is not possible to reliably determine whether the geochemical model has successfully recorded the mass of tephra contamination contributed to each isotope sample.

![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)
Despite a significant positive correlation between XRF and light microscope estimates of tephra abundance ($r = 0.42$, $P < 0.01$, $n = 63$), XRF-inferred estimates of tephra contribution exceed counted abundance in all but 9 of the 63 samples, with an average residual of $+6.06 \pm 6.77\%$ ($\pm 1\sigma$, $\%_{\text{XRF}} - \%_{\text{Counted}}$). Disagreements with light microscope counts are expected as the latter fail to account for variable volume or density between diatom frustules and tephra. Nevertheless, sieving samples to <20 μm as well as a subsequent use of SPLITT fractionation in which density is a critical determinant, reduces the potential for changes in size or density to explain observed underestimation by light microscopy. Furthermore, diatom frustules occupied a range of sizes up to ~20 μm in all samples and were poorly distinguished by density in earlier attempts to float tephra contaminants from diatom frustules at densities of ~1.9-2.3 s.g. A possible mechanism to explain XRF overestimation is duplication of tephra abundance when modelling rhyolite and basalt separately. This has undoubtedly occurred as minor amounts of rhyolitic indicator major oxides and trace elements were present in basaltic tephra (AVF 8 and 24), and vice versa in rhyolitic tephra (Rotoehu and Rotoma). Consequently, it is likely that mass-balanced contributions of volcanic glass represent overestimates of contaminant abundance, particularly in those samples whose contaminant tephra exhibits a geochemistry similar to both rhyolitic and basaltic end members. Hence, tephra encountered in the Pupuke composite sequence vary markedly in their geochemistry (Molloy et al., 2009) so that it can be hard to distinguish rhyolitic or basaltic input by a fixed abundance of a major oxide or trace element. This point is exemplified by the lack of a significant correlation between geochemical indicators of basaltic tephra abundance (Table 6.9). Greater agreement between rhyolitic geochemical indicators enables combined XRF estimates of tephra to be significantly correlated with light microscope counts. Hence a significant draw-back to adopting XRF-mass balance models of contaminants is the requirement that contaminant geochemistry is relatively stable and very well captured by end-member geochemistry employed in subsequent modelling (Brewer et al., 2008). In particular, a fixed geochemistry of the diatom end member assumes no changes occur to the geochemistry of pure diatom silica throughout a paleolimnological series. Whilst no studies have explored whether the trace element geochemistry of diatom silica varies with changing lacustrine or marine hydrochemistry, it is feasible that the abundance of trace elements within diatom silica will vary with paleolimnological changes to hydrochemistry (e.g., with changes to pH or solubility during growth and later during deposition). Choosing a single estimate of pure diatom silica geochemistry can therefore lead to over-estimation of contaminant contribution when those elements or major oxides indicative of contamination become more readily available as dissolved forms and if these are incorporated into diatom silica. Further work is needed to establish whether the geochemistry of diatom silica varies in response to changing hydrochemistry to ensure that mass balance corrections can accurately model contaminant abundance.

Table 6.9: Correlation matrix of inferred tephra abundance between individual geochemical indicators within rhyolite and basalt.

<table>
<thead>
<tr>
<th>Correlation Matrix</th>
<th>Basaltic Glass Abundance ($n = 63$)</th>
<th>Rhyolitic Glass Abundance ($n = 63$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$MgO$</td>
<td>$TiO_2$</td>
</tr>
<tr>
<td>$MgO$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$TiO_2$</td>
<td>0.10</td>
<td>1</td>
</tr>
<tr>
<td>$Fe_2O_3$</td>
<td>0.11</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Despite a potential for contaminant over-estimation, correction for tephra content in Pupuke core samples has not greatly altered the trends present in $\delta^{18}O_{\text{Diatom}}$ or $\delta^{30}Si_{\text{Diatom}}$ (Figure 6.18). This reflects the fact that downcore $\delta^{18}O_{\text{Diatom}}$ undergoes considerable fractionation (15.06 and 18.79 ‰ [uncorrected and tephra-free]) thereby preventing changes in contamination dominating inferred paleoenvironmental responses, and $\delta^{30}Si_{\text{Diatom}}$ undergoes little change due to tephra contamination.

6.5.2 Silica Maturation Effects

The impacts of post-depositional changes in silica maturity upon $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ are largely unknown (Swann et al., 2008, 2010). Although, contemporary samples exhibit a weak and insignificant negative correlation between FTIR-inferred maturity and corresponding $\delta^{18}O_{\text{Diatom}}$ ($r_{\text{Maturity,} \delta^{18}O} = -0.25, P > 0.01, n = 4$) and a stronger but also insignificant correlation with $\delta^{30}Si_{\text{Diatom}}$ ($r_{\text{Maturity,} \delta^{30}Si} = -0.66, P > 0.01, n = 4$), several studies have identified that silica maturation during sedimentation and burial can generate enrichment of $\delta^{18}O_{\text{Diatom}}$ by up to ~10 ‰ (Schmidt et al., 1997, 2001; Brandriss et al., 1998; Moschen et al., 2006). Moschen et al (2006) further suggested that an exponential increase in silica maturity is likely over time assuming a gradual loss of protective organic coatings and similar pore-water conditions over the sedimentary record. Examination of the tephra-free composite $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ downcore series demonstrates little similarity to changing maturity ($r_{\text{Maturity,} \delta^{18}O} = 0.29, P > 0.01, n = 55$; $r_{\text{Maturity,} \delta^{30}Si} = 0.36, P > 0.01, n = 20$). Little correlation is also demonstrated in uncorrected $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ ($r_{\text{Maturity,} \delta^{18}O} = 0.39, P < 0.01, n = 55$; $r_{\text{Maturity,} \delta^{30}Si} = 0.39, P > 0.01, n = 20$). The exponential increase in silica maturity proposed by Moschen et al (2006) is not evident in FTIR-inferred maturity (Figure 6.18). This might reflect changes in the rate of sedimentation over the Pupuke composite sequence with rapid and slower sedimentation leading to lesser and greater reduction of Si-OH respectively (Moschen et al., 2006). However, contemporary Lake Pupuke samples suggest the inverse – most mature diatom silica occurs during overturn (rapid sedimentation) and least mature during stratification (slower sedimentation through a developed thermocline) (refer to Table 6.8). However, the limited number of contemporary samples ($n = 4$) preclude evaluation of the causes of greater and lesser maturity. Nevertheless, the absence of a significant maturity associated effect in downcore isotope signatures confirms that $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ can be successfully employed to reconstruct aspects of the paleolimnology at Lake Pupuke. Based on the many reviews that cite observed trends between contemporary diatom isotope signatures and corresponding water chemistry as well as between paleo-$\delta^{18}O_{\text{Diatom}}$ series and other $\delta^{18}O$/proxy data in multi-proxy investigations (e.g., Leng and Barker, 2006; Tyler et al., 2008; Swann and Leng, 2009; Swann et al., 2010), it is reasonable to exclude changes in maturity as a cause of downcore variation in $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}Si_{\text{Diatom}}$ within the Pupuke composite sequence.
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.
6.5.3 Taxonomic Vital Effects

Changes in diatom community structure might be capable of altering diatom isotopic composition (Moschen et al., 2005). For instance, variable fractionation rates between diatom taxa could elicit changes to sedimentary $\delta^{18}$O$_{\text{Diatom}}$ or $\delta^{30}$Si$_{\text{Diatom}}$ by community structural change under homogenous paleoenvironmental conditions (Leng and Barker, 2006). Despite the importance taxonomic changes might have on paleolimnological studies, little research has been conducted into the existence of a taxonomic vital effect, of which only one has demonstrated an effect greater than analytical uncertainty within fluorination approaches (Brandriss et al., 1998), who demonstrated a vital effect of 0.6 ‰ ($\delta^{18}$O$_{\text{Diatom}}$) between two cultured diatom species. Accordingly, to be able to present a robust paleolimnological record from the Pupuke composite isotope sequence, changes in diatom community structure must be examined downcore. High-resolution diatom taxonomic analysis has already been undertaken on the Pupuke composite sequence. Although SPLITT-fractionation of composite sediment might have preferentially biased purified diatom extracts to smaller (<20 μm) diatom taxa, the continued dominance of small, centric diatoms (e.g., *Aulacoseira granulata* var. *ambigua*, *Discotella stelligera*, *Staurosira microstriata*) over the last ~44 kyrs likely limits variation between taxonomic and SPLITT purified diatom taxonomy. Accordingly diatom taxonomic changes have been interpolated by simple linear regression to isotope composite sample depths (Figure 6.19).

Correlation analyses revealed no significant trend between composite $\delta^{18}$O$_{\text{Diatom}}$ or $\delta^{30}$Si$_{\text{Diatom}}$ and either habitat preference (e.g., planktic, facultative planktic, tychoplanktic, benthic, aerophilic) or dominant taxon (e.g., *A. granulata* var. *ambigua*, *D. stelligera*, *S. microstriata*) (Table 6.10). Although interpolation between diatom taxonomic and isotopic samples will have failed to capture some rapid species turnover, earlier taxonomic investigations demonstrated limited variation about the dominance of *D. stelligera* until ~22.5 cal. kyr BP and thereafter *S. microstriata* until ~8.2 cal. kyr BP (Section 5.3.3. Diversity). Increased species turnover only occurs during the last ~8.2 kyrs (Figure 6.19). Thus only mid-to-late Holocene samples are likely to have experienced rapid changes in community structure, conferring older interpolated estimates of diatom abundance greater reliability. The absence of a significant correlation between dominant taxa or habitat preference suggests the absence of either a taxonomic or habitat vital effect governing changes in the downcore composite isotope series, particularly before ~8.2 cal. kyr BP. This is also supported by recent reviews of diatom isotope paleolimnology which stress the lack of a taxonomic or size-related effect in experimental cultures and sediment trap samples (Binz, 1987; Brandriss et al., 1998; Moschen et al., 2005; Cardinal et al., 2007; Schiff et al., 2009). Given the likelihood of limited if any taxonomic or habitat-specific vital effect and the magnitude of downcore variation (~15.06 and 18.79 ‰ [uncorrected and tephra-free]), the composite $\delta^{18}$O$_{\text{Diatom}}$ sequence is likely to offer an accurate record of changes to water chemistry.
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 ($\delta^{30}$Si) 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 $\delta^{30}$Si 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 $\delta^{30}$Si.
The lower magnitude of changes observed in $\delta^{30}\text{Si}_{\text{Diatom}}$ (~0.73 and 0.81 ‰ [uncorrected and tephra-free]) and paucity of research into taxonomic vital effects adds more uncertainty to its interpretation, although a lack of significant ($P < 0.01$) changes to dominant diatom flora or habitat preference also confers greater reliability that composite $\delta^{30}\text{Si}_{\text{Diatom}}$ signatures record changes to DSi availability and uptake during the last ~48 kyrs (Table 6.10). A greater, positive correlation to $A$. granulata var. ambiguа ($r_{A.granulata,\delta^{30}\text{Si}} = 0.42$, $P > 0.01$, $n = 22$) likely reflects the greater nutrient demands associated with intense stratification that in turn favour this taxon. Rapid growth during overturn (July to August) would place greater demand upon DSi thereby favouring enrichment (e.g., greater abundance of $A$. granulata var. ambiguа coincides with more enriched $\delta^{30}\text{Si}_{\text{Diatom}}$ indicative of stronger thermal stratification).

Table 6.10: Correlation coefficients between $\delta^{18}\text{O}_{\text{Diatom}}$ 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>
<thead>
<tr>
<th>Correlation Matrix</th>
<th>$\delta^{18}\text{O}_{\text{Diatom}}$ ($n = 60$)</th>
<th>$\delta^{30}\text{Si}_{\text{Diatom}}$ ($n = 22$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shannon-Weiner (Alpha diversity)</td>
<td>-0.037</td>
<td>-0.102</td>
</tr>
<tr>
<td>Hoagland Similarity Index (Beta diversity)</td>
<td>0.122</td>
<td>0.180</td>
</tr>
<tr>
<td>Planktic</td>
<td>0.016</td>
<td>0.390</td>
</tr>
<tr>
<td>Facultative Planktic</td>
<td>-0.188</td>
<td>-0.212</td>
</tr>
<tr>
<td>Tychoplanktic</td>
<td>0.146</td>
<td>-0.363</td>
</tr>
<tr>
<td>Benthic</td>
<td>-0.082</td>
<td>0.082</td>
</tr>
<tr>
<td>Aerophilic</td>
<td>-0.281</td>
<td>0.200</td>
</tr>
<tr>
<td>$A$. granulata var. ambiguа</td>
<td>-0.188</td>
<td>0.416</td>
</tr>
<tr>
<td>$D$. stelligera</td>
<td>-0.003</td>
<td>-0.213</td>
</tr>
<tr>
<td>$S$. microstriata</td>
<td>0.130</td>
<td>-0.299</td>
</tr>
</tbody>
</table>

6.5.4 Paleoenvironmental Reconstruction

6.5.4.1 Lacustrine Residence Time, Total and Effective Precipitation ($\delta^{18}\text{O}_{\text{Diatom}}$)

The Oxygen stable isotope composition of diatom silica precipitated in equilibrium with lakewater, is governed by a thermodynamic mass-dependent fractionation (Leng et al., 2009). Although the precise nature of the latter is debated, a thermal coefficient of $\sim-0.2 \%\text{o}/^\circ\text{C}$ is believed to be systematic across freshwater diatom taxa. In Lake Pupuke however, any thermodynamic relationship is likely to be hidden amongst more marked changes in $\delta^{18}\text{O}_{\text{Lake}}$ driven by the balance between isotopic composition of inputs (precipitation temperature, source and amount effects) and outputs (evaporative enrichment and groundwater loss). Despite its mid-latitude location, Lake Pupuke exhibits marked evaporative enrichment of $\sim+6.15 \%\text{o}$ on amount-weighted annual precipitation (e.g., $\delta^{18}\text{O}_{\text{Lake}} - \delta^{18}\text{O}_{\text{Precipitation}}$). Although a significant thermal relationship exists in $\delta^{18}\text{O}_{\text{Precipitation}}$ (+0.4 $\%\text{o}/^\circ\text{C}$) the effect of changes in temperature are likely to be markedly altered by changes in effective precipitation as evaporation from the lake surface is the dominant mechanism of changes to $\delta^{18}\text{O}_{\text{Lake}}$. More depleted $\delta^{18}\text{O}_{\text{Diatom}}$ values correspond to shorter lake residence times and reduced capacity to accumulate evaporative effects, whilst greater values represent a deeper lake whose longer residence time enables $\delta^{18}\text{O}_{\text{Lake}}$ to enrich far beyond $\delta^{18}\text{O}_{\text{Precipitation}}$. Whilst this prevents the composite $\delta^{18}\text{O}_{\text{Diatom}}$ record from responding directly to changes in temperature, the greater magnitude of changes in $\delta^{18}\text{O}_{\text{Lake}}$ associated with a closed basin lake, reduce the impacts of changes in source water or the balance of multiple sources upon the downcore isotope series.
Without a dissolution, maturity, habitat or taxonomic vital effect, the composite δ¹⁸O_Diatom sequence provides a record of changes in effective precipitation, particularly as groundwater outflow effectively ceases when lake levels decline by ~1 m on present levels isolating inputs and outputs to precipitation and evaporation alone (Salter et al., 2005). The composite δ¹⁸O_Diatom record therefore records changes to: (1) residence time (e.g., a positive relationship with greater residence time equating to greater enrichment from δ¹⁸O_Precipitation); and (2) effective precipitation (e.g., greater and lesser relative evaporation will enrich and deplete δ¹⁸O_Lake respectively).

The composite δ¹⁸O_Diatom sequence displays a range of ~15.06 and 18.79 ‰ (uncorrected and tephra-free). A thermal coefficient of ~+0.2 ‰/ºC in diatoms (Brandriss et al., 1998) and ~+0.4 ‰/ºC in local precipitation (Section 6.2.2.3. Thermal (‘Dansgaard’) and Amount Relationship in δ¹⁸O_Precipitation) yields a combined thermal coefficient of ~+0.2 ‰/ºC (e.g., -0.2 + 0.4 = +0.2). Thus if changes in downcore δ¹⁸O_Diatom were solely the result of temperature change, over ~75 and 93 ºC has occurred during the last ~48 kyrs at Lake Pupuke in uncorrected and tephra-free isotope series respectively (e.g., 15.06/0.2 = 75 and 18.79/0.2 = 93). This is therefore conclusive evidence that the Oxygen isotope cycle within Lake Pupuke is governed by changes in effective precipitation, swamping any thermodynamic relationship in δ¹⁸O_Diatom.

Inspection of the uncorrected and tephra-free composite δ¹⁸O_Diatom record reveals three periods of marked change to residence time at Pupuke: (3) high residence time from ~0.5 to 18.5 cal. kyr BP; (2) lesser residence time from ~18.5 to 28.6 cal. kyr BP; and (1) a return to greater residence time from ~28.6 to 48.2 cal. kyr BP (Figure 6.20). These boundaries align well with published data on variations to effective precipitation within the Northern North Island (NNI) of New Zealand, particularly the overlap of Zone 2 with the Last Glacial Coldest Period (LGCP; ~28.5 to 18.5 cal. kyr BP [Alloway et al., 2007]), an interval of lower effective precipitation than either the earlier Moerangi interstadial during Marine Oxygen Isotope Stage (MIS) 3 or the return of interglacial conditions during MIS 1 (post-18.5 cal. kyr BP). Although unusual, the greater enrichment of composite δ¹⁸O_Diatom signatures in Zone 1 can be explained by the greater effective precipitation (~85% wetter [Ogden et al., 1993]) and mild (~2-3 ºC cooler [Ogden et al., 1993]) conditions associated with MIS 3 in the NNI (e.g., Newnham, 1999; Newnham et al., 2007a). Relatively cool and wet conditions would favour a deeper water column whose greater lake residence time would permit greater evaporative enrichment of δ¹⁸O_Lake and hence δ¹⁸O_Diatom beyond δ¹⁸O_Precipitation. For instance, the present lake residence time of ~30 yrs has enabled the δ¹⁸O_Lake composition of Lake Pupuke to become enriched by ~6.15 ‰ on the amount-weighted mean regional precipitation. That δ¹⁸O_Diatom during MIS 3 is more enriched than during either MIS 2 or 1 suggests a deep lake coupled to longer residence time. This hypothesis is supported by the observation that any increase in precipitation amount, necessary to the formation of a deeper lake, would include an amount effect as greater volumes of precipitation tend to be associated with a depletion of δ¹⁸O_Precipitation (Clark and Fritz, 1997). Thus to retain an enriched δ¹⁸O_Lake signature during a particularly wet, cool period would necessitate marked increases in residence time and a greater capacity to accumulate evaporative enrichment effects. Furthermore, the limited variation of δ¹⁸O_Diatom in Zone 1 (± 1.26 and 2.06 ‰ [1σ uncorrected and tephra-free]) suggests a relatively stable paleohydrological regime (refer to Figure 6.20). Particularly stable and taxonomically similar diatom
communities throughout much of this interval, as well as dominance by open-water planktic taxa (e.g., *Discotella stelligera*, *Cyclotella* cf. *planctonica*), support the inference of limited hydrological change (Figure 6.20). Overall diatom productivity during this period is high and might therefore reflect the greater availability of open-water habitat as well as the likely increase in supply of nutrients leached from surrounding catchment under a wetter, mild climate (Figure 6.20).

A transition to drier paleoclimate is indicated by relatively depleted $\delta^{18}O_{\text{Diatom}}$ between ~30.5 and 28.6 cal. kyr BP. Low sampling resolution precludes a more precise delineation of the onset of reduced residence time during MIS 2. However, coincident changes to diatom taxonomy (e.g., rise in aerophilic taxa), physical sediment characteristics (e.g., increased grain size) and geochemical changes (e.g., lower TS-concentration and flux, more enriched bulk sediment $\delta^{13}C$) suggest onset of the LGCP at ~28.5-29.0 cal. kyr BP (Figure 6.20). As geochemical, physical and ecological proxy indicators each suggest shallowing, a corresponding decline in effective precipitation at Lake Pupuke is likely. The LGCP corresponds to an exchange of *Agathis australis*-dominated forest (warm) for *Nothofagus truncata* (cold) (Newnham, 1992; Newnham et al., 1993; Ogden et al., 1993). Compared to today, a corresponding decline of ~4-5 ºC in annual average temperatures within the NNI is not sufficient to explain the palynological observations and instead a response to declining effective precipitation between ~29.0 and 18.5 cal. kyr BP has been inferred by Newnham (1999) and Alloway et al (2007).

Three periods of particularly depleted $\delta^{18}O_{\text{Diatom}}$ occur in Zone 2, from ~28.5 to 27.9 cal. kyr BP, ~27.0 to 24.9 cal. kyr BP and from ~21.7 to 19.1 cal. kyr BP. Each represents a period of reduced residence time and evaporative enrichment (e.g., shallowest lake stand). Importantly, correcting for tephra-contamination has not altered the trends to depleted $\delta^{18}O_{\text{Diatom}}$ signatures although absolute values during intervening periods of relative enrichment are markedly greater in tephra-free samples. Coincident reductions in biological productivity between ~27.8 and 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP suggest that the LGCP reductions in $\delta^{18}O_{\text{Diatom}}$ support a decline in effective precipitation amidst a cooler, drier climate which in turn reduced biological productivity. Palynological investigations of the Auckland region record an increase in wildfire frequency during the LGCP accompanied by a reduction in tall tree abundance (Sandiford et al., 2002, 2003; Newnham et al., 2007a; Augustinus et al., 2010). Indeed the late LGCP (~22.5 to 19.0 cal. kyr BP) is associated with expansion of Poaceae and Asteraceae representing a likely maximum extent of glacial cooling coincident with a marked decline in $\delta^{18}O_{\text{Diatom}}$ compared to early LGCP conditions (Figure 6.20) (Newnham, 1999). Importantly, the lower temperatures during the LGCP in New Zealand would have resulted in reduced evaporation, necessitating a marked decline in precipitation to explain the depletion of $\delta^{18}O_{\text{Diatom}}$. With lower precipitation, any changes to moisture source region or the $\delta^{18}O$ of source water would not readily become expressed meaning these cannot explain the marked variation in $\delta^{18}O_{\text{Diatom}}$ and support the likelihood that the Pupuke composite isotope sequence preserves a record of changes to overall and effective precipitation. The Pupuke $\delta^{18}O_{\text{Diatom}}$ record thereby corroborates paleoenvironmental evidence from Northland of a drier (~65% less precipitation on today [Elliot et al., 2005]) and cooler climate (~4-5 ºC on today [Newnham et al., 2004; Elliot et al., 2005]) during the LGCP, albeit a variable cooler and drier paleoclimate (e.g., Newnham, 1992; Elliott, 2001; Sandiford et al., 2002).
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 (3) greater (~18.5 cal. kyr BP to today), (2) reduced (~28.6 to 18.5 cal. kyr BP) and (1) greater effective precipitation are recorded (~48.2 to 28.6 cal. kyr BP). Zone 3 corresponds to the Holocene and Last Glacial Interglacial Transition (LGIT), Zone 2 the Last Glacial Coldest Period (LGCP) and Zone 1 the earlier Moerangi Interstadial (MIS 1, 2 and 3 respectively). Zone 1 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.
The return to increased total and effective precipitation characteristic of Termination 1 and the onset of MIS 1 is recorded by a return to enriched δ18O_Diatom signatures between ~19.1 and 18.5 cal. kyr BP. Coeval changes to geochemical and physical indicators also imply an onset of warming and a return to greater total precipitation through greater productivity from ~18.5 cal. kyr BP (Figure 6.20). Similarly, declining abundance of aerophilous diatom taxa and increased abundance of tychoplanktic diatoms support a return to higher lake level and longer residence time (refer to Figure 6.20). Warming associated with the onset of MIS 1 would likely have caused enrichment of δ18O_Precipitation (at source) thereby accentuating any increase in cumulative evaporative enrichment. However, the magnitude of isotope change between Zones 3 and 2 (~7.61 and 5.52‰ [uncorrected and tephra-free]) would require an unrealistic temperature rise of ~38 and 28 °C respectively, stressing the continued dominance of evaporative effects upon the Last Glacial Interglacial Transition (LGIT) and Holocene δ18O_Diatom stratigraphy. Marked variation about the uncorrected and tephra-free zonal average δ18O_Diatom signature indicates variable paleohydrology at Lake Pupuke including an initial rise in δ18O_Diatom at ~18.5 cal. kyr BP indicative of particularly wet, warm conditions favouring both high rates of evaporation but also sufficient lake volume to accumulate greater evaporative effects. A similar event occurs during a phase of reduced clastic influx and markedly greater biological productivity between ~14.0 and 13.0 cal. kyr BP (refer to Figure 6.20). Lower δ18O_Diatom values prior to this mid-LGIT peak in productivity also correspond to heightened clastic influx and erosion at ~14.0 cal. kyr BP which implies marked cooling and reduced evaporation prior to a mid-LGIT peak in δ18O_Diatom.

The mid-to-late Holocene δ18O_Diatom series records greater enrichment prior to ~7.6 cal. kyr BP reinforcing earlier inferences of a particularly wet and mild Early Holocene Warm Period, before the onset of drier conditions associated with strengthened westerly and southwesterly circulation from ~5-6 cal. kyr BP (Shulmeister and Lees, 1995; Shulmeister et al., 2001). For instance, declining abundance of the drought-intolerant taxon, Ascarina lucida, has been noted throughout the NNI from ~5-6 cal. kyr BP in line with a shift to particularly dry summers and wet winters (Newnham et al., 1989, 1995; Newnham, 1999; Gomez et al., 2004; Elliot et al., 2005; Newnham et al., 2007a). A subtle enrichment in δ18O_Diatom occurs from ~5.0 cal. kyr BP to today which is coincident with a hydrological regime of thermal stratification. Enrichment likely records the effects of enhanced stratification during diatom growth seasons rather than a simple response to changing residence time alone.

However, the most important isotope feature of the late Holocene is a trend to markedly depleted δ18O_Diatom from ~0.8 cal. kyr BP. Three samples (~0.8, 0.6 and 0.5 cal. kyr BP) record a continued trend of declining δ18O_Diatom. Coeval increases in clastic influx occur within the Pupuke composite sequence from ~0.6-0.8 cal. kyr BP which in the absence of lake level variation were inferred to indicate the arrival of Polynesian migrants (Section 4.5. Discussion).

The absence of marked changes to lake level over the late Holocene is demonstrated by reduced clastic influx until ~0.4 cal. kyr BP, as well as dominantly planktic diatom assemblages and continued reduction of dissolved nitrate and nitrite to ammonia (Section 4.5.4. Change to Mixing and Benthic REDOX and 5.3.3.1. Habitat Preference). Consequently, the depletion of δ18O_Diatom from ~0.8 cal. kyr BP is unlikely to represent a response to
a decreased lake volume (e.g., as occurred during the LGCP). Although tentative, an explanatory hypothesis involves catchment clearance practices undertaken by early Maori communities (e.g., Newnham, 1999) linking depletion in $\delta^{18}O_{\text{Diatom}}$ to anthropogenic activity. Under relatively wet conditions, reduced vegetation cover could increase runoff and result in the heightened erosion observed in the composite sequence. Therein, greater inflow via enhanced runoff could effectively result in a high lake level (as at today) but with relatively lower residence time due to enhanced discharge from the Thorne Bay Springs (e.g., under greater hydraulic head), and a corresponding reduction in the accumulation of evaporative enrichment in $\delta^{18}O_{\text{Lake}}$. For instance, Lamb et al (2002) developed a similar mechanism to explain historic depletion of $\delta^{18}O_{\text{Lake}}$ in Lake Awassa, a closed basin Ethiopian maar crater lake.

6.5.4.2 The Silica Cycle ($\delta^{30}\text{Si}_{\text{Diatom}}$)

In contrast to Oxygen, little is known of Silicon stable isotope cycles within lakes or diatom silica, reflecting its novelty in paleolimnology (Leng et al., 2009). However, the absence of a thermodynamic relationship in $\delta^{30}\text{Si}_{\text{Diatom}}$ ensures that $\delta^{30}\text{Si}_{\text{Diatom}}$ will reflect the availability and source of dissolved Silica (DSi) in much the same way as the $\delta^{13}\text{C}$ content of lacustrine organic matter reflects changes to the availability and sources of dissolved inorganic Carbon (DIC) (De La Rocha et al., 1997, 2000; Varela et al., 2004; Cardinal et al., 2005). Hence the relatively simple hydrology of Lake Pupuke permits limited groundwater effects and no fluvial impacts (e.g., fluvial filtering [Alleman et al., 2005]). Given the limited source pathway (e.g., runoff) a simple $\delta^{30}\text{Si}$ model can be constructed for Lake Pupuke whereby changes to precipitation, lake mixing and biological uptake control the $\delta^{30}\text{Si}_{\text{Diatom}}$ signature of composite sediment. Changes in precipitation alter weathering intensity; greater precipitation generates greater runoff and dissolution of surface silicates, a process that favours depletion of $\delta^{30}\text{Si}$ in DSi (Sommer et al., 2006; Engstrom et al., 2010). Terrestrial biological productivity can moderate any runoff effect by preferentially enriching pore-water DSi in the formation of isotopically lighter opal phytoliths (Leng et al., 2009). However, in a review of mechanisms capable of altering terrestrial and fluvial Si-pools, Sommer et al (2006) rank runoff of greatest importance whereby even highly productive catchments are likely to demonstrate a strong positive relationship between DSi and runoff. Hence the effect of changing runoff upon DSi is therefore likely to alter $\delta^{30}\text{Si}_{\text{Lake}}$ far more than corresponding changes in terrestrial biomass, particularly within the small catchment of Lake Pupuke.

Consequently, greater precipitation and runoff is likely to result in depletion of $\delta^{30}\text{Si}_{\text{Lake}}$ and by association $\delta^{30}\text{Si}_{\text{Diatom}}$. However, any runoff effect will be altered by diatom productivity whereby changes in biological productivity will result in a positive relationship to $\delta^{30}\text{Si}_{\text{Lake}}$ and $\delta^{30}\text{Si}_{\text{Diatom}}$ (e.g., greater uptake will result in nutrient scarcity and Si-limitation thereby leading to incorporation of isotopically heavier $^{30}\text{Si}$ within diatom silica). Productive enrichment of $\delta^{30}\text{Si}_{\text{Diatom}}$ will only occur where DSi is limited and thus changes to mixing within Lake Pupuke will also be expressed in $\delta^{30}\text{Si}_{\text{Diatom}}$. For instance, contemporary $\delta^{30}\text{Si}_{\text{Diatom}}$ signatures exhibit a close relationship to $\delta^{13}\text{C}$ of organic matter in sediment ($r_{\delta^{13}\text{C},\delta^{30}\text{Si}} = 0.73, P > 0.1, n = 4$). Alleman et al (2005) also recorded the effects of thermal stratification upon DSi-availability and $\delta^{29}\text{Si}$ within Lake Tanganyika (East Africa).
Lake Tanganyika is permanently stratified such that diatom productivity is controlled by changes in the depth of the thermocline with increased wave-induced mixing, resulting in greater productivity through release of nutrients trapped in deeper waters (Alleman et al., 2005). However, imposed upon a seasonal trend of greater and lesser mixing in line with wet and dry seasons, are brief periods of heightened productivity associated with storms which supply DSI to epilimnetic waters via surface runoff (Alleman et al., 2005). Three such events during 2002-2003 led to the marked depletion of $\delta^{29}$Si$_{Lake}$ and $\delta^{30}$Si$_{Diatom}$, stressing the role of mixing upon lacustrine DSI-availability and isotopic composition (Alleman et al., 2005). Despite its monomictic status, similar responses can be expected in Lake Pupuke whereby the onset of thermal stratification would be expected to enrich corresponding $\delta^{30}$Si$_{Diatom}$ by resource limitation. In a similar vein, heightened diatom productivity would be expected to result in DSI-competition and enrichment of downcore composite $\delta^{30}$Si$_{Diatom}$ values. These changes will however, be imposed upon changes to DSI-delivery (e.g., effective precipitation) which alter the baseline in $\delta^{30}$Si upon which mixing and productivity selectively enrich the lacustrine reservoir.

A notable property of the Pupuke composite $\delta^{30}$Si$_{Diatom}$ sequence is the limited impact of tephra contamination and the similarity of uncorrected and tephra-free profiles (Figure 6.21). Despite potential over-estimation of glass shard abundance, average rhyolitic and basaltic contamination across the 22 samples is only $\sim$10.86 ± 8.94 wt. % ($\mu$ ± 1σ) which leads to an average isotopic enrichment of $\sim$0.04 ± 0.05 ‰ ($\mu$ ± 1σ) within tephra-free signatures which vary by 0.73 and 0.81 ‰ (uncorrected and tephra-free) in the composite sequence. Accordingly, tephra-contamination is substantially reduced within the $\delta^{30}$Si$_{Diatom}$ series, reducing the uncertainty attached to its interpretation.

The Pupuke composite $\delta^{30}$Si$_{Diatom}$ sequence can be split into 3 broad zones: (3) relatively enriched values from $\sim$5.0 cal. kyr BP to today; (2) relatively depleted values from the Last Termination at $\sim$18.5 cal. kyr BP until $\sim$5.0 cal. kyr BP; and (1) relatively enriched values prior to the Last Termination at $\sim$18.5 cal. kyr BP. Zone 1 therefore fails to record the reduction in effective precipitation at $\sim$28.5 cal. kyr BP although a possible mechanism for a relatively enriched $\delta^{30}$Si$_{Diatom}$ during the wetter Moerangi interstadial are the correspondingly high diatom influx rates (Figure 6.21). The possible depletion of $\delta^{30}$Si$_{Lake}$ by increased runoff under a wetter paleoclimate from $\sim$48.2 to 31.3 cal. kyr BP is countered by particularly high demands upon DSI due to higher diatom productivity. In contrast the precipitation during the LGCP is characterised by low diatom influx and productivity meaning continued enriched $\delta^{30}$Si$_{Diatom}$ must have arisen through reduced input (e.g., lesser precipitation and runoff supplied less DSI). Enriched $\delta^{30}$Si$_{Diatom}$ during the LGCP until the (last) Termination record the lower effective precipitation of MIS 2 within the NNI. Marked $\delta^{30}$Si$_{Diatom}$ depletion commencing with the termination of the LGCP ($\sim$18.5 cal. kyr BP) coincides with increasing catchment and lake productivity under a return to warmer and wetter paleoclimate (see above). Depletion of $\delta^{30}$Si$_{Diatom}$ until $\sim$5.0 cal. kyr BP therefore records the increased supply of DSI by greater runoff under a wetter climate during the Last Glacial-Interglacial Transition (LGIT). Importantly, the lack of any change in diatom influx at Termination 1 precludes depletion of $\delta^{30}$Si$_{Diatom}$ by reduced productivity and instead stresses the role of greater total and effective precipitation in delivering more DSI to Lake Pupuke. A brief reversal with enrichment of $\delta^{30}$Si$_{Diatom}$ between $\sim$14.0 and 13.6 cal. kyr BP
corresponds to an LGIT peak in productivity (Figure 6.21). Increased diatom influx occurs between ~13.9 and 13.0 cal. kyr BP offering a mechanism to explain relatively enriched $\delta^{30}\text{Si}_{\text{Diatom}}$ through greater demand on lacustrine DSi during an otherwise wetter period of greater DSi supply. An alternative hypothesis involving reduced DSi input can be excluded as this would reduce overall diatom productivity.

Depleted $\delta^{30}\text{Si}_{\text{Diatom}}$ values continue into the early Holocene but are abruptly interrupted and reversed by marked enrichment at ~5.0 cal. kyr BP. Enrichment of bulk sedimentary $\delta^{15}\text{N}$ at this time indicates marked benthic anoxia permitting denitrification and the enrichment of remaining nitrogenous organic matter (OM) (refer to Figure 6.21). Coeval changes in diatom taxa and inferred water chemistry support the inference of ~5.6 cal. kyr BP as the onset of thermal stratification (Section 5.4.3. Paleo-REDOX and Mixing). Thermal stratification effectively limits the availability of dissolved nutrients within the present epilimnion resulting in a seasonally-distinct bloom of Si-rich *A. granulata* during holomixis (July to August) (Cassie, 1989; Holmes, 1994). Thus the onset of thermal stratification implied by sedimentary REDOX indicators at ~5 to 6 cal. kyr BP (e.g. $\delta^{15}\text{N}$, Mn/Fe ratio; Figure 6.21), offers an explanatory mechanism of more enriched $\delta^{30}\text{Si}_{\text{Diatom}}$ by reducing available DSi to the epilimnion. A lack of marked change in effective precipitation during the middle Holocene makes a decline in DSi supply unlikely and underscores the importance of thermal stratification in governing dissolved nutrient availability.

The concomitant rise in abundance of *A. granulata var. ambigua* after ~5.0 cal. kyr BP offers the potential for $\delta^{30}\text{Si}_{\text{Diatom}}$ to be subject to a taxonomic effect ($r = 0.42$, $P > 0.01$, $n = 22$). However, the absence of coincident changes in $\delta^{30}\text{Si}_{\text{Diatom}}$ with other shifts in diatom assemblage structure (e.g., shift from planktic to tychoplanktic dominance at ~22.5 cal. kyr BP) as well as an absence of a taxonomic vital effect in other Si-isotope studies of diatom silica suggest that this is unlikely (e.g., Swann and Leng, 2009). The dependence of *A. granulata var. ambigua* upon thermal stratification and in particular, overturn for resuspension, links changes in $\delta^{30}\text{Si}_{\text{Diatom}}$ to the abundance of this meroplankton. The heavy silicification of *A. granulata var. ambigua* would also positively feedback upon reduced DSi availability during stratified months, by placing greater demand upon DSi within the photic zone during a narrowly defined period of overturn. Consequently, variations in the downcore composite $\delta^{30}\text{Si}_{\text{Diatom}}$ sequence during the last ~5 kyrs likely records varying intensity of thermal stratification which also governs the dominance of meroplanktic diatoms. Given the dependence of thermal stratification upon calm, dry summers, the composite $\delta^{30}\text{Si}_{\text{Diatom}}$ record also offers a potential record of the dominance of zonal summer airflow whereby strengthened westerlies and southwesterlies during the mid-to-late Holocene could explain observed changes to $\delta^{30}\text{Si}_{\text{Diatom}}$ (e.g., Shulmeister et al., 2006).
Figure 6.21: Paleoclimatic shifts in Si-cycling, uptake and availability recorded by changes to $\delta^{30}$Si$_{Diatom}$ within the Pupuke composite sequence. Three broad zones of (3) greater (~5.0 cal. kyr BP to today), (2) lower (~18.5 to 5.0 cal. kyr BP) and (1) greater enrichment are recorded (~48.2 to 18.5 cal. kyr BP). Zone 3 corresponds to the mid-to-late Holocene, Zone 2 the early Holocene and Last Glacial Interglacial Transition (LGIT) and Zone 1 the Last Glacial Coldest Period (LGCP) and earlier Moerangi Interstadial. Zone 2 is interrupted by enriched $\delta^{30}$Si$_{Diatom}$ between ~14.0 and 13.6 cal. kyr BP indicative of an LGIT peak in diatom and total productivity.
6.6 Summary

A novel approach to diatom isotope paleolimnology, employing chemical, physical and mathematical techniques has been applied to the Pupuke composite sequence. Following standard chemical treatments, core samples were subject to a physical separation procedure employing SPLITT fractionation to isolate biogenic silica from surrounding contaminants. The approach proved exceptionally powerful and reduced average sample contamination to ~3.3 % by count. Subsequent SEM analyses revealed the absence of clay contaminants but the presence of volcanic tephra in nearly all samples. Application of a geochemical mixture model to calculate the abundance of rhyolitic and basaltic tephra generated a greater average estimate of contamination (~9.7 % by mass). Application of average δ\(^{18}\)O and δ\(^{30}\)Si to each estimate has enabled removal of the tephra contaminant effect. This meets the second aim of this thesis (e.g., ‘Development of novel paleolimnologic proxies’).

Nevertheless, this approach is limited to removal of geochemically distinct contaminants with evidence of over-estimation of tephra abundance in the purified samples analysed here. Fortunately, correction of sample composition has not altered overall trends in the Pupuke composite δ\(^{18}\)O\(_{\text{Diatom}}\) and δ\(^{30}\)Si\(_{\text{Diatom}}\) records, such that three broad intervals can be identified in each isotope sequence.

Greater residence time and a deeper lake existed prior to ~28.6 cal. kyr BP whereupon depleted δ\(^{18}\)O\(_{\text{Diatom}}\) records a loss of lake volume and residence time until ~18.5 cal. kyr BP, after which a continued higher lake level under a wetter paleoclimate persisted to today. Short-term variation about these average states highlights marked changes in effective precipitation including several depleted phases during the LGCP, representing particularly low rates of evaporation combined with low overall precipitation. Particularly enriched δ\(^{18}\)O\(_{\text{Diatom}}\) between ~14.0 and 13.0 cal. kyr BP also records a brief period of greater precipitation leading to greater residence time necessary to enrich δ\(^{18}\)O\(_{\text{Diatom}}\).

The Pupuke composite δ\(^{30}\)Si\(_{\text{Diatom}}\) sequence records changes to DSI input via runoff, uptake via productivity and isolation of dissolved nutrients by thermal stratification. Enriched δ\(^{30}\)Si\(_{\text{Diatom}}\) values prior to ~18.5 cal. kyr BP record a mix of higher DSi demand prior to MIS 2 and then reduced supply under a drier LGCP climate. The termination of the LGCP and MIS 2 is observed by depletion of δ\(^{30}\)Si\(_{\text{Diatom}}\) under a wetter climate delivering greater quantities of DSI in greater runoff. A brief reversal to enriched δ\(^{30}\)Si\(_{\text{Diatom}}\) between ~14.0 and 13.6 cal. kyr BP records an increase in diatom productivity coeval with earlier inferences of an LGIT peak in overall productivity (Section 4.5.2. Paleoproductivity). Subsequently, values of δ\(^{30}\)Si\(_{\text{Diatom}}\) remain depleted until ~5.0 cal. kyr BP, and enriched thereafter until today. Corresponding changes in sediment geochemistry and diatom taxonomy indicate the onset of thermal stratification at ~5.6 cal. kyr BP (Section 5.4.3. Paleo-REDOX and Mixing) which presently limits the availability of dissolved nutrients in Lake Pupuke. Thus the Pupuke composite δ\(^{30}\)Si\(_{\text{Diatom}}\) stratigraphy records the onset of intense thermal stratification within Lake Pupuke from ~5.0 cal. kyr BP through the isolation of DSI within bottom waters during seasonal stratification, and the production of \(^{30}\)Si-enriched diatom silica.
CHAPTER SEVEN

The Combined Paleolimnology of Lake Pupuke and Comparison to the NZ-INTIMATE Climate Event Stratigraphy

7.1 Introduction

In previous chapters the paleolimnology of Lake Pupuke has been described using a series of proxies: geochemical and physical indicators (Chapter 4), biotic indicators (Chapter 5) and novel, stable isotopic indicators of environmental change (Chapter 6). Each has been discussed separately to facilitate their interpretation although together they demonstrate coeval paleolimnological changes across a range of processes (e.g., erosion, lake level, mixing and biological productivity). Whilst Chapter 3 meets the first aim of this thesis (e.g., development of a robust chronology) and Chapter 6 the second (e.g., application of novel paleolimnological proxies to the Pupuke composite sequence), it now remains to construct a multi-proxy climate event stratigraphy for Lake Pupuke in this chapter (e.g., Section 1.3. Research Objectives). The chapter finishes in a regional comparison to the Northern North Island (NNI) and high-value NZ-INTIMATE paleo-records.

7.2 A Paleoclimate Event Stratigraphy for Lake Pupuke

A paleolimnological record of Lake Pupuke including changes in erosion, lake level, mixing and biological productivity derived from multiple indicators of past environment, is presented in Table 7.1 and Figure 7.1. Inferred boundaries of marked paleoclimatic change record the transition from Marine Isotope Stage (MIS) 3 to 2 at ~28.5 cal. kyr BP and from MIS 2 to 1 in the Holocene.
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.
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>
<thead>
<tr>
<th>Interval</th>
<th>Erosion</th>
<th>Lake level</th>
<th>Biomass</th>
<th>Holoclimatology of Lake Pupuke</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3.2 cal. kyr BP to Today</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Holocene (Deep, productive lake)</td>
</tr>
<tr>
<td>~5.7 to 3.2 cal. kyr BP</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>• Higher diatom influx and greater nutrient availability coupled to enhanced seasonality from ~5.6 cal. kyr BP associated with strengthened westerly airflow, more frequent summer zonal regimes and negative ENSO phases. Changes to seasonality affect degree of mixing which controls nutrient availability and diatom suspension recorded by composite geochemistry ($\delta^{13}$N, $\delta^{30}$Si$_{dissoc}$, Mn/Fe), lower diatom SIMI scores (shifts between euplankton, tychoplankton and meroplankton) as well as highly variable DI-EC, DI-TP, DI-DRP and DI-Chl a. Changes in $\delta^{18}$O offer record of zonal regime frequency through changes to westerly circulation (e.g., coeval Southern Alps glacial response).</td>
</tr>
<tr>
<td>~7.6 to 5.7 cal. kyr BP</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>• Period of heightened catchment disturbance (~7.6 to 5.7 cal. kyr BP) during which TOC, TN and C/N ratios decline indicating reduced terrestrial OM influx. Diatom productivity high and greater nutrient availability (e.g., high DI-EC, DI-TP, DI-DRP and DI-Chl a) records high aquatic biomass which in absence of stratification indicators (e.g., depleted $\delta^{13}$N, reduced Mn/Fe) implies reduced seasonality and influx of nutrients from catchment soils. Very low SIMI scores demonstrate marked diatom species turnover.</td>
</tr>
<tr>
<td>~10.2 to 7.6 cal. kyr BP</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>• Early Holocene Warm Period (~10.2 to 8.0 cal. kyr BP) of greater terrestrial and aquatic biomass, limited diatom productivity though stable communities with little seasonality (e.g., absence of thermal stratification despite high lake level). Greater MAR because of increased biological productivity.</td>
</tr>
<tr>
<td>~12.8 to 10.2 cal. kyr BP</td>
<td>Low</td>
<td>Rising</td>
<td>Rising</td>
<td>LGIT (Deepening, increasingly productive lake)</td>
</tr>
<tr>
<td>~13.6 to 12.8 cal. kyr BP</td>
<td>Falling</td>
<td>High</td>
<td>High</td>
<td>• LGIT transitional conditions to greater precipitation and warmth occurred from ~12.8 to 10.2 cal. kyr BP prevents ready definition of the Holocene onset. Depleted $\delta^{30}$Si suggests increasing wet conditions (e.g., greater runoff) but limited diatom productivity indicates presence of a limiting factor (e.g., competition, habitat).</td>
</tr>
<tr>
<td>~14.4 to 13.6 cal. kyr BP</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>• LGR event (~14.4 to 13.6 cal. kyr BP) recorded by marked increase to MAR of minerogenic sediment (e.g., greater DBD) coeval with reductions in terrestrial and aquatic biomass (e.g., reduced TOC, TN and TS concentration) and markedly different diatom communities to later and earlier LGIT assemblages. Rising abundance of autotrophic taxa from ~15.5 to 13.8 cal. kyr BP is coeval with onset of rising grain-size and heightened erosion.</td>
</tr>
<tr>
<td>~18.5 to 14.4 cal. kyr BP</td>
<td>Falling</td>
<td>Rising</td>
<td>Rising</td>
<td>• LGIT onset evident in reduced erosional influx (e.g., reduced Ti abundance, smaller grain-size), increased terrestrial biomass and increased pCO$_2$ (e.g., depleted $\delta^{13}$C), coeval with warming in EPICA DML ice sequence (EPICA, 2006). Aquatic biomass recovery is delayed by ~2 kyrs but recorded by increasing DI-DRP, DI-TP and DI-Chl a from ~16.5 cal. kyr BP. High SIMI scores suggest continued trend to improved paleoclimate until LGR (~14.4 cal. kyr BP).</td>
</tr>
<tr>
<td>~21.0 to 18.5 cal. kyr BP</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>LGR (Shallow, unproductive lake)</td>
</tr>
<tr>
<td>~26.0 to 21.0 cal. kyr BP</td>
<td>Moderate</td>
<td>Low</td>
<td>Moderate</td>
<td>• Enhanced erosional influx is recorded by increased MAR of minerogenic sediment (e.g., high DBD) and coarser grain-size from ~23.5 to 18.5 cal. kyr BP. Reduced biomass is noted from ~21.0 to 18.5 cal. kyr BP. A coeval decline in C/N ratios suggests reduction in terrestrial vegetation during a period of already reduced aquatic biomass (e.g., shift to thinly vegetated catchment).</td>
</tr>
<tr>
<td>~27.6 to 26.0 cal. kyr BP</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>• Enhanced erosional influx is recorded by coarser grain-size although with little change to MAR or lithology. Reduced terrestrial vegetation cover from ~27.6 to 26.0 cal. kyr BP is recorded by a decline in TOC, TN and C/N ratios during a period of reduced aquatic biomass.</td>
</tr>
<tr>
<td>~28.5 to 27.6 cal. kyr BP</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td>• The LGCP is marked by a reduction in aquatic biomass (e.g., reduced DI-DRP, DI-Chl a, TS) and the onset of rising abundance of autotrophic diatoms (~28.5 cal. kyr BP as well as reduced pCO$_2$ (e.g., enriched $\delta^{13}$C)). A coeval rise in C/N indicates increased terrestrial OM input in response to declining lake levels.</td>
</tr>
<tr>
<td>~31.3 to 28.5 cal. kyr BP</td>
<td>Rising</td>
<td>Falling</td>
<td>Moderate</td>
<td>Pre-LGCP (Deep [shallowing], moderately productive lake)</td>
</tr>
<tr>
<td>~48.2 to 31.3 cal. kyr BP</td>
<td>Low</td>
<td>Very high</td>
<td>Moderate</td>
<td>• The interval prior to the LGCP is marked by declining lake level recorded by increasing grain-size and reducing diatom influx from ~31.3 cal. kyr BP. Stable, deepwater communities of euplanktic diatoms continue to dominate until ~28.5 cal. kyr BP recording the presence of a deep lake until the start of the LGCP. A reduction in pCO$_2$ (e.g., enriched $\delta^{13}$C) is recorded from ~31.4 cal. kyr BP.</td>
</tr>
<tr>
<td>~48.2 to 31.3 cal. kyr BP</td>
<td>Low</td>
<td>Very high</td>
<td>Moderate</td>
<td>• Moderate abundance of catchment vegetation including greater aquatic biomass is recorded by a rise in TN, TS and DI-DRP concentrations. Diatom influx is also very high approaching values more indicative of the late Holocene and resulting in enrichment of $\delta^{30}$Si$<em>{dissoc}$ by greater uptake. Higher lake level is recorded by enriched $\delta^{15}$O$</em>{oxygen}$. Stable diatom communities coupled to the absence of thermal stratification indicators record the likely absence of marked seasonality.</td>
</tr>
</tbody>
</table>
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 (δ13C), Nitrogen stable isotope (δ15N), Hoagland similarity index scores (SIMI), diatom taxa (planktic, tychoplanktic, meroplanktic, benthic and aerophilic), diatom-inferred dissolved reactive Phosphorus (DI-DRP), diatom sample DCA Axis 1 scores, diatom Oxygen isotope (δ18ODiatom) and diatom Silicon isotope composition (δ30SiDiatom).
7.2.1 Pre-LGCP (~48.2 ± 4.7 to 28.5 ± 2.3 cal. kyr BP [± 95% uncertainty])

A deep lake existed at Pupuke from ~48.2 to 31.5 cal. kyr BP under a climate sufficiently wet and only moderately cooler than present to enrich δ¹⁸O_Lake and δ¹⁸O_Diatom to contemporary values (Figure 7.2). Little paleohydrological variability occurred to lake residence time or level as recorded by relatively stable δ¹⁸O_Diatom, the continued dominance of planktic diatoms (including Discotella stelligera) and low beta diversity amongst diatom communities until ~28.5 cal. kyr BP (Figure 7.2). The absence of intense thermal stratification until the middle Holocene is indicated by relatively depleted δ¹⁵N of bulk sediment until ~5.5 cal. kyr BP and the absence of stratification-adapted diatoms until ~6.9 cal. kyr BP. The existence of a deep lake and absence of intense seasonal overturn between ~48.2 and 28.5 cal. kyr BP effectively limited mixing and recirculation of nutrients held in bottom waters by sedimentary organic matter (OM). Sediments deposited during MIS 3 are therefore indicative of low biological productivity although a moderate concentration of total Sulphur (TS) and diatom-inferred dissolved reactive Phosphorus (DI-DRP) indicates aquatic producers contributed significantly to the limited biomass (refer to Figure 7.2).

The transition to cooler paleoclimate indicative of the Last Glacial Coldest Period (LGCP) might have started as early as ~31.5 cal. kyr BP as suggested by enhanced particle size, although substantial changes to most paleoenvironmental indicators only occurs after ~28.5 cal. kyr BP. A decline in TS concentration occurs after ~31.6 cal. kyr BP coeval with an increasing proportion of coarse sediment influx (>32 μm). A decline in lake level can explain the loss of TS through a reduction in aquatic productivity and less reducing conditions at depth (i.e., limiting reduction of sulphate to iron pyrite). A shallower lake would also expose more of the lake catchment to erosion explaining the coeval increase in abundance of coarse sediment. A decline in planktic and rise of tychoplanktic diatoms starts at ~31.3 cal. kyr BP although a consistent shift only occurs from ~29.3 cal. kyr BP and records increased shallowing. Thus, transitional changes between high and low lake level could have started at ~31.5 cal. kyr BP but were not substantial until later as demonstrated by continued enrichment of δ¹⁸O_Diatom until ~28.6 cal. kyr BP.

7.2.2 LGCP (~28.5 ± 2.3 to 18.5 ± 1.4 cal. kyr BP [± 95% uncertainty])

Erosional indicators record a shallower lake at Pupuke during the LGCP. For instance, the proportion of coarse (% >32 μm) sediment is heightened throughout the period ~28.5 to 18.5 cal. kyr BP (refer to Figure 7.2). A decline in the abundance of planktic vs. tychoplanktic diatoms also occurs throughout the LGCP. Moreover, the proportion of aerophilic diatoms rises markedly between ~28.5 and 18.4 cal. kyr BP requiring more catchment to be exposed and a drop in lake level as these diatoms inhabit ephemeral ponds (Dam et al., 2001). A drop in the concentration of DI-DRP from ~28.5 to 16.7 cal. kyr BP demonstrates a coeval decline in aquatic biomass during the LGCP because DRP is dominantly aquatic in origin (Wetzel, 2001). Furthermore, the concentration of TS drops consistently from ~31.5 to 16.5 cal. kyr BP underscoring the inferred drop in lake level and aquatic productivity to favour greater oxygenation at the sediment-water interface and prevent reduction of dissolved or
organic sulphate. The composite $\delta^{13}$C record offers a detailed insight into atmospheric $p$CO$_2$ availability and indicates the onset and termination of the LGCP through reduced dissolved inorganic Carbon (DIC) availability from ~28.8 to 18.3 cal. kyr BP. Coeval depletion of $\delta^{18}$O$_{\text{Diatom}}$ from ~28.6 until 18.5 cal. kyr BP further confirms the timing and duration of the LGCP at Lake Pupuke as it is driven by reduced lake level, residence time and limited evaporation under a markedly cooler and drier paleoclimate.

Several shorter duration climate events can also be identified within the LGCP. Two phases of drier and cooler paleoclimate occur from ~27.6 to 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP respectively. Both intervals display depleted $\delta^{18}$O$_{\text{Diatom}}$ as well as reduced total organic Carbon (TOC) and Nitrogen (TN) concentration suggesting reduced lake residence time and overall biomass. The absence of changes in TS (already reduced) and declining C/N of organic matter (OM) demonstrate that reductions in biomass occurred largely in the terrestrial components, with aquatic components already reduced through lower lake level. A shift from beech-conifer forest to open grass and shrubland could explain the observed changes in sediment geochemistry during these two intervals with the latter period recording the most marked change to paleoclimate during the LGCP just prior to Termination 1 (T1). During this inferred cool phase erosional influx increased markedly from ~23.5 to 18.4 cal. kyr BP driving a consequent increase in the dry bulk density and mass accumulation rate (MAR) of composite sediment (Figure 7.2).

### 7.2.3 LGIT and Holocene (~18.5 ± 1.4 cal. kyr BP to today [± 95% uncertainty])

The LGCP terminates abruptly at ~18.5 cal. kyr BP indicated by a change to wetter, warmer paleoclimate necessary to enrich $\delta^{18}$O$_{\text{Diatom}}$ by increasing lake residence time and depth, as well as permitting greater evaporative enrichment. Further indication of increasing precipitation is recorded by depletion of $\delta^{30}$Si$_{\text{Diatom}}$ through greater dissolved Silicon (DSi) supply via increased runoff from ~18.5 cal. kyr BP. A coeval depletion of $\delta^{13}$C also demonstrates the abrupt termination of the LGCP at ~18.3 cal. kyr BP. Thus the period ~18.5 to 10.2 cal. kyr BP marks the transition from full glacial to interglacial paleoclimate and is referred to here as the Last Glacial Interglacial Transition (LGIT).

Although terrestrial biomass increased markedly following climatic amelioration from ~18.5 cal. kyr BP (through increased TOC and TN coupled to greater C/N), aquatic biomass only increased from ~16.5 cal. kyr BP indicating a ~2 kyr BP delay to climate amelioration (refer to Figure 7.2). For instance, diatom-inferred DRP rises from ~16.7 cal. kyr BP, a decline in aerophilous diatoms occurs from ~16.7 cal. kyr BP coincident with a shift to relatively stable tychoplanktic diatom communities (e.g., *Staurosira microstriata*, *S. aff. venter* and *S. parasitoides*), and the concentration of TS increases markedly from ~16.5 cal. kyr BP (Figure 7.2). This might reflect the bathymetry of Lake Pupuke and the steep crater sides which would require a water column of ~30-35 m depth prior to inundation of more expansive gently-grading shelves (Section 2.3. Bathymetry and Morphometry). Thus lake shallowing during the LGCP likely resulted in a period of 2 kyr following the LGCP during which water depth rose sufficiently to approach values more indicative of the present interglacial.
Alternatively, increased temperature and evaporation rate resulted in greater loss of surface water from ~18.5 cal. kyr BP until a shift to markedly wetter paleoclimate at ~16.5 cal. kyr BP. However, the former is more likely as declining percentage of coarse sediment (>32 μm), magnetic susceptibility (MS) and concentration of Titanium (Ti) from ~18.5 cal. kyr BP indicate reduced erosional influx which would be expected under a rising lake level (refer to Figure 7.2).

Variable hydrological conditions occurred during the LGIT at Lake Pupuke. Increased erosional influx occurred from ~15.5 to 13.8 cal. kyr BP as recorded by greater clastic inwash. Reduced biological productivity and biomass occurred from ~14.4 to 13.8 cal. kyr BP and a coeval decline in lake level is recorded by the increased abundance of aerophilous diatoms between ~15.1 and 13.4 cal. kyr BP (refer to Figure 7.2). Likewise, depletion of $\delta^{18}$O$_{\text{Diatom}}$ occurred between ~15.1 and 13.6 cal. kyr BP indicating a reduction in lake level and residence time as per the LGCP. This inferred drop in lake level is abruptly reversed between ~13.6 and 13.0 cal. kyr BP (recorded by the enrichment of $\delta^{18}$O$_{\text{Diatom}}$) through a return to a deeper, more evaporatively-enriched lake. Increased lake level is also suggested by greater TS-concentration, decline in the abundance of aerophilous diatoms and increase in overall biological productivity (Figure 7.2). The concentration of TOC and TN rises markedly from ~13.8 cal. kyr BP which is also demonstrated in greater TOC and TN flux which drive a marked rise in MAR between ~14.8 and 12.7 cal. kyr BP (Figure 7.2). Diatom influx peaked at ~13.5 cal. kyr BP after which biological productivity falls between ~12.8 and 12.0 cal. kyr BP (Figure 7.2). Increasing DCA Axis 1 sample scores throughout the LGIT also record a general trend to increasing nutrient availability thereby supporting geochemical evidence for greater productivity during the transition to the early Holocene (Figure 7.2).

The early Holocene is a period of particularly high biological productivity in both terrestrial and aquatic components between ~10.2 and 8.0 cal. kyr BP (Figure 7.2). A coeval increase in MAR corresponds to this accumulation of highly organic sediment suggesting that the paleoclimate of the early Holocene was particularly conducive to increased primary production (e.g., warmer and wetter than present). However, an abrupt decline in terrestrial productivity occurs between ~7.6 and 5.7 cal. kyr BP. A coeval rise in the proportion of coarse (>32 μm) sediment indicates heightened erosion accompanied the decline in terrestrial biomass. In contrast, diatom productivity reaches a peak at ~6.9 cal. kyr BP. Likewise, diatom-inferred water chemistry reaches several maxima (e.g., in conductivity [DI-EC], aquatic biomass [DI-Chl a], total and dissolved reactive phosphorus [DI-TP and DI-DRP]) suggesting the cause of increased catchment disturbance and heightened erosion favoured aquatic producers. An absence of marked change in aerophilous or benthic taxa as well as $\delta^{18}$O$_{\text{Diatom}}$ precludes a drop in lake level as the cause of heightened erosion (e.g., as experienced in the LGCP). Instead increased erosive influx likely occurred in response to more frequent destructive windstorms which restricted terrestrial producers through tree throw but favoured aquatic producers through greater inwash and recirculation of essential nutrients by deeper wave bases. Greater abundance of heavily silicified meroplankton further confirms the likelihood of increased windiness and mixing driving a corresponding increase in diatom productivity between ~7.6 and 5.7 cal. kyr BP.
A natural eutrophication of Lake Pupuke occurred from ~6.2 cal. kyr BP as recorded by greater algal contribution to composite sediment (e.g., reduced C/N). A broadly coeval onset of thermal stratification is evident by the more intense reducing potential necessary to enrich sedimentary δ¹⁵N from ~5.6 cal. kyr BP. Likewise, enrichment of δ³⁰SiDiatom occurred by 5.0 cal. kyr BP (refer to Figure 7.2). Thermal stratification of the lake presently limits the availability of dissolved silica (DSi) in much the same way as DIC such that biogenic silica precipitated during stratified months has a characteristically enriched δ³⁰SiDiatom signature (Section 6.2.2.5. Diatom Isotope Seasonality). Thus, enrichment of δ³⁰SiDiatom is likely a response to the restricted availability of DSi from ~5 to 6 cal. kyr BP to present. An initial response to stratification is also evident in the diatom stratigraphy whereby increased abundance of oligotrophic, benthic diatoms occurs from ~5.5 cal. kyr BP (Figure 7.2). This could record greater inundation of shallow surrounding basin shelves, but as little change occurs to δ¹⁸O Diatom, the change more likely records a loss of tychoplanktic diatoms through more restricted summer nutrient availability and increased water clarity permitting greater aquatic macrophyte growth and a corresponding increase in periphytic diatoms. However, the most marked changes in sediment geochemistry and diatom taxonomy occurs following intensification of thermal stratification from ~3.2 cal. kyr BP (Figure 7.2). Contamination of TN by inorganic sources occurs and is indicative of greater ammonification through a more intensely reducing seasonal hypolimnion (Wetzel, 2001). Similarly, increased abundance of meroplanktic diatoms (e.g., Aulacoseira granulata var. ambigua) occurs from ~3.3 cal. kyr BP to present. The latter are highly adapted to thermal stratification with resting stages capable of surviving deep anoxia and heavily silicified adult forms requiring strong mixing at overturn to become suspended in Lake Pupuke (Harper et al., 1986).

The onset of strong thermal stratification within Lake Pupuke is therefore associated with limited nutrient availability until intensification of mixing from ~3.2 cal. kyr BP which permitted greater turbulence (e.g., the sudden collapse of a thermocline permits overturning waters to more intensively mix and suspend nutrients lost to deeper waters than through wave mixing alone [Holmes, 1994]). Seasonal ventilation of deeper waters offers a mechanism of natural eutrophication with stratified conditions resulting in release of phosphate and ammonia from organic detritus (Wetzel, 2001). Overturning returns these nutrients to productive surface waters where ammonia is nitrified by cyanobacteria to dissolved nitrate, which, combined with TP release, results in fertilization of aquatic producers (Wetzel, 2001). Thus intensification of thermal stratification likely resulted in eutrophication of Lake Pupuke and can explain the coeval rise in diatom influx to composite sediment from ~3.3 cal. kyr BP. Variability in the intensity of thermal stratification in line with changing seasonality throughout the mid-to-late Holocene also offers a mechanism capable of explaining the δ¹³C record. Less and more DIC is returned to surface waters by weaker and stronger mixing respectively, and resulting in changes to DIC-availability recorded by the relative enrichment and depletion respectively of corresponding δ¹³C in OM. Changes in the intensity of mixing and nutrient recycling can also explain greater variability in diatom community structure from ~3.3 cal. kyr BP to today characterised by alternating dominance of A. granulata var. ambigua, S. microstriata and D. stelligera.
Chapter Seven

The arrival of Polynesian settlers at Lake Pupuke after ~0.6 cal. kyr BP can be inferred from increased erosion and sediment delivery, reduced terrestrial biomass, and depletion of $\delta^{18}O_{\text{Diatom}}$ and $\delta^{30}S_{\text{Diatom}}$. Polynesian settlers practiced catchment clearance techniques which increased sediment delivery to surrounding water bodies (Goff, 1997; Kasai et al., 2005; Page et al., 2007). Thus increased erosion and in particular, the reduction in C/N ratios of composite sediment, likely record catchment clearance and a thinning of terrestrial vegetation at Lake Pupuke. Depletion of lacustrine O and Si stable isotope reservoirs occurred through greater runoff supplying DSi and reducing the residence time of waters within Lake Pupuke. A reduction in the residence time of Lake Pupuke would reduce the accumulated evaporative effects upon $\delta^{18}O_{\text{Lake}}$ and thereby favour depletion of $\delta^{18}O_{\text{Diatom}}$.

7.3 Regional comparison with Northern North Island paleoclimate records

The Pupuke event stratigraphy offers the most detailed and continuous proxy record for late Quaternary terrestrial paleoenvironment from mid-latitude New Zealand. However, to assess the reliability of attached paleoclimatic inferences and whether these are regional or local responses to climatic change, it is necessary to compare the Pupuke event stratigraphy with other paleoclimate records of the Northern North Island (NNI). Fortunately, several records of late Quaternary paleoclimate exist for the NNI and have been reviewed in Newnham (1999), Alloway et al (2007) and Newnham et al (2007a). Within the Auckland region, the Pupuke composite sequence can be compared to several other paleoenvironmental investigations, namely Pukaki maar (Sandiford et al., 2001, 2003), Onepoto maar (Shane and Hoverd, 2002; Pepper et al., 2004; Augustinus et al., 2011a,b) and Lake Pupuke (Augustinus et al., 2006, 2008; Striewski et al., 2009). Although none of these offer a continuous investigation of paleoclimate from present through to the LGCP, several major events have been defined, namely: the LGCP (~28.0 to 18.0 cal. kyr BP), a Late Glacial Reversal (LGR, ~14.0 to 11.0 cal. kyr BP) and an Early Holocene Warming (EHW, ~11.0 to 10.0 cal. kyr BP).

Relatively few studies explore the NNI paleoclimate during and prior to the LGCP (e.g., Dodson et al., 1988; Dodson, 1998; Newnham et al., 1993; Ogden et al., 1993; Shane and Sandiford, 2003; Newnham et al., 2007a). The interval ~48.2 to 28.5 cal. kyr BP includes much of MIS 3 and is marked across the NNI by a transition from the warmer Moerangi interstadial to cooler conditions associated with a return to intense glacial conditions at ~28 cal. kyr BP (Alloway et al., 2007). During this interval however, drops in mean annual temperature were not severe (~2-3 °C less than today) whilst several palynological reconstructions within Northland and offshore of eastern Northland noted increased precipitation (~85% wetter than today) (e.g., Newnham et al., 1993; Ogden et al., 1993; Wright et al., 1995). The presence of a similar, relatively mild paleoclimate is evident in Pupuke prior to the transition to harsher paleoclimatic conditions from ~31.5 cal. kyr BP and full glacial conditions by ~28.5 cal. kyr BP. For instance, values of DI-DRP, TS and $\delta^{18}O_{\text{Diatom}}$ approximate those seen in the late Holocene, implying sufficient lake depth and aquatic biomass to generate anoxic benthic conditions necessary to reduce sulphate to iron pyrite and/or organic compounds. A recent study of Onepoto maar also highlights the period ~30 to 28.5 cal. kyr BP as a transitional period to greater environmental stress resulting in greater cladoceran ephippia
Debate centres on the extent of forest cover across Northland prior to the LGCP (e.g., Newnham, 1999; Newnham et al., 2007a). The inferred higher lake level and total precipitation at Pupuke between ~48.2 and 31.5 cal. kyr BP lends credence to substantive vegetative cover in Auckland prior to the LGCP, as do palynological reconstructions at Onepoto maar in Shane and Sandiford (2003). The cool but moist paleoclimate during much of MIS 3 permitted survival of dense conifer-angiosperm forest within the NNI (Newnham, 1992; Newnham et al., 1993; Ogden et al., 1993). Retention of conifer-angiosperm forest further distinguishes Northland’s interstadial paleoclimate during MIS 3 from much of New Zealand including the bordering Southern North Island regional paleoclimate zone in which shrub and grassland predominated (McGlone, 1985; Newnham, 1999). Evidence of decreasing aquatic biomass and increasing influx of inorganic matter at Lake Pupuke from ~31.5 cal. kyr BP likely reflects decreasing annual precipitation resulting in lake level lowering. Newnham et al (2007a) suggest a complex coincident response by vegetation within Auckland including expanded thermophilous taxa from ~32 to 31 cal. kyr BP prior to further expansion of lowland-montane conifers from ~31 to 29 cal. kyr BP. Such a shift to drier, windier paleoclimate coeval with increased disturbance and erosional influx likely involved a shift to less dense, shrubland or grassland within Auckland (e.g., Shane and Sandiford, 2003; Newnham et al., 2007a).

The onset of the LGCP resulted in climatic deterioration in New Zealand due to enhanced southerly and southwesterly airflow which led to greater cooling and aridity (Shulmeister et al., 2001). The LGCP has been inferred within Auckland by a decline in the abundance of podocarp forest relative to grassland, reduced concentration of TOC and enrichment of δ¹³C approximately ~1.0 kyrs before deposition of the Kawakawa tephra (~27.1 ± 1.0 cal. kyr BP) (Sandiford et al., 2003; Newnham et al., 2007a; Augustinus et al., 2011a). The poor age uncertainty attached to this tephra has prevented a precise boundary being set for the onset of the LGCP in Auckland. Onset of the LGCP within the Pupuke composite sequence at ~28.5 cal. kyr BP is therefore plausible. Indeed palynological reconstructions at Otakairangi, Northland also indicate marked cooling and increased aridity from ~29 cal. kyr BP (Newnham, 1992). Overall, increased aridity and cooling during the LGCP was sufficient for the northerly migration of Nothofagus menziesii, which presently occurs south of 38 °S or above ~550 m elevation, such that its expansion within Auckland necessitated a cooling of 4-5 °C below present (Sandiford et al., 2002; Shane and Sandiford, 2003). Other palynological changes associated with drying and cooling during the LGCP include the loss of Dacydium cupressinum (rimu), rarity of Cyathea dealbata (tree ferns) and expansion of Poaceae (grasses) (Lancashire et al., 2002; Sandiford et al., 2002; Augustinus et al., 2011a). Accordingly during the LGCP, Auckland likely retained patches of beech-dominated forest within a shrubland-grassland ecotone resulting from the enhanced aridity and cooling of full glacial paleoclimate (Sandiford et al., 2002, 2003; Newnham et al., 2007a).

The Pupuke composite sequence offers a clear response to reduced total and effective precipitation during the LGCP through depleted δ¹⁸O_Diatom, reduced TS and DI-DRP concentration, and diatom floristic changes (e.g., shift from planktic to tychoplanktic taxa, increased abundance of aerophilic diatoms) from ~28.5 to 18.5 cal. kyr
BP. The similarity in timing and duration of the LGCP at Pupuke to earlier studies is reassuring as it stresses the sensitivity of the site to changes in total and effective precipitation through its closed hydrological status (Section 6.2.3. Summary of Modern Stable Isotope Systematics). A similar timing and duration of the LGCP is also evident at Onepoto maar which records evidence of lake level lowering from ~28.5 to 16.0 cal. kyr BP through expansion of wetland vegetation (e.g., Restionaceae and Leptospermum spp.) and increased dominance of tychoplanktic diatoms (e.g., Pseudostaurosira brevistriata, Staurosirella pinnata) (Augustinus et al., 2010). Furthermore, coeval palynological changes indicative of reduced lake level occur at Pukaki maar from ~28.0 to 18.0 cal. kyr BP (Sandiford et al., 2003). Together this enables a reliable date for the LGCP to be defined within Auckland as from ~28.5 cal. kyr BP to ~18.5 cal. kyr BP.

Importantly, marked paleoenvironmental variability occurred in Auckland during the LGCP. For instance, Newnham et al (2007a) noted a period of grassland expansion between ~29 and 28 cal. kyr BP following a shift to increasing beech forest cover at Mt. Richmond and Lake Kohuora. A marked reduction in biogenic silica concentration, enrichment of δ¹³C and greater erosional influx occurred at Onepoto from ~27.5 to 25.0 cal. kyr BP whilst increased abundance of the aerophilic diatom, Diatomella balfouriana, and erosional influx also occurred from ~23.0 to 20.0 cal. kyr BP (Augustinus et al., 2011b). A shift to greater abundance of Poaceae and Asteraceae in the face of declining tree and shrub taxa also occurs from ~22.7 to 21.7 cal. kyr BP within the Pukaki sediment sequence (Sandiford et al., 2002). Hence the coolest and driest phases of the LGCP were likely its onset (~28.5 to 25 cal. kyr BP) and near-termination (~23 to 20 cal. kyr BP) (Sandiford et al., 2003; Newnham et al., 2007a; Augustinus et al., 2011a). These correspond to two periods of significant reduction in terrestrial biological productivity and biomass at Pupuke (e.g., markedly reduced TOC and TN, reduced C/N) coeval with a decline in lake level (e.g., increased abundance of D. balfouriana) from ~27.8 to 26.0 cal. kyr BP and ~21.0 to 19.0 cal. kyr BP (Figure 7.2). The LGCP is therefore likely to comprise two distinct periods of enhanced aridity separated by a milder mid-LGCP paleoclimate commensurate with warming in Antarctica, expressed as Antarctic Isotope Maxima 2 (AIM 2; ~25.4 to 23.0 cal. kyr BP) (EPICA, 2006; Newnham et al., 2007a; Augustinus et al., 2011a). Combined with the overall duration of the LGCP (~10.5 kyrs), the onset of the first of these peaks in glacial climate at ~28.5 cal. kyr BP further underscores the likelihood of significant regional departure from the Northern Hemisphere insolation forcing model of Quaternary climate change (e.g., Vandergoes et al., 2005) as the latter recognises the onset of full glacial conditions in a Last Glacial Maximum between ~23 and 19 cal. kyr BP. Therein, the onset of the LGCP within the Pupuke sequence at ~28.5 cal. kyr BP closely matches cooling following AIM 3 in the EPICA Dronning Maud Land (EDML) ice core sequence at ~27.9 cal. kyr BP (EPICA, 2006), whilst enhanced glacial conditions from ~21.0 cal. kyr BP within the Pupuke sequence also broadly coincides with cooling following AIM 2 at ~23.0 cal. kyr BP (EPICA, 2006). Importantly therefore, the Pupuke sequence provides further evidence that mid-latitude New Zealand observed an in-phase relationship to Antarctic late-Quaternary paleoclimate, at least during the LGCP (e.g., Augustinus et al., 2011a).

Reduced abundance of tall podocarp trees within New Zealand during the LGCP was abruptly reversed at ~18.0 cal. kyr BP by climatic amelioration to warmer, wetter conditions of lesser seasonal extremes, concomitant with a contraction of grassland (Alloway et al., 2007). The boundary of T1 at ~18.5 cal. kyr BP within the Pupuke
composite sequence therefore closely ties with previous research as does a delay of ~2.0 kyr in the onset of increased aquatic productivity. For instance, a delay of ~2.0 kyr in recovery of aquatic biomass occurred within Onepoto where podocarp forest expansion began at ~18.0 cal. kyr BP but which initially resulted in little change to aquatic biomass until ~16.0 cal. kyr BP, possibly recording a delayed increase in precipitation but more likely, local site morphometry (e.g., steep sides require marked increase to lake level prior to significant change in available photic zone and aquatic biomass) (Augustinus et al., 2011b).

A distinguishing feature of the LGIT within the NNI is the complexity of responses exhibited at sites, which has prevented identification of a Late Glacial Reversal (LGR) as either a corollary to the Antarctic Cold Reversal (ACR; ~14.7 to 12.5 cal. kyr BP) or Younger Dryas (YD; ~12.9 to 11.6 cal. kyr BP) (Alloway et al., 2007). The brief extent of an ACR or YD event further inhibits the identification of an LGR within many proxy records, in particular, palynological floras which might not record much change were the LGR either short in duration or of low magnitude. Likewise, the maritime climate and lower elevation of sedimentary archives in the NNI might dampen any response to the ACR or YD (Newnham et al., 2007a). Thus although Sandiford et al (2003) found little evidence of an LGR within the Pukaki pollen sequence, the authors note that the site flora might have been insensitive to changes noted by increased landscape disturbance and cooling in Northland (Newnham, 1992), offshore (Wright et al., 1995) and within the central North Island (McGlone and Topping, 1977; Newnham and Lowe, 2000). A consensus is emerging of a return to relatively dry, cool paleoclimatic coeval with an LGR in New Zealand between ~14 and 11 cal. kyr BP (Turney et al., 2003; Alloway et al., 2007; Williams et al., 2009). For instance, Newnham and Lowe (2000) detail grassland expansion at Kaipo wetland between ~13.8 and 12.4 cal. kyr BP. Likewise, McGlone and Topping (1977) noted the restriction of warmer temperate forest taxa at Otamangakau wetland from ~15.5 to 14.7 cal. kyr BP and a more marked expansion of grassland taxa prior to deposition of the Waiohau tephra (~13.6 ± 0.2 cal. kyr BP). An LGR has also been noted within Auckland where it occurs as a short-lived decline in lake levels and expansion of grassland (Alloway et al., 2007; Newnham et al., 2007a). For instance, a decrease in the Pukaki LPG ratio and Onepoto TOC-concentration have been proposed as the LGR although the latter commenced broadly coeval with the Waiohau tephra (Augustinus, 2007). Augustinus et al. (2011a,b) also note shallowing and increased water stress at Onepoto which resulted in greater erosional influx, decrease in biogenic silica concentration and reduced abundance of *D. cupressinum* from ~14.0 to 12.5 cal. kyr BP. Analysis of laminations within the Onepoto sediment sequence also revealed an ACR response through greater spectral power (~2-7, 15-30, and 70-120 yr band) in lamination thicknesses following the Rotorua tephra (~15.4 ± 0.3 cal. kyr BP) and prior to the Waiohau tephra (Pepper et al., 2004). These spectral bands are believed to be associated with El Nino Southern Oscillation (ENSO; 2-7 yr) and Inter-decadal Pacific Oscillation (IPO; 15-20 and 50-70 yr) behaviour which likely briefly ‘switched on’ during the LGR by greater southwesterly airflow and consequent zonal regimes (e.g., cooling and drying) (Pepper et al., 2004).

The Pupuke composite sequence records marked paleoclimatic change coeval with the ACR. Initial cooling and increased aridity occurred from ~14.4 to 13.8 cal. kyr BP as recorded by a reduction in biological productivity, heightened erosion and depletion of δ¹⁸O_Diatom (Figure 7.2). An abrupt return to ameliorating climate occurred from ~13.8 to 12.8 cal. kyr BP, and resulted in substantial influx of highly organic sediment, increasing MAR and
mirrored by increased biomass, reduced erosional influx as well as hydrochemical changes that support a warmer, more productive interval (e.g., greater TS and DI-DRP concentration) (Figure 7.2). Although marked increases to biomass and productivity cease by ~12.8 cal. kyr BP, a lack of corresponding changes in erosional influx suggests this period marks the return to transitional paleoclimate of lower warmth/moisture availability to that of the prior LGIT peak. The Pupuke composite sequence suggests the YD chronozone was a period of resumed warming whilst the ACR corresponds to a marked cooling and drying of paleoclimate of short duration. In addition to earlier coeval declines in productivity and biomass proceeding AIM 3 and 2, the presence of an ACR-like climatic reversal within the Pupuke composite sequence further demonstrates an in-phase relationship with Antarctica.

The early Holocene (~12 to 10 cal. kyr BP) was a highly productive period throughout the NNI as recorded by palynological floras which record a shift from a conifer-hardwood forest composed mostly of *D. cupressinum* (Rimu) and *Prumnopitys taxifolia* (Matai) to more frost-sensitive and thermophilous taxa including an expansion of *Metrosideros* spp. (Pohutakawa) (Newnham and Lowe, 1991; Ogden et al., 1992; Newnham et al., 1995). Notable increases in the abundance of tree ferns and *Ascarina lucida* (Hutu) from ~11 to 9 cal. kyr BP also demonstrate increased moisture availability at Pukaki maar (Sandiford et al., 2003) as does increased concentration of TOC and enrichment of δ¹³C within Onepoto maar (Augustinus et al., 2011a), and similar expansion of thermophilous forest vegetation at Lake Kohuora (Newnham et al., 2007a). Horrocks et al (2005) also noted increased TOC concentration at Lake Pupuke including increased terrestrial biomass that recorded a shift to more complex forest. Heightened productivity is also recorded in the Pupuke composite sequence during the early Holocene (~10.2 to 8.0 cal. kyr BP) by greater TOC, TN and TS influx as well as enriched δ¹³C, whilst coeval increases in C/N ratios imply a change to OM-source to favour terrestrial biomass. This marks the expansion of thermophilous forest within the Auckland region as well as the presence of frost-sensitive flora (e.g., *A. lucida*), implying a shift in regional airflow to a more stable regime of mild, moist paleoclimate during a ‘thermal optimum’ (Newnham et al., 2007a). Likewise, the Waitomo master speleothem δ¹⁸O sequence observes more enriched values from a peak wet period at ~10.8 cal. kyr BP (Williams et al., 2004).

The mid-to-late Holocene is poorly understood in the Auckland region due to a postglacial marine transgression that breached several crater maars ~7-8 cal. kyr BP with the exception of Lake Pupuke (e.g., Horrocks et al., 2005). However, several paleoclimatic records exist for other sites within the NNI which demonstrate a mid-to-late Holocene (~7-6 cal. kyr BP) expansion of mixed-Kauri (*Agathis australis*) forest communities (Newnham et al., 1993; Newnham, 1999, 2007a). A shift from moist early Holocene conditions to markedly drier paleoclimate likely resulted in greater disturbance and landscape-scale forest destruction by fire and drought (Kershaw and Strickland, 1988; Ogden et al., 1992; Horrocks et al., 2005). Kauri expansion was therefore at the expense of less disturbance-resistant forest taxa (Newnham, 1999). Abrupt declines in terrestrial biomass and increased erosion occurred at Pupuke from ~7.6 to 5.7 cal. kyr BP supporting a proposed increase in catchment disturbance. Heightened coeval diatom productivity, especially amongst meroplanktic taxa, suggests limited change to lake level and precludes the likelihood of drought as the cause of disturbance at Pupuke. Likewise, Lancashire et al (2002) reconstructed high lake levels and intermittent flooding from diatom assemblages at
Crater Hill from ~7.5 to 5.0 cal. kyr BP offering little support for greater aridity within Auckland at this time. The expansion of Kauri within Auckland from ~7 cal. kyr BP might therefore record a response to greater canopy exposure through more frequent destructive windstorms (Ogden et al., 1992).

A shift from relatively moist to drier conditions occurred throughout the NNI from ~6 cal. kyr BP, marked by the expansion of drought-tolerant taxa (e.g., Libocedris spp., Phyllocladus spp., A. australis) (Ogden et al., 1998; Newnham, 1999; Newnham et al., 2007a). The coeval onset of thermal stratification at Lake Pupuke from ~5 to 6 cal. kyr BP indicates increasing frequency of dry, clear summers (e.g., clear skies would permit greater insolation and generation of a strong thermocline). Likewise the onset of rising aquatic nutrient availability, biomass, and benthic mixing from ~5.7 cal. kyr BP confirms the onset of strengthened thermally-stratified conditions at Pupuke accompanied by strong overturn and diatom community shifts first to benthic than to meroplanktic taxa. A coeval rise in Pupuke composite sequence C/N ratios >20 also demonstrates a return to greater terrestrial OM influx and productivity following a reduction in catchment disturbance. Thus the onset of thermal stratification at Lake Pupuke is tied to reduced disturbance, greater biomass and increasingly dry, clear summers to encourage formation of a stable thermocline. Drier paleoclimate has also been reconstructed from ~6.2 cal. kyr BP in the Waitomo master speleothem record in which δ18O values oscillate about a declining trend that peaks at ~3 cal. kyr BP (Williams et al., 2004). Increased seasonality is evident in the Pupuke composite sequence from ~3.2 cal. kyr BP through more intensely reducing conditions (necessary to enrich δ15N) and oxidising conditions at overturn (to increase Mn/Fe ratios). Moderate concentrations of TS over the last ~5.5 kyrs underscores the greater oxygenation of bottom waters by overturn as greater overall biomass would otherwise have resulted in much higher sedimentary TS abundance (e.g., as per the early Holocene). Increased seasonality has also been noted in several reviews of Holocene paleoclimate with more frequent droughts in the NNI from ~3-4 cal. kyr BP (e.g., Newnham et al., 1999, 2007a).

Warm, dry conditions across the NNI presently accompany westerly airflow and zonal regimes (Lorrey et al., 2007). Thus reduced effective precipitation through enhanced westerly and southwesterly airflow from ~6 cal. kyr BP, intensifying from ~3 cal. kyr BP, might explain the concomitant onset of thermal stratification and its subsequent intensification at Lake Pupuke by ~5.7 and ~3.2 cal. kyr BP respectively. An increasing gradient in polar-equatorial air pressure from ~5-6 cal. kyr BP, resulting in strengthened westerly airflow and zonal regimes, has been suggested as a cause of greater coeval Southern Hemisphere seasonality (Shulmeister et al., 2004; McGlone et al., 2010; Putnam et al., 2010). It is also worth noting that enhanced southerly and southwesterly airflow was also accompanied by strengthened El Niño Southern Oscillation (ENSO) within the Southern Hemisphere (Shulmeister et al., 2006). ENSO activity is associated with marked seasonality in temperature and precipitation patterns (Lorrey et al., 2007). For instance, positive excursions in the Southern Oscillation Index (SOI), so-called La Nina events, generate frequent warmer and wetter trough regimes (Kidson, 2000). Negative excursions (El Niño events) result in cooler and drier zonal regimes (Kidson, 2000). Thus the combination of heightened westerly and southwesterly airflow, more frequent zonal regimes and enhanced ENSO variability from ~5-6 cal. kyr BP, intensifying further from ~3.2 cal. kyr BP, offers an explanation of observed paleolimnological change in the Pupuke composite sequence. The absence of inferred changes in lake level at
Pupuke from ~5.7 cal. kyr BP until today necessitates a complex reorganisation of seasonal airflow across the NNI favouring greater zonal airflow in summer and greater trough or blocking regimes in winter (e.g., drier summers, wetter winters). Continued zonal dominance would otherwise reduce lake level possibly to the point of inhibiting thermal stratification at the site due to its unusually deep thermocline (~20-30 m) (Section 2.4.1.2. Temperature and Thermal Stratification). This is also reflected by modern climate at Lake Pupuke which exhibits marked seasonal variation in precipitation including dry (~130 mm), calm summers and wet (~405 mm), windy winters (Section 2.4. Climatology).

The arrival of human migrants to New Zealand is a topic of great debate (e.g., Anderson, 1991; Sutton, 1994). Increasing proxy evidence supports a date of ~0.7-0.8 cal. kyr BP (e.g., McFadgen, 1994; Ogden et al., 1998; McGlone and Wilmshurst, 1999; Horrocks et al., 1999, 2001). Heightened erosion, reduced terrestrial biomass and greater runoff tied to the arrival of Polynesian settlers at Lake Pupuke have been inferred from greater clastic influx, reduced C/N and depleted δ¹⁸O_Diatom and δ³⁰Si_Diatom of composite sediments from ~0.7 cal. kyr BP to present. The coincidence of changes in erosional influx, nutrient availability, algal ecology and stable isotope cycles at Pupuke thereby indicate the onset of anthropogenic catchment modification. The strongest evidence of anthropogenic activity within the Pupuke composite sequence is presented by the order of magnitude change to Magnetic Susceptibility (MS) and MAR observed from ~0.7 cal. kyr BP to present which is also noted at Pupuke in Horrocks et al (2005) and Striewski et al (2009) (Figure 7.2). Both studies tie the latter to fire clearance generating greater erosion and influx of catchment soils. For instance, Horrocks et al (2005) note a corresponding increase in charcoal and Pteridium spp. spore concentration coeval with a decline in tall tree pollen at the onset of exponential increases to MAR just after deposition of the Rangitoto tephra (~504 ± 5 cal. yr BP). Moreover, increased MS, sediment influx and reduction in terrestrial biomass have also been applied to infer Polynesian arrival at a number of lake and swamp sites throughout the NNI (McGlone, 1983; McGlone et al., 1994; Elliot et al., 1995, 1998; Higham and Jones, 2004). Extensive use of fire to clear native vegetation would explain a concomitant decrease in the proportion of terrestrial OM reaching Lake Pupuke from ~0.7 cal. kyr BP. Similarly, reduced catchment vegetation would increase rates of soil erosion offering an explanation for coincident rises in sedimentary MS and Ti-abundance. A consequent increase in runoff would also result in the observed depletion of δ¹⁸O_Diatom through an associated increase in effective precipitation. The continuation of heightened erosion, limited terrestrial biomass and greater runoff is evidence of continued catchment modification through the interval of European colonisation of the NNI (e.g., from the 19th Century [Augustinus et al., 2006]). For instance, a corresponding intensification of land use resulted in even greater deforestation across the NNI (to ~55 % of pre-indigenous levels [Newnham, 1999]). Although the Pupuke composite sequence has not been sampled in sufficient detail here to record historic changes, a high-resolution reconstruction by Augustinus et al (2006) has presented a date for European arrival in Auckland through associated catchment activity and exotic flora from ~1840 AD.
7.4 **Comparison with the NZ-INTIMATE Climate Event Stratigraphy**

The degree of similarity between the Pupuke composite sequence and regional changes within the NNI highlight the likelihood that it is an accurate and detailed record of late glacial terrestrial paleoclimate in New Zealand. It can therefore add to the NZ-INTIMATE climate event stratigraphy constructed by Alloway et al. (2007). What follows is a brief comparison of NZ paleoclimatic stratigraphy to the Pupuke composite sequence drawing upon key palynological, glacial, speleothem and marine records beyond the Northern North Island.

7.4.1 **Palynological Records**

A large number of palynological investigations of late Quaternary paleoclimate have been mounted in New Zealand (e.g., Newnham et al., 1999, 2007a; Williams et al., 2009). Despite the wealth of studies available, many lack sufficient chronological control or demonstrate sufficient sensitivity to permit their incorporation into the NZ-INTIMATE CES (Alloway et al., 2007). However, three sites contributed significantly to the latter: (1) Otamangakau wetland, Northern North Island (McGlone and Topping, 1977 [previously discussed above]); (2) Kaipo wetland, Eastern Northern Island (ENI) (Lowe et al., 1999 [previously discussed above]); and (3) Okarito Pakihi wetland, Western South Island (WSI) (Newnham et al., 2007b).

The Okarito-Pakihi sequence offers the longest continuous palynological sequence in New Zealand spanning MIS 6 to today (Newnham et al., 2007b). Importantly, the Okarito-Pakihi sequence offers further evidence of the in-phase relationship between changes in mid-latitude New Zealand and Antarctic paleoclimate. For instance, the onset of the LGCP is coincident with cooling in Antarctica from ~30 to 27 cal. kyr BP, manifest in an expansion of grassland communities (Newnham et al., 2007b). A similar expansion of grassland is also recorded from ~21 to 18 cal. kyr BP (Newnham et al., 2007b). These peaks in cooling and declining tree line in the WSI separate a milder interval of paleoclimate evident in greater abundance of podocarp/hardwood forest (Newnham et al., 2007b). LGCP changes in paleoclimate at Okarito-Pakihi closely match those recorded in Pupuke, notably reduced terrestrial biomass from ~27.6 to 26.0 and ~21.0 to 18.0 cal. kyr BP. The earlier onset of the LGCP within the Okarito-Pakihi sequence also supports a Southern Hemisphere ‘lead’ into the LGCP (Vandergoes et al., 2005). Consequently, Vandergoes et al. (2005) have proposed strong cooling in the Southern Hemisphere commenced after perihelion during the Austral winter (~30-35 cal. kyr BP) and a minimum in local insolation propagated throughout the Southern Ocean by changes to oceanic-atmospheric circulation related to variation in Antarctic sea ice extent. This model necessitates that positive changes to regional insolation during the mid-LGCP were insufficient to counter marked Northern Hemisphere cooling at the onset of the LGM (~24 cal. kyr BP) but might explain a possible mid-LGCP interstadial (Newnham et al., 2007b). Similarly, a maximum of Southern Hemisphere insolation at ~22 cal. kyr BP (Berger, 1992) offers a mechanism to explain the earlier deglacial warming exhibited at Okarito-Pakihi (~17-18 cal. kyr BP) and also exhibited at Pupuke (~18-19 cal. kyr BP), compared to Northern Hemisphere warming in the Bölling/Allerød (~14-15 cal. kyr BP) (Alloway et al., 2007).
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).
The Okarito-Pakiri sequence also records an LGR response indicated by catchment disturbance and accompanied by a reversal in montane forest expansion (shift to subalpine shrubland) between ~14 and 11 cal. kyr BP (Figure 7.3) (Newnham et al., 2007b). The latter is however, poorly constrained and moreover, there is mounting evidence of a delay in palynological responses to rapid climate change within New Zealand (e.g., Williams et al., 2009). For instance, a detailed record of LGIT vegetation change has been recovered from Boundary Stream Tarn over the period ~17.5 to 10.0 cal. kyr BP in which pollen and chironomid proxies for paleoclimate disagree in the timing of an LGR event (Vandergoes et al., 2008). Pollen microfossils suggest cooling commenced from ~13.2 cal. kyr BP whilst faunal microfossils offer a more detailed response including a ~2.5 °C drop on modern annual temperature from ~14.2 to 13.5 cal. kyr BP (Figure 7.3) (Vandergoes et al., 2008). Vandergoes et al (2008) note that different seasonal signatures might explain the temporal offset, although Williams et al (2009) suggest a delay in regional vegetation reorganisation is more likely. This offers an explanation of the younger inferred palynological date for the LGR at Boundary Stream Tarn relative to Lake Pupuke (and Kaipo Bog, see below), whilst chironomid-inferred estimates of the LGR from ~14.2 to 13.5 therefore support an inferred LGR from ~14.4 to 13.8 cal. kyr BP at Lake Pupuke.

The palynological record of the LGIT has been substantially improved by the Kaipo bog sequence, 4.4 m of peat with an exceptional tephra (n = 16) and radiocarbon (n = 51) chronology from the late glacial to early Holocene (Lowe et al., 1999; Newnham and Lowe, 2000; Hajdas et al., 2006). The Kaipo sequence offers clear evidence for the LGR. Climatic amelioration occurs from ~18.0 to ~13.8 cal. kyr BP after which expansion of grassland at the expense of lowland podocarp trees occurs until ~12.8 cal. kyr BP (Hajdas et al., 2006). A return to more productive conditions occurs from ~12.8-12.4 cal. kyr BP until Holocene communities are attained by ~11.0 cal. kyr BP (Newnham and Lowe, 2000). The Kaipo sequence thereby supports inferences from Pupuke that an LGR punctuated the LGIT although the precise boundaries of the LGR plainly disagree. As noted however, marked discrepancies between palynological floras and other paleoclimatic proxies have been noted in New Zealand (e.g., Williams et al., 2009). Furthermore, other palynological floras do record marked cooling within the South Island coeval with the LGR inferred at Pupuke. For instance, McGlone et al (2004) demonstrate the presence of an LGR coeval with the ACR at Kettlehole Bog, Eastern South Island (ESI) by forest retreat and grassland expansion from ~14.6 to 13.6 cal. kyr BP. Marked improvement of paleoclimate occurred following the LGR (~13.6 cal. kyr BP) until the early Holocene meaning the YD chronozone was a period of sustained warmth within the ESI as at Pupuke. Palynological evidence for renewed warming during the YD has also been recovered at Durham Road, Southwest North Island (SWNI) in which an LGR event is indicated by grassland expansion between ~14.7 and 13.7 cal. kyr BP followed by expansion of drought- and frost-sensitive taxa (*Ascarina lucida*) until ~12.0 cal. kyr BP and establishment of lowland warm temperate vegetation (Alloway et al., 1992; Turney et al., 2003).

Together these palynological records suggest the onset of deglaciation occurred earlier in New Zealand than typical for a mid-latitude Northern Hemisphere location, and was first expressed in the North Island of New Zealand by ~18 cal. kyr BP before marked warming and expansion of lowland forests in the South Island by ~16 cal. kyr BP (Turney et al., 2003). Climatic amelioration halted and/or reversed to cooler/drier conditions in the
mid-LGIT. Although widely varying dates have been published for the LGR (~14-11 cal. kyr BP; Alloway et al., 2007) more recent palynological as well as beetle and chironomid proxies suggest an LGR response attuned to the ACR (~14.7 to 12.5 cal. kyr BP) with evidence of a potential delay in some palynological floras (Williams et al., 2009).

### 7.4.2 Glacial Records

Glacial records from the South Island of New Zealand are employed here to offer a further comparison to the NZ-INTIMATE CES (e.g., Alloway et al., 2007). Radiocarbon and cosmogenic exposure ages record advances at ~28, 24.5-21.5 and 20.5-19 cal. kyr BP with widespread deglaciation thereafter (Almond et al., 2001; Suggate and Almond, 2005; Schaefer et al., 2006; Williams et al., 2009). The onset of major glacial advances at ~28 cal. kyr BP corresponds to cooling in the EPICA DML ice core record following AIM 3 (e.g., EPICA, 2006), coeval with palynological evidence for a reduction in treelines within the South Island (e.g., Newnham et al., 2007b), as well as the onset of the LGCP within the Pupuke sequence (refer to Figure 7.2). Across the South Island the emerging picture is one of complex glacial behaviour within the LGCP including major glaciation prior to peak cooling in the Northern Hemisphere peak cooling (~24.5-21.5 cal. kyr BP) (Williams et al., 2009).

A highly complex record of glacial advance/retreat further complicated by the uncertainties of exposure dating, exists in the South Island throughout the LGIT and Holocene (Suggate and Almond, 2005; Schaefer et al., 2006; Alloway et al., 2007). Accordingly the evidence for a glacial response to the LGR is equivocal, particularly as lower elevation glaciers subsequently did not undergo marked advances during the LGIT whereas central South Island glaciers record possible ice advances including the contentious Waiho Loop Moraine which has been tied to the YD (Denton and Hendy, 1994), ACR (Turney et al., 2007) and very early Holocene (Barrows et al., 2007a). A recent examination of the Waiho Loop Moraine composition has demonstrated the moraine might represent the end product of a major landslide onto the Franz Josef Glacier (Tovar et al., 2008). A subsequent modelling exercise demonstrated the need for further research to accurately describe glacier dynamics, but stressed that a large landslide could indeed advance the Franz Josef Glacier during the LGIT (Vacco et al., 2010). Thus although evidence exists to suggest an LGR response attuned to cooling in the ACR (e.g., Schaefer et al., 2006; Putnam et al., 2010), until the debate behind its cause can be addressed (e.g., climatic vs. topographic) little can be reliably inferred by comparison to the Pupuke paleorecord.

Less debatable are the mid-to-late Holocene Western South Island (WSI) glacial advances noted by Schaefer et al (2009) at the Mueller, Hooker and Tasman valley glaciers. A salient point is that these glacial ice advances, like those of the LGIT, are restricted to higher elevations within the Southern Alps (Schaefer et al., 2009). The greater elevation and evidence for limited Holocene temperature change within the South Island indicate that variation in precipitation is most likely to have controlled WSI glacial dynamics during the last ~7 kyrs (Colhoun and Shulmeister, 2007). Zonal and trough regimes deliver greater precipitation to the central South Island (Lorrey et al., 2007). Therefore the timing of proposed glacial advances is critical because this helps to identify intervals of greater westerly and southwesterly airflow, generating greater trough and zonal regimes in the WSI.
Atmospheric circulation changes in the southwest Pacific therefore likely control Holocene glacier fluctuations in New Zealand and offer an explanation of their asynchrony with Northern Hemisphere mid-latitude mountain glaciers (e.g., Schaefer et al., 2009). For instance, a total of ~15 pulses of glacier advance and retreat were observed during the last ~7 kyrs: peak glacial advances having occurred at ~6.5 cal. kyr BP, ~3.7-3.2 cal. kyr BP, ~2.3 cal. kyr BP, ~2.0-1.7 cal. kyr BP, ~1.4 cal. kyr BP, ~1.0 cal. kyr BP, ~0.9 cal. kyr BP, ~0.8 cal. kyr BP, ~0.7-0.6 cal. kyr BP, ~0.4 cal. kyr BP and ~0.3 cal. kyr BP (Schaefer et al., 2009). Maximum Holocene ice extent occurred in the South Island at ~6.5 cal. kyr BP, well before the Northern Hemisphere maximum during the Little Ice Age (~0.7-0.2 cal. kyr BP) (Schaefer et al., 2009). More recently, the Interdecadal Pacific Oscillation (IPO) has altered historic glacial extent (e.g., from ~1940 to 1978 negative IPO phase delivered warm, dry conditions in the WSI; from ~1978 positive IPO phase delivered colder, wetter conditions) (Lorrey et al., 2008). The IPO modulates ENSO behaviour on a decadal to multi-decadal time scale (Salinger and Mullan, 1999). Thus, combined changes to the IPO and ENSO might have induced changes to Holocene atmospheric circulation (e.g., trough, zonal and blocking) within the WSI and either in-phase or opposing regimes in the NNI (e.g., Lorrey et al., 2007). The potential for sustained shifts in atmospheric circulation were highlighted by Harrington (1952) who observed that a southward shift of the southern westerlies in response to migration of the Subtropical Front (STF) would cause fewer cold, moist Southern Ocean airmasses to transect the Southern Alps, thereby reducing precipitation and instigating glacial retreat (Putnam et al., 2010). The inverse has been cited by Denton et al (2010) as a potential explanation of the LGR within New Zealand, namely that warm conditions in the North Atlantic (during the Bölling/Allerød interstadial) permitted northward-migration of the STF, an expanded polar cell in the Southern Ocean and northward-shifted westerlies (e.g., ice advance in response to equatorward migration of the STF followed by poleward retreat and a resumption of warming during the YD). In a similar vein, mid-to-late Holocene glacial advances could record greater southwesterly airflow through concomitant equatorward migration of the STF. If so, the mid-Holocene peak in glacial extent therefore ties with the proposed intensification of southwesterly airflow and zonal regimes in New Zealand through intensification of ENSO variability from ~5-6 cal. kyr BP (Shulmeister et al., 2004).

Peaks in the Pupuke composite δ13C record might offer a corollary to the Southern Alp glacial records as increased westerly and southwesterly circulation delivers more frequent zonal regimes to the WSI (Lorrey et al., 2007). Antiphased responses within the NNI to increased zonal regimes include greater warmth, reduced effective precipitation and clearer skies (Lorrey et al., 2007), permitting the development of a more stable thermocline for a longer seasonal period within Lake Pupuke. Increased stability of thermal stratification at Lake Pupuke would effectively starve primary producers of dissolved inorganic Carbon (DIC) which would remain trapped in the hypolimnion, resulting in the uptake of bicarbonate (e.g., δ13C enrichment of organic Carbon). Thus enrichment peaks in composite δ13C from ~6.5 to 5.7 cal. kyr BP, ~4.2 to 2.9 cal. kyr BP and ~1.7 to 1.1 cal. kyr BP could correspond to glacial advances at ~6.5, ~3.7-3.2, and ~2.0-1.7, ~1.4 and ~1.0 cal. kyr BP, provided the latter are indeed responses to equatorward migration of the STF accompanied by increased westerlies and southwesterlies (refer to Figure 7.4). The above links are tentative but improved dating and high-resolution sampling of the Pupuke composite sequence for stratification indicators (e.g., for δ13C, diatom
taxonomy) could offer an exciting proposal because if the case, the continuous sedimentary archive at Lake Pupuke might offer a high-resolution record of changing ocean-atmosphere dynamics in the South Pacific throughout the Holocene through changes to the Subtropical Front (STF) and a strengthening of ENSO, whose capacity to alter the strength of zonal westerlies offers a link to valley glaciers in the central South Island (e.g., Putnam et al., 2010).

Figure 7.4: Holocene glacial advances near Mount Cook in New Zealand’s Southern Alps, together with published 14C ages on soils buried by Mount Cook glacier expansion events over the past 4000 years (probability plots are derived from 10Be 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 δ13C. 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 δ13C at Lake Pupuke. (Modified from Schaefer et al., 2009: 625).
7.4.3 Marine Records

Several continuous marine sediment cores are available for comparison to the Pupuke composite sequence including the SO136-GC3 (42º18’S, 169º53’E on the Challenger Plateau), DSDP site 594 (45º31.41’S, 174º55.85’E east of New Zealand) and the MD97-2120 core (45º32.06’S, 174º55.85’E east of New Zealand). From these, Barrows et al (2007b) demonstrate a close temporal connection between reconstructed sea surface temperatures (SSTs) in the Southern Ocean and southern New Zealand. Greater variability and cooling occurred from ~35 to 20 cal. kyr BP with maximum cooling expressed in the LGM (Barrows et al., 2007a). Likewise, the onset of the LGCP and increased cooling recorded by terrestrial flora from ~29 to 27 cal. kyr BP is also evident in rapidly fluctuating SSTs both east and south of New Zealand (Barrows et al., 2007a). Thus a similar response in the Pupuke composite sequence from ~27.6 to 26.0 cal. kyr BP might record enhanced glacial conditions during the early LGCP.

Abrupt warming is recorded by increased SSTs in the Southern Ocean from ~20-18 cal. kyr BP (Barrows et al., 2007a) coeval with increased biomass, reduced erosion and increasing lake level at Lake Pupuke from ~18.5 cal. kyr BP (refer to Figure 7.5). Deglacial warming was complex with evidence for surface warming at MD97-2121 from ~21 cal. kyr BP, nearly ~3 kyrs ahead of benthic waters (Figure 7.5) (Carter et al., 2008). Warming permitted SSTs to approach Holocene values by ~15 cal. kyr BP (Carter et al., 2008). However, the warming was not monotonic although the cooling associated with the ACR was likely weak, preventing its precise definition (Williams et al., 2009). For instance, whilst Barrows et al (2007b) found little evidence of an ACR or YD chronozone, Carter et al (2008) provide evidence of the ACR at MD97-2121, a site particularly sensitive to the influxes of sub-tropical water (STW) and sub-Antarctic water (SAW). A deglacial trend to more depleted benthic foraminifera δ¹⁸O halted from ~14.1 cal. kyr BP to ~12.4 cal. kyr BP (Carter et al., 2008). Corresponding SST estimates were relatively stable at ~15-16 ºC from ~13 to 11 cal. kyr BP whilst seasonality also reduced until ~11.5 cal. kyr BP (Carter et al., 2008). Calvo et al (2007) also record the ACR in core MD03-2611 (36º44’S, 136º33’E Great Australian Bight) through a two-step deglaciation from 11 ºC at ~19 cal. kyr BP to 19.3 ºC by the Holocene, including a pause in warming from ~15 to 13.3 cal. kyr BP. Further evidence for an Antarctic-type deglacial pattern is observed in other Southern Ocean marine cores, though again the response is muted (e.g., Pahnke et al., 2003; Lamy et al., 2004; Kaiser et al., 2005). Together these also demonstrate resumed warming following a weakened cold reversal meaning an LGR response at Pupuke between ~14.4 and 13.8 cal. kyr BP followed by a return to warming during the YD is plausible. A coeval increase in windiness and mixing of the upper ocean during the LGR indicates the likelihood of enhanced southerly and southwesterly airflow as a mechanism of reduced temperature in mid-latitude New Zealand, driven by northward migration of the Subtropical Front (STF) (Carter et al., 2008). Northward migration of the STF would permit a greater pressure gradient to develop across mid-latitudes thereby enhancing southerly and southwesterly airflow and resulting in more frequent zonal regimes (Shulmeister et al., 2004).

The early Holocene (~9 to 7 cal. kyr BP) is an interval of greater seasonality and peak SSTs at MD97-2121, SO136-GC11 and DSDP 594 (Carter et al., 2008). Coeval changes within Pupuke including greater biological productivity and biomass also record improved terrestrial paleoclimate. Warmer SSTs in the Southern Ocean
record greater influx of STW and could therefore offer a cause of enhanced productivity at Pupuke through a concomitant increase of moist subtropical airflow resulting in greater precipitation and warmth.

The diffuse signal of changes to the Southern Ocean in the vicinity of New Zealand offers further support for an in-phase response to Antarctica, including cooling between ~35 and 20 cal. kyr BP (Carter et al., 2008). A later but broadly coeval terrestrial response in the NNI at Lake Pupuke (~28.5 to 18.5 cal. kyr BP) is therefore highly plausible. A synchronous onset of deglacial warming of the Southern Ocean at ~20-19 cal. kyr BP suggests the importance of oceanic processes in transmitting Antarctic warming to mid-latitude New Zealand (Carter et al., 2008). However, the muted and delayed response to the ACR within the Southern Ocean (e.g., Pahnke et al., 2003; Lamy et al., 2004; Kaiser et al., 2005) implies a more complex atmospheric/oceanic mechanism (Carter et al., 2008) preventing ready comparison to the Pupuke composite sequence. A resumption of warming during the YD is less equivocal beginning from ~13-13.5 cal. kyr BP (Barrows et al., 2007a; Carter et al., 2008). A broadly coeval increase in biological productivity and biomass commencing from ~13.6 cal. kyr BP at Pupuke is therefore supported by marine core inferences of a close link between mid- and high-southern latitudes. An early Holocene period of heightened productivity at Pupuke is also supported by warmer regional SSTs through greater influx of STW prior to a subsequent decrease in SST and reduced effective precipitation from ~6.5 cal. kyr BP (Nelson et al., 2000; Carter et al., 2008).
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 Globotheria 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 U°37 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).
7.4.4 Speleothem Records

Speleothems provide valuable terrestrial archives of paleoclimate within New Zealand because of their independent chronologies and high-resolution (Alloway et al., 2007). A master speleothem record has been compiled for the North Island (Williams et al., 2004) and the South Island (Williams et al., 2005), which have been reviewed in Williams et al. (2010). The speleothem archive covers the last ~30 kyrs to today with several important climatic events evident in the composite δ¹⁸O and δ¹³C speleothem records (Figure 7.6). The onset of colder climate within the South Island master speleothem is delayed compared to vegetation and glacial changes throughout New Zealand, including Lake Pupuke (~27.6 to 26.0 cal. kyr BP), as cold paleoclimate was not recorded until ~26 cal. kyr BP (Alloway et al., 2007). Low sampling frequency is believed to have led to this discrepancy (Williams et al., 2010). Nonetheless, the speleothem master sequence provides evidence for a ‘mid-LGCP warming complex’ (Alloway et al., 2007: 24) similar in timing to AIM 2 (~24.4 to 22.7 kyr). However, the latter occurred between ~22.4 and 20.8 kyr in the master speleothem sequence, placing it well after corresponding palynological evidence (e.g., ~27 to 21 cal. kyr BP) (Newnham et al., 2007a). Despite the likelihood of delayed responses in the master speleothem sequence, enhanced glacial conditions can be inferred from ~28 to 18 kyr (Williams et al., 2010), coeval with South Island glacial advances and reduced tree-lines throughout New Zealand, and importantly, lake shallowing and increased erosive influx at Lake Pupuke. Enhanced though variable, glacial conditions were inferred from ~23 to 19 kyr (Williams et al., 2005). This could therefore correspond with markedly cooler, drier paleoclimate during the late LGCP at Lake Pupuke from ~21.0 to 19.0 cal. kyr BP.

The South Island master speleothem sequence records climatic amelioration and the onset of the LGIT between ~19.6 and 17.9 kyr (Williams et al., 2005), coeval with increased terrestrial productivity at Lake Pupuke from ~18.5 cal. kyr BP. Increased temperature and precipitation likely continued until an LGR event from ~13.5 to 11.2 kyr (Williams et al., 2005). Whilst the timing of the latter disagrees markedly with the Pupuke composite sequence and palynological evidence from the Kaipo bog sequence (e.g., ~13.8 to 12.8 cal. kyr BP; Hajdas et al., 2006) and Kettlehole Bog sequence (e.g., ~14.6 to 13.6 cal. kyr BP; McGlone et al., 2004), it further establishes the likelihood of an ACR type response, with the YD chronozone a period of resumed warming as recorded by more enriched δ¹⁸O values from ~12.7 kyr (Williams et al., 2005). Several factors could account for the offset in timing of the LGR notably the age uncertainties attached to chronologies and/or regional paleoclimate zone responses being out of phase (e.g., Lorrey et al., 2007). Importantly however, the South and North Island composite speleothem sequences offer further evidence of an early Holocene warm period culminating at ~10.8 kyr as well as a wetter interval from ~10.4 to 8.0 kyr (e.g., recorded by depletion of δ¹³C and δ¹⁸O) (Williams et al., 2010), coeval with heightened productivity at Pupuke from ~10.2 to 8.0 cal. kyr BP. Thereafter relatively mild conditions are inferred from North and South Island speleothems until ~6.5 kyr at which point more, cooler, drier conditions prevailed until ~3.2 kyr (Williams et al., 2010).
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 δ¹⁸O has been corrected for ice-volume effects on δ¹⁸O_Precipitation. (Modified from Williams et al., 2010: 103-104).
CHAPTER EIGHT

Conclusion and Future Research

8.1 Conclusion

The objectives of this thesis were threefold: (1) to develop a high-resolution chronology for the Pupuke sediment sequence; (2) apply novel stable isotopic proxies for paleolimnology to the Pupuke composite sequence; and (3) reconstruct a climate event stratigraphy at Lake Pupuke from ~48 cal. kyr BP to today. A tephra and radiocarbon-based chronology in conjunction with a mixed-effect regression (MER) age-depth model has met objective (1) by providing accurate and precise ages for the entire Lake Pupuke sequence in conjunction with estimates of 95% uncertainty in estimated age. In keeping with INTIMATE protocols, the application of isochronous tephra layers permitted the accurate inter-comparison of the Pupuke composite sequence to other paleo-records from New Zealand (Section 7.4. National Comparison to the NZ-INTIMATE Climate Event Stratigraphy).

Objective (2) has been met through the development of a novel approach to diatom purification including the physical separation and mathematical mixture-modelling of tephra contaminant effects, in addition to the novel application of changes in δ$_{30}$Si$_{Diatom}$ to the paleo-record from Lake Pupuke. A modern lacustrine stable isotope study showed that large variability in lake water δ$_{18}$O and δD occurs due to thermal stratification whilst the lengthy residence time (~30 yrs) coupled to the closed hydrological status, produces evaporative enrichment effects in Lake Pupuke. Consequently, the δ$_{18}$O$_{Diatom}$ record from the Lake Pupuke sequence has offered a remarkable insight into changes in residence time and effective precipitation since ~48 cal. kyr BP. Monitoring of the stable isotopic composition of contemporary diatom silica in Lake Pupuke has also demonstrated the control exerted by thermal stratification upon dissolved nutrients including dissolved Silicon (DSi). Consequently, δ$_{30}$Si$_{Diatom}$ has also been demonstrated to record paleoclimate through changes to DSi-input in runoff, DSi-recycling by mixing and DSi-uptake by diatoms. Coeval changes in δ$_{30}$Si$_{Diatom}$, indicators of effective precipitation (δ$_{18}$O$_{Diatom}$) and diatom abundance further underscore the potential for changes in the Silicon cycle to reconstruct paleoclimate.

The synthesis of multi-proxy paleoclimate inferences at Lake Pupuke from ~48 cal. kyr BP to today in Chapter 7 meets objective (3). Knowledge of the contemporary controls on sediment geochemistry, biological productivity and diatom autecologies has improved the reliability of paleolimnological inferences derived from the Pupuke composite sequence. Combined with the precision of the MER age-depth model, three phases of paleoclimate have been inferred, spanning the last ~48 cal. kyr BP at Lake Pupuke: (1) prior to the Last Glacial Coldest
Period (LGCP) (~48.2-28.5 cal. kyr BP); (2) the LGCP (~28.5-18.5 cal. kyr BP); and (3) the Last Glacial-Interglacial Transition (LGIT) and Holocene (~18.5 cal. kyr BP to today). The timings of paleoclimatic changes inferred at Lake Pupuke closely match those observed in the Northern North Island (NNI) regional climate zone (e.g., Newnham et al., 2007a) as well as those observed in the NZ-INTIMATE climate event stratigraphy (e.g., Alloway et al., 2007).

The period prior to the LGCP at Lake Pupuke is one of relatively high lake level and effective precipitation including a significant aquatic component to the overall biomass. Limited beta diversity in diatom assemblages prior to the LGCP demonstrates that stable hydrological conditions prevailed until ~28.5 cal. kyr BP. However, overall biological productivity was relatively low prior to the LGCP whose onset is very clearly recorded through increases in erosion and sediment supply, reduced lake level and aquatic biomass. Inferred changes in paleoclimate between ~28.5 and 18.5 cal. kyr BP support a reduction in effective precipitation at Lake Pupuke, a trend noted throughout Auckland (e.g., Sandiford et al., 2003; Newnham et al., 2007a). Coeval changes in sediment δ¹³C record the reduction in global pCO₂ during Marine Oxygen Isotope Stage 2 (MIS 2). The Lake Pupuke record provides further evidence of paleoclimatic variability during the LGCP with two phases of severe glacial climate inferred near its onset (~27.6 to 26.0 cal. kyr BP) and termination (~21.0 to 19.0 cal. kyr BP). A return to less severe glacial climate during the interim (~26.0 to 21.0 cal. kyr BP) might record a relatively mild LGCP-interstadial (e.g., Newnham et al., 2007b; Augustinus et al., 2011a).

The onset of warming following the LGCP occurs throughout New Zealand at ~18 cal. kyr BP (e.g., Turney et al., 2006; Newnham et al., 2007a,b; Williams et al., 2010), coeval with warming in the EPICA DML isotope sequence (EPICA community members, 2006) and punctuated by a Late Glacial Reversal (LGR) between ~14 and 12 cal. kyr BP (e.g., Lowe et al., 1999; Williams et al., 2005; Alloway et al., 2007; Calvo et al., 2007; Carter et al., 2008; Vandergoes et al., 2008; Williams et al., 2009). Within the Lake Pupuke paleoenvironmental-record the onset of the Last Glacial-Interglacial Transition (LGIT) is recorded by a shift to warmer, wetter climate from ~18.5 cal. kyr BP. The LGIT is interrupted by a complex climatic reversal from ~14.4 to 13.8 cal. kyr BP which resulted in a decline in lake level and biological productivity accompanied by increased erosion. The timing of the LGR at Lake Pupuke thus overlaps with the Antarctic Cold Reversal (ACR) within the EPICA Dronning Maud Land isotope record (~14.7 to 12.5 cal. kyr BP [EPICA community members, 2006]). The LGR within the Pupuke sediment record is followed by enhanced biological productivity, higher lake level and reduced erosion including a peak in the sedimentation of organic matter between ~13.8 and 12.8 cal. kyr BP which continues though at reduced level into the early Holocene. The Younger Dryas (YD) Chronozone was therefore a period of ameliorating climate at Lake Pupuke.

The early Holocene is noted at Lake Pupuke by greater terrestrial and aquatic biomass from ~10.2 to 8.0 cal. kyr BP followed by a period of increased disturbance and reduced terrestrial biomass, though with continued high lake level and aquatic biomass from ~7.6 to 5.7 cal. kyr BP. The onset of intense thermal stratification at ~5.6 cal. kyr BP is coeval with estimates of heightened westerly circulation across New Zealand and likely
corresponds to an increased frequency of zonal regimes (e.g., Shulmeister et al., 2004, 2006), permitting seasonal development of a stable thermocline at Lake Pupuke. Further intensification of seasonality occurred from ~3.2 cal. kyr BP resulting in greater disturbance of bottom waters at overturn, resuspension of key limiting nutrients and the dominance of heavily silicified meroplanktic diatoms which are reliant upon overturning circulation for their resuspension in Lake Pupuke (Cassie, 1989). Natural eutrophication of Lake Pupuke occurred from ~5-6 cal. kyr BP likely as a consequence of intense thermal stratification which permits the release of phosphate and nitrates in benthic anoxia and their return to the photic zone by stronger mixing at overturn (Holmes, 1994). A trend to higher nutrient loads was accentuated by the likely arrival of Polynesian settlers at Lake Pupuke ~0.6 cal. kyr BP, inferred from greater coeval catchment disturbance, sediment delivery and reduced terrestrial biomass.

8.2 Future Research and Improvement

Several lines of future research can be identified from work explored in this thesis. There is a clear need for additional investigations of the paleoenvironmental records of other maar craters in Auckland as despite the multi-proxy approach applied here, the possibility remains that the changes in Lake Pupuke are site-specific and therefore not representative of changes in the wider Auckland region and beyond. The priority for further work on the Pupuke sediment record includes:

1. Age control – further analysis of cryptotephra can identify the presence of as yet unidentified tephra markers to better refine the age-depth model employed for the Lake Pupuke sequence. Further radiocarbon analyses can also offer improved chronological control of the Pupuke sediment record.

2. Proxy sampling – further analysis of sedimentary geochemistry ($\delta^{13}$C, $\delta^{15}$N) and diatom taxonomy can offer valuable insight into nature and intensity of Holocene seasonality. It was noted that the frequency of zonal regimes has likely resulted in contemporary seasonality which is a key driver of thermal stratification at Lake Pupuke. Thus a higher-resolution sampling approach might offer further insights to changes in mid-latitude circulation within the Southern Hemisphere. Likewise higher-resolution sampling of the interval ~14.5 to 12.0 cal. kyr BP is needed to further define the extent and nature of the inferred LGR event in the Lake Pupuke record.

3. Proxy development – the application of $\delta^{30}$Si$_{\text{Diatom}}$ to the Pupuke sediment record has demonstrated the capacity of this approach to record changes in paleoclimate. However, as with $\delta^{18}$O$_{\text{Diatom}}$, downcore paleoenvironmental inferences are hindered by uncertainty regarding the impact of diatom stable isotope vital effects. Therefore further research is needed to assess the extent to which inter- and intra-species isotopic variation exists, the importance of silica maturation on isotopic composition and whether a post-depositional effect exists (e.g., whether $\delta^{18}$O$_{\text{Diatom}}$ and $\delta^{30}$Si$_{\text{Diatom}}$ signatures correspond to life or death of the algae). If isotopic signatures correspond to death of the algae, further research is also needed to
identify whether this signature is fixed during settling through a water column, or whether diatom isotopic signatures are relatively mobile and entrained over a longer period through sediment pore-water interactions. High resolution sampling is required to provide a detailed record of $\delta^{18}$O$_{\text{Diatom}}$ changes over the last ~0.6 kyrs of the Lake Pupuke record, and whether a trend to increasingly depleted $\delta^{18}$O$_{\text{Diatom}}$ values corresponds to paleolimnological changes in other proxies for hydrology, or whether this represents a natural process of enrichment in biogenic silica over time.

4. Extension of the sediment record – deeper coring of Lake Pupuke sediment could recover a continuous paleoclimatic history of mid-latitude New Zealand from the formation of the maar crater lake (~250 cal. kyr BP). Given the evidence that Lake Pupuke has captured a record of changing regional oceanic/atmospheric circulation during the last ~48 kyrs, extending the paleoenvironmental record through two glacial-interglacial cycles could prove of exceptional value in the debate regarding the nature and drivers of inter-hemispheric climate teleconnections.

5. The application of $\delta^{30}$Si$_{\text{Diatom}}$ to paleolimnology is reliant upon an improved understanding of the lacustrine controls on DSi-availability. Further investigations are needed to establish the contemporary DSi regime at Lake Pupuke so as to better understand the likely response of $\delta^{30}$Si$_{\text{Diatom}}$ to lacustrine or catchment forcing factors. For instance, non-terrestrial sources of DSi could potentially contribute to the lacustrine DSi reservoir despite limited evidence for such influences in SEM micrographs (e.g., absence of clays or aeolian sands). If aeolian influx of DSi is substantial, glacial-interglacial changes to $\delta^{30}$Si$_{\text{Diatom}}$ might record changes in aeolian transportation of exposed coastal shelf sediments.

This thesis also examined the application of lake cellulose purification approaches for lake sediment with the aim of reconstructing a complimentary $\delta^{18}$O$_{\text{Lake}}$ record to that provided by $\delta^{18}$O$_{\text{Diatom}}$ for the Pupuke sediment record. Aquatic cellulose offers an indirect record of $\delta^{18}$O$_{\text{Lake}}$ but one which does not suffer from taxonomic or other vital effects (Wolfe et al., 2007). Instead aquatic cellulose is enriched by +27 ‰ on $\delta^{18}$O$_{\text{Lake}}$ (Wolfe et al., 2007). Two alternative approaches to cellulose purification were undertaken that involved a detailed chemical and physical purification approach (Wolfe et al., 2007; Wissel et al., 2008) but which could not isolate pure cellulose of sufficient quality to permit IRMS analysis (refer to Appendix G). Transmitted-light microscopy demonstrated that silicates were extracted with cellulose by the Wolfe et al., (2007) procedure and non-organic inclusions were demonstrated to contaminate precipitates extracted by the Wissel et al., (2008) method. The published methods were also adapted with the inclusion of additional stages for bleaching lignins and the introduction of an acid-leaching stage as per Wolfe et al., (2007) in the cellulose precipitation approach of Wissel et al., (2008). The latter removed iron and manganese oxides as evident in the change from red/brown to white/yellow precipitates but elemental analyses indicated contributions of non-organic material to sample extracts. Further research is needed to permit the isolation of pure cellulose from sediments with contaminants of similar density and capable of dissolution under leaching approaches prior to attempts to employ this proxy for paleolimnology in Lake Pupuke.
Appendix A

APPENDIX A

Sediment Core Logs

Please refer to the CD included with this thesis.
APPENDIX B

Autecologies of subdominant (30% > n > 5%) diatom taxa in the Pupuke composite sequence

*Cocconeis placentula*: is a moderately-sized (<10 to 100 μm) epiphytic member of a relatively small genus comprised of elliptical members (Round et al, 1990). Despite limited diversity, the genus is very widely tolerant of pH (circumneutral to alkaliphilous) and trophic state (exception: intolerant of oligotrophy) (Van Dam et al, 1994). *C. placentula* is suited to benthic habitats and readily attaches to exposed substrates (e.g., macrophytes, rock, algae) such that it is a good indicator of well-mixed water columns (Cassie, 1989). In Lake Pupuke the species is associated with summer stratification where it blooms upon *Valisneria gigantea* rafts which collect on shallow shelves and yield essential nutrients (Cassie, 1989). The taxon has moderate Oxygen requirements (>50% saturation) and is β-mesosaprobous (Van Dam et al, 1994).

*Cyclotella cf. planctonica*: is a small (<10 to 40 μm), freshwater, circular, planktonic taxon within a very large genus (>100 spp. described) (Round et al, 1990). They are a Spring and late Summer-Autumn blooming species indicative of oligo/mesotrophic systems (Brugam, 1983, 1993; Bradbury, 1988). The species has fairly high Oxygen requirements (>75% saturation) and is β-mesosaprobous (Van Dam et al, 1994).

*Cymbella microcephala*: is a small (10 to 30 μm), elliptical or elongate, benthic taxon indicative of epilithic habitats in rivers and lakes (Round et al, 1990). It is also known to exist in aerophilous habitats and prefers oligotrophic systems (Round et al, 1990). Accordingly, it is indicative of high levels of dissolved Oxygen (continuously high, >100% saturation) and is oligosaprobous (Van Dam et al, 1994).

*Diatomella balfouriana*: is a small (10 to 50 μm), elliptical to linear, benthic taxon indicative of lower nutrient loads (Van Dam et al, 1994). The species is also tolerant of semi-aquatic aerophilous environments and is thus an indicator of ephemeral aquatic habitats and highly variable lake level (Dam et al, 2001). The species is tolerant of moderate Oxygen levels (>50% saturation) and is α-mesosaprobous (Van Dam et al, 1994).

*Epithemia adnata and Epithemia sorex* (described together as they share similar autecologies): are moderately-sized (30 to 150 μm), elliptical or elongated, freshwater, benthic taxa that attach readily to exposed plant or rock surfaces (Round et al, 1990). They are capable of fixing atmospheric Nitrogen via endosymbiotic cyanobacteria and tolerate moderate nutrient concentrations (meso/eutrophic) as well as alkaline environments (alkalibiontic) (Round et al, 1990). The species have fairly high Oxygen requirements (>75% saturation) and are β-mesosaprobous (Van Dam et al, 1994). Accordingly the species currently blooms throughout stratified summers during nutrient scarcity in which *Epithemia* spp. can synthesis nitrate and nitrite (Cassie, 1989).
*Gomphonema exiguum*: is a moderately-sized (<10 to 100 μm), freshwater, elongate to elliptical benthic taxon indicative of epiphytic and epilithic habitats (Round et al, 1990). The species is circumneutral but requires continuously high levels of Oxygen (~100 % saturation) and is β-mesosaprobous (Van Dam et al, 1994). Accordingly the genus is pollution sensitive and indicative of mesotrophy (Van Dam et al, 1990).

*Nitzschia amphibia*: is a moderately-sized (<10 to 70 μm), freshwater, elliptical or lanceolate taxon indicative of benthic habitats and neutral to alkaline waters (alkaliphilous) (Round et al, 1990). It is tolerant of high nutrient loads and is polytrophic (Van Dam et al, 1994). Likewise it has only moderate Oxygen requirements (>50 % saturation) and is α-mesosaprobous (Van Dam et al, 1994). Cassie (1989) and Holmes (1994) note Nitzschia spp. bloom throughout mild winter months in Lake Pupuke.

*Staurosira pinnata* (previously recorded as *Staurosirella pinnata*) and *Staurosira aff. venter* (described together as limited taxonomic information available on latter): is a small (<10 to 35 μm), freshwater, elliptical to elongate taxon indicative of open-water and benthic habitats (Round et al, 1990). The taxon is alkaliphilous and indicative of mesotrophic conditions (Van Dam et al, 1994). This species is also tychoplanktonic and requires continuously high Oxygen levels (~100 % saturation) as well as limited BOD (β-mesosaprobous) (Van Dam et al, 1994).

*Stephanodiscus cf. alpinus*: is a small (<10 to 40 μm), freshwater, planktonic taxon (Round et al, 1990). Many species within the genus are associated with productive waters and are robust indicators of eutrophication (Van Dam et al, 1994). Similar species within the *Stephanodiscus* genus (*S.meyerii*, *S.parvus* and *S.flabellatus*) are typical of high Phosphorus content, warm and shallow water where heavy mixing favours turbid conditions (Bradbury et al, 1994). Consequently, the species is tolerant of moderate Oxygen availability (>50 % saturation) and BOD (α-mesosaprobous) (Van Dam et al, 1994).

*Synedra capitata*: is a large (120 to 500 μm), linear, freshwater, benthic taxon indicative of low to moderate nutrient loads (oligo/mesotrophy) and pH (alkaliphilous) (Round et al, 1990). The large size of species in this genus necessitates relatively elevated levels of dissolved Si present in a water body (Bradbury et al, 1994). Morley (2005) employed *Synedra acus* as an indicator of enhanced catchment erosion within Lake Baikal. Similarly, experiments have demonstrated *S.acus* to be favoured by lower Phosphorus availability (Interlandi et al, 1999). Indeed the species cannot tolerate much less than continuously high levels of Oxygen availability (~100 % saturation) and is oligosaprobous (Van Dam et al, 1994). Thus conditions of nutrient scarcity, limited biomass and enhanced competition favour *Synedra* spp. growth in addition to greater Si-availability endearing the taxon potential to indicate short-lived influxes of Si (e.g., changes to erosion, ashfall).
APPENDIX C

Diatom Species List

Achnanthidium minutissimum
Amphora libyca
Amphora veneta
Aulacoseira alpigena
Aulacoseira crenulata
Aulacoseira granulata/ambigua
Brachysira vitrea
Caloneis bacillum
Cocconeis neodiminuta
Cocconeis placentula
Craticula cuspidata
Cyclotella cf. planctonica
Cyclotella meneghiniana
Cymbella affinis
Cymbella aspera
Cymbella delicatula
Cymbella gracilis
Cymbella microcephala
Cymbella minutum
Diadesmis contenta
Diatomella balfouriana
Diploneis subovalis
Discostella stelligera <10 mic
Discostella stelligera >10 mic
Epithemia adnata
Epithemia sorex
Eunotia formica
Fragilaria capucina var. capucina
Fragilaria capucina var. vaucheriae
Fragilaria exigua
Fragilaria ulna
Frustulia rhomboides
Gomphonema augur
Gomphonema exiguum
Gomphonema gracile
Hantzschia amphioxys
Karayevia clevei
Mastogloia exigua
Navicula angusta
Navicula cryptotenella
Navicula difficillima
Navicula gastrum
Navicula ignota var. palustris
Navicula peregrina
Navicula rhyncocephala
Navicula vitabunda
Neidium ampliatum
Nitzschia amphibia
Pinnularia gibba
Planothidium frequentissimum
Psammothidium sacculum
Rhopalodia novae zealandiae
Sellaphora bacillum
Sellaphora pupula
Staurosira aff. venter 1a
Staurosira aff. venter 1c
Staurosira aff. venter 3
Staurosira girdle view <10 mic
Staurosira girdle view >10 mic
Staurosira microstriata
Staurosira microstriata B
Staurosira parasitoides
Staurosira pinnata sl. A
Staurosira pinnata sl. B
Staurosira pinnata sl. C
Stephanodiscus cf. alpinus
Surirella ovalis
cf. Synedra capitata
Tabellaria fenestrata
APPENDIX D

Uncertainty and Error in Diatom Isotope Paleolimnology

6.1. Vital Effects

Natural systems are inherently complex involving feedbacks operating between biological organisms and their physicochemical environment (Cronin, 1999). Isotope paleolimnology aims to elicit a simple response between a biogenic or inorganic precipitate and one or two environmental factors (e.g., temperature or P/E balance). Such approaches are inherently reductionist and necessitate some simplification of the complexity of natural responses (Cronin, 1999). Since the 1950s, researchers have known that organic precipitates secreted under similar chemical conditions often display heterogeneous isotope signatures due to some biologically mediated affect (e.g., Urey et al, 1951; Epstein et al, 1951). Subsequently, the term has come to define nearly all biologically mediated processes that are poorly understood (Broecker, 1982). Kinetic and equilibrium vital effects can be distinguished: kinetic vital effects associated with diatom ontogeny and taxonomy; and equilibrium vital effects of variation in season and habitat of dominant diatom taxa. Given the propensity for isotopic records to reflect processes more reliant on diatom taxonomy, age, and size, rather than hydrology, the latter are highly contentious (Swann and Leng, 2009). This is especially true of vital effects within δ^{30}Si_{Diatom} owing to typically less downcore variation in the latter than δ^{18}O_{Diatom} (e.g., Street-Perrott et al, 2008; Swann et al, 2010). De La Rocha (2006) identifies changes to δ^{30}Si_{Diatom} correlated to changes in species composition within a Southern Ocean sediment series, thereby emphasising the potential existence of δ^{30}Si_{Diatom} vital effects (see also Jacot Des Combes et al, 2008).

Overall however, diatom culture and down-core stable isotope studies have revealed little evidence for a taxonomic vital effect (Binz, 1987; Shemesh et al, 1995; Brandriss et al, 1998; Schmidt et al, 2001; Swann et al, 2006). There are exceptions such as Brandriss et al (1998) who suggested a 0.6 ‰ δ^{18}O_{Diatom} offset between 2 cultured diatom species. Thus uncertainty surrounds whether diatom frustules are precipitated in isotopic equilibrium with their aquatic environment, or at the very least suffer a systematic disequilibrium which is independent of temperature and can be calibrated by living specimens (Leng and Marshall, 2004). For instance, a marine δ^{18}O_{Diatom} record over the interval 2.84 Myr to 2.57 Myr, from ODP site 882 (Pacific Ocean), revealed a substantial size-dependent effect: 1.23 ‰ mean variation between two separate size classes (75-150µm and >150µm) (max. 3.51 ‰, n = 25) (Swann et al, 2007). However, subsequent analyses of sediment deposited at the same site during the last 200 kyr revealed, contrary to earlier findings, that no single fraction consistently retains an enriched or depleted signature despite large isotopic differences by size. Instead multiple processes
Appendix D

(e.g., paleoenvironmental changes in oceanic hydrochemistry and nutrient availability, changes in contributing bloom season and influx of taxa from widely dispersed source water locations) are believed to be responsible for the observed size-related $\delta^{18}O_{\text{Diatom}}$ offsets (Swann et al, 2007). To circumvent these problems, Swann and Leng (2009) suggest selecting size- and taxonomic-specific fractions of sedimentary BSi. As many diatoms are habitat- and season-specific this overcomes problems of spatial variability and seasonality in $\delta^{18}O_{\text{Lake}}$ or $\delta^{30}Si_{\text{Lake}}$ (Swann and Leng, 2009). Sieving offers a simple approach to isolate size classes (e.g., Morley et al, 2004) whilst the process of SPLITT fractionation, applied in this thesis, offers the ability to isolate individual taxa based on their hydrodynamic behaviour under laminar flow (e.g., by hydraulic resistance, density, grain size) (Rings et al, 2004).

6.2. Silica Maturation

To be accurately employed as a stable isotope proxy for paleolimnology, diatom frustules must undergo limited secondary isotope exchange during sedimentation and diagenesis (Leng and Marshall, 2004). Empirical evidence between cultured and sedimentary diatoms has revealed that sedimenting frustules undergo a process of maturation whereby fresh diatoms are $\sim$3 to 10 ‰ depleted compared to fossil equivalents (Schmidt et al, 1997, 2001; Brandriss et al, 1998). This property was first observed by Juillet (1980) who reported enrichment of fresh diatom silica by 1.8 to 5.3 ‰ following chemical digestion of surficial layers. Schmidt et al (2001) demonstrated that temperature-related fractionation could not explain this offset but that the ratio of Si-O-Si/Si-OH correlated with a $\sim$3 to 10 ‰ $\delta^{18}O_{\text{Diatom}}$ enrichment from fresh to sedimentary silica. Open-system cultivation experiments revealed that frustules were isotopically homogenous and therefore any change in fractionation between living and senescent diatoms were not due to dissolution (Schmidt et al, 2001). Instead slow internal condensation reactions are thought to occur in surficial sediments in which the relative proportion of hydroxyl silica (Si-OH) reduces with a concomitant increase in $\delta^{18}O_{\text{Diatom}}$ by nucleophilic addition, as follows:

$$\text{Si}^{18}\text{OH} + \text{H}^{16}\text{O-Si} \rightarrow \text{Si}^{18}\text{O-Si} + \text{H}_2^{16}\text{O}$$

(Proposed condensation reaction in diatom silica [Source: Schmidt et al, 2001: 207])

Supporting this theory, Lewin (1961) observed that the surfaces of fresh diatom frustules are more reactive than their sub-fossil or fossilised counterparts whilst others too have demonstrated greater volume of adsorbed water on fresher frustules than fossil diatomite (e.g., Hurd et al, 1981; Barker et al, 1994; Brandriss et al, 1998). To investigate this finding further, Moschen et al (2006) performed a series of Infra-Red (IR) spectroscopic analyses of the characteristic IR-absorption bands attributed to Si-OH (945 cm$^{-1}$) and Si-O-Si (800 cm$^{-1}$) groups. Cultured and freshly harvested diatom opal (Cyclotella meneghiniana) possessed distinct vibrational bands at both frequencies although the 945 cm$^{-1}$ band was markedly weaker in near-surface and sub-fossil samples indicating
the loss of Si-OH groups (Figure 6.22). Thus the authors argue for a selective loss of Si-OH groups during early diagenesis to result in enrichment of fossil $\delta^{18}O_{\text{Diatom}}$ and living specimens (~2.5 $\%$ [Moschen et al, 2006]). Dehydroxylation of unstable Si-OH bonded silanol groups causes the selective enrichment of diatom silica due to the lower bond energy of $^{16}$O-containing water molecules (Schmidt et al, 2001; Gendron-Badou et al, 2003).

Without further research the implications of cryptic silica maturation for sedimentary $\delta^{18}O_{\text{Diatom}}$ remain uncertain (Swann and Leng, 2009). Deviations of 3-10 $\%$ could easily disguise an environmental effect and instead record changes in the degree of maturation (Swann and Leng, 2009). Debate centres on whether sedimentary $\delta^{18}O_{\text{Diatom}}$ values correspond to ambient conditions during productivity or burial (e.g., surface versus benthic or pore-water) although a strong correlation between $\delta^{18}O_{\text{Diatom}}$ and other surface water hydrological proxies suggests the former (e.g., Tyler et al, 2008). As long as the fractionation factor associated with dehydroxylation ($f$) is constant, then inspection of trends in $\delta^{18}O_{\text{Diatom}}$ and silica maturity will reveal a systematic and predictable

Figure 6.22: IR absorption spectra of 4 diatom samples from laboratory and field (Lake Holzmaar, Germany) cultures demonstrating markedly reduced Si-OH groups (945 cm$^{-1}$) in sub-fossil and surficial sediments vs. living and 7m (epilimnion) sediment trap material (Source: Moschen et al, 2006: 4376).
offset (see below) (Swann and Leng, 2009). As such $f$ will need to be constant in space (between cores), time (downcore) and taxonomy to avoid introducing a $\delta^{18}\text{O}_{\text{Diatom}}$ vital effect (Swann and Leng, 2009).

$$\delta^{18}\text{O}_{\text{Diatom}} = \delta^{18}\text{O}_{\text{Si-O-Si}} + \delta^{18}\text{O}_{\text{Dehydroxyl}}$$

(Composition of $\delta^{18}\text{O}_{\text{Diatom}}$ signatures by constituent Si-O and Si-OH components [Source: Swann and Leng, 2009: 393])

$$\delta^{18}\text{O}_{\text{Dehydroxyl}} = f[\delta^{18}\text{O}_{\text{Si-OH}}]$$

(Proportion of Si-OH can be demonstrated by a corresponding $\delta^{18}\text{O}$ effect [f] [Source: Swann and Leng, 2009: 394])

### 6.3. Dissolution and/or Reprecipitation

Many lacustrine systems are under-saturated with relation to Si resulting in the dissolution of silicate compounds, particularly high pH systems (Swann and Leng, 2009). BSi is even susceptible to dissolution within the sedimentary Si-asymptotic concentration zone (generally <30 cm beneath the sediment-water interface) (Swann and Leng, 2009). Consequently, diatom silica is subject to dissolution either in transit to or in sediment. Approximately 10% to 100% of diatom silica is typically recycled in the water column with the remainder contributing to lake and marine sediment (Leng and Barker, 2007). Dissolution may alter sedimentary assemblages as those that are more resistant to dissolution (e.g., more densely silicified) remain in lake sediment (Moschen et al, 2006). Parameters influencing dissolution rates include: temperature, sedimentation rate, alkalinity, trace metals, inorganic and organic coating, detritivory, abundance of detrital minerals, and structure, aggregation and degree of silicification (Swann and Leng, 2009). Consequently, there is considerable potential for dissolution rate to alter sedimentary diatom assemblage structure (e.g., species richness and morphology) and to vary over time in line with changing pore-water hydrochemistry (Swann and Leng, 2009).

Secondary dissolution has the capacity to alter soil water $\delta^{28}\text{Si}$ by preferentially leaching lighter $^{28}\text{Si}$ and $^{29}\text{Si}$ through mass-dependent fractionation (Cardinal et al, 2010). A similar effect has been demonstrated in detrital diatom silica during dissolution (enrichment of up to $\sim+0.55\%\delta^{30}\text{Si}$ [Demarest et al, 2009]). Likewise reprecipitation of DSi results in the enrichment of consequent, secondary Si-precipitates (Opfergelt et al, 2008). Similar effects can be expressed in $\delta^{18}\text{O}_{\text{Diatom}}$ values (enrichment of up to $\sim+6.9\%\delta^{18}\text{O}$ [Schmidt et al, 2001]). Accordingly if dissolution/reprecipitation effects are constant a systematic offset can be introduced to account for taphonomic enrichment. However, any change in the rate of dissolution/reprecipitation (e.g., due to changing hydrology) will result in a dynamic effect in downcore $\delta^{18}\text{O}_{\text{Diatom}}$ or $\delta^{30}\text{Si}_{\text{Diatom}}$ (Swann and Leng, 2009).
Only a few investigations of diatom dissolution have attempted to quantify the effect on diatom O or Si-isotope signatures (e.g., Schmidt et al, 2001; Moschen et al, 2006; Demarest et al, 2009). Schmidt et al (2001) demonstrated enrichment of marine $\delta^{18}$O_Diatom over several hundred metres depth, and Demarest et al (2009) reported dissolution of marine $\delta^{30}$Si_Diatom under laboratory conditions of low DSi. However, it is uncertain whether such effects would be limited by shallower depths and more rapid burial in Lake Pupuke. Rapid burial in a reduced hypolimnion could be particularly important because this favours retention of protective organic coatings on diatom frustules, which effectively limit dissolution (Bidle et al, 2003). For instance, whilst marked $\delta^{18}$O_Diatom enrichment occurs in alkaline waters (pH >9.0; +6.9 ‰ [C. meneghiniana]; +1.6 ‰ [Fragilaria crotonensis]), this was only following treatment with a strong oxidising agent (H$_2$O$_2$) (Moschen et al, 2006). Uncertainty surrounds whether such effects would therefore be expressed in the natural realm. Accordingly, the approach outlined in Swann and Leng (2009) is adopted here, employing light and scanning electron microscopy (SEM) to identify and exclude samples subject to marked dissolution/reprecipitation (see 6.3.5.1. Light and Electron Microscopical Analyses).
APPENDIX E

Modern Isotope Hydrological Modelling

For each tracer ($\varepsilon^+, \Delta\varepsilon$ and $\alpha$) values were derived empirically from Horita and Wesolowski (1994) based on the formulae:

\[
10^3 \ln \alpha (\delta D) = 1158.8 \left( \frac{T^3}{10^9} \right) - 1620.1 \left( \frac{T^2}{10^6} \right) + 794.84 \left( \frac{T}{10^3} \right) - 161.04 + 2.9992 \left( \frac{10^9}{T^3} \right)
\]

\[
10^3 \ln \alpha (\delta^{18}O) = -7.685 + 6.7123 \left( \frac{10^3}{T} \right) - 1.6664 \left( \frac{10^6}{T^2} \right) + 0.35041 \left( \frac{10^9}{T^3} \right)
\]

where $T$ is temperature of water (K).

\[
\varepsilon^+ = \alpha - 1
\]

\[
\Delta\varepsilon = n C_K^\theta (1 - h)
\]

where $C_K^\theta$ is 25.0 %o and 28.6 %o for $\delta D$ and $\delta^{18}O$ respectively, $n = \frac{1}{2}$ for open water bodies and $n = 1$ for soil water, $\theta = 1$ for small water bodies and $h$ is relative humidity (Gibson et al, 2008).

Values for $\delta E$ were estimated from the linear resistance model of Craig and Gordon (1965), using Gonfiattini (1986):

\[
\delta_E = \frac{(\delta_L - \varepsilon^+)/((\alpha - h\delta_A - \Delta\varepsilon))}{1 - h - \Delta\varepsilon}
\]
Appendix E

Equations here employ δ and ε values in decimal notation. δ-values are multiplied by 1000 and expressed in per mil (‰).

Values for δA were computed using the precipitation-equilibrium assumption of Gibson et al (2008):

$$\delta_A = (\delta_p - \varepsilon^+)/\alpha$$

As per Gibson et al (2008) the exchange terms δA, ε+, Δε and h were evaluated on a monthly basis and evaporation-flux weighted to simulate the expected annual δD and δ18O trajectories. Likewise annual precipitation (δP) values were amount-weighted from monthly data to better model the annual average source water to Lake Pupuke.
Theoretical limits to SPLITT fractionation are governed by Stokes’ Law. Assuming spherical particles under constant gravitational acceleration, the sinking velocity ($v_s$) is governed by particle (particle density [$\rho_p$], diameter [d], frictional ratio [$f/f_0$]) and liquid properties (liquid density [$\rho_l$], viscosity [$\eta$]):

$$V_s = g \frac{d^2}{18 \eta f/f_0} (\rho_p - \rho_l)$$

(Stokes’ Law for settling velocity [$V_s$] of spherical particles)

In a homogenous carrier fluid and constant gravitational force, $V_s$ is governed by d and $\rho_p$. Consequently, particles can possess identical $V_s$ despite differences in d provided there is a concomitant and inverse change in $\rho_p$, so-called “corresponding density or size” (Rings et al, 2004:27) (Figure 6.23).

Figure 6.23: Dependency of sedimentation velocity ($V_s$) on particle size (d) for different particle densities ($\rho_p$) (double log scale). Density of the liquid = 0.998 g/cm$^3$. Note a light spherical particle ($\rho_p1 = 2$ g/cm$^3$) of $d_1 = 14$ µm diameter has the same $V_s$ as a denser particle ($\rho_p2 = 3$ g/cm$^3$) of $d_2 = 9.9$ µm diameter (source: Rings et al, 2004: 27).
Corresponding densities or sizes limit the ability of SPLITT cells to separate different particles as these govern the smallest possible grains capable of being separated from diatom frustules (Rings et al, 2004). A wide range of grain size and densities increase the likelihood of larger corresponding size or density intervals. Consequently, it is recommended that silicate fractions are sieved prior to SPLITT separation. Even if particles are of identical shape and densities, there will be a region of overlapping particle size separated into both outlets a and b (Giddings, 1992; Rings et al, 2004). The range of this size interval will be dependent on flow rate, channel and ISP geometry and particle interactions (Rings et al, 2004). Thus whilst \( V_s \) can be calculated for biogenic opal (\( \rho = 1.95 - 2.20 \, \text{g/cm}^3 \)) of varying diameters observed in a sample and flow rate modified to ensure sufficient time is given for sedimentation in the SPLITT cell, this calculated time will be heavily modified by particle-particle interactions and varying particle sizes present in a sample. Accordingly, a trial and error approach was employed to ensure cleaned diatom frustules were collected.
APPENDIX G

Cellulose Purification Approach

Aquatic cellulose is enriched by ~+27-28‰ on \( \delta^{18}O_{\text{Lake}} \), independent of changes in water temperature or plant species (Sternberg, 1989; Wolfe et al., 2007). Stratigraphic changes in \( \delta^{18}O_{\text{Cellulose}} \) can therefore record past changes to \( \delta^{18}O_{\text{Lake}} \) indicative of paleoenvironmental or climatic change (Edwards et al., 2004; Wolfe et al., 2005). There are two approaches for isolating aquatic cellulose from lake sediment that employ a complex series of chemical treatments (Wolfe et al., 2007) and a less complex, dissolution-precipitation treatment (Wissell et al., 2008). Each has been applied to the Pupuke sediment record to offer a complimentary record of changes to \( \delta^{18}O_{\text{Lake}} \) from which to test paleohydrologic inferences. Details of the methods are summarised below (rinsing with ultra-pure water between stages):

1. Wolfe et al. (2007): acid-washing (45 ml, 1N HCl, 2 hrs, 60°C); solvent extraction to remove lipids (45 ml, Toluene/Ethanol overnight; 50 ml acetone overnight); bleaching to remove lignin (0.3 ml glacial acetic acid; 0.3 g sodium chlorite at 70°C); alkaline hydrolysis to remove xylan, mannan and other polysaccharides (50 ml 17% sodium hydroxide); and acid-leaching to remove Fe- and Mn-oxhydroxides as per Wolfe et al. (2001). Acid-leaching stages were repeated until the precipitate lost no further red or brown colour (necessary due to the high abundance of basaltic particles in sediment samples). A further heavy-liquid flotation stage was added using sodium polytungstate at a specific gravity of 1.9 as per Wolfe et al. (2007). Cellulose flotant was dried and crushed for oxygen isotope analysis.

2. Wissell et al. (2008): bleaching to remove lignin (0.3 ml glacial acetic acid; 0.3 g sodium chlorite at 70°C) prior to cellulose dissolution in cuprous ammonium solution (20-30 ml CUAM solution; 15 g copper hydroxide; 900 ml ammonium hydroxide solution [25%]; 100 ml deionised water). The cellulose is precipitated from the CUAM supernatant by adding 3 ml H\(_2\)SO\(_4\) (20% v/v), centrifuged at x4000 rpm for 25 min. Additional H\(_2\)SO\(_4\) was added until the CUAM solution became transparent.

The application of lake sediment aquatic cellulose to paleolimnology depends on isolating pure aquatic cellulose (Wolfe et al., 2007). The analysis of non-aquatic cellulose will introduce variable fractionation rates and additional Oxygen isotopic reservoirs into downcore \( \delta^{18}O_{\text{Cellulose}} \) variation. Thus, the purity of cellulose extracts underpins the reliability of \( \delta^{18}O_{\text{Cellulose}} \) inferences (Wolfe et al., 2007). The cellulose isolated by the Wolfe et al. (2007) approach contained numerous tephra particles and was therefore not analysed for \( \delta^{18}O_{\text{Cellulose}} \) by IRMS. To permit the latter approach within Auckland maar crater lakes, whose exposure to ash-fall raises the likelihood of further tephra contamination, further investigation is needed to determine how best to separate tephra from cellulose precipitates. This might involve additional stages of sodium hydroxide leaching to remove silicates or adjustment to the specific gravity of SPT to better float cellulose from tephra. In comparison, light microscopical
examination of CUAM-derive cellulose extracts revealed little if any visible contamination. However, analysis of these extracts by IRMS revealed widely varying stratigraphic changes in $\delta^{18}O_{\text{Cellulose}}$, whose pattern did not approximate changes to $\delta^{18}O_{\text{Diatom}}$ (Figure 8.1). As $\delta^{18}O_{\text{Diatom}}$ has been demonstrated to offer a reliable and sensitive record of past changes to $\delta^{18}O_{\text{Lake}}$, these differences suggest $\delta^{18}O_{\text{Cellulose}}$ values suffer from one or more vital effects that distort paleohydrologic changes in $\delta^{18}O_{\text{Lake}}$ (e.g., through inclusion of non-lacustrine cellulose, diagenetic alteration). Further, marked variation in the $\delta^{18}O_{\text{Cellulose}}$ signature of laboratory cellulose standards that were subject to the CUAM treatment suggests this approach can alter the Oxygen isotopic composition of derived cellulose (Table 8.1). Thus, despite the potential for the CUAM approach to overcome the limitations inherent to physical separation by the Wolfe et al. (2007) approach, further research is needed into the cause of analytical uncertainty in $\delta^{18}O_{\text{Cellulose}}$ values. Without this and despite the potential for aquatic lake cellulose to provide a valuable record of stable isotope paleohydrology, the CUAM approach cannot be employed to investigate the paleolimnology of Auckland maar crater lakes.

Figure 8.1: Preliminary $\delta^{18}O_{\text{Cellulose}}$ (CUAM extract) plotted by $\delta^{18}O_{\text{Diatom}}$ demonstrating marked differences in stratigraphic variation and suggesting the presence of vital effects in $\delta^{18}O_{\text{Cellulose}}$ distorting the link to $\delta^{18}O_{\text{Lake}}$ within the Pupuke sediment record.
Table 8.1: Preliminary $\delta^{18}O_{\text{Cellulose}}$ (CUAM extract) variation in laboratory cellulose standards suggesting the CUAM method introduces marked variation to the isotopic composition of cellulose extracts.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>$\delta^{18}O_{\text{Cellulose}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Standard</td>
<td>27.30</td>
</tr>
<tr>
<td>Standard</td>
<td>27.87</td>
</tr>
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</tr>
<tr>
<td>CUAM</td>
<td>26.17</td>
</tr>
</tbody>
</table>

* Samples denoted by 'CUAM' were treated with the CUAM method whereas those denoted by 'Standard' were untreated.


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