Origin, Formation and Environmental Significance of Sapropels in Shallow Holocene Coastal Lakes of Southeastern Australia

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September 2007

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ACKNOWLEDGEMENTS

To my three supervisors: Assoc. Prof. David McKirdy, Prof. Martin Williams and Dr. Evelyn Krull. Thank you for your guidance over the years and for your enthusiasm and encouragement along the way. The three different styles of supervision and the varied fields of expertise always kept things interesting, and no doubt contributed to a more rounded, complete piece of work than that which would otherwise have been the case.

I gratefully acknowledge financial support from the Cooperative Research Centre for Landscape, Environments and Mineral Exploration, and from Martin Williams (XRD analyses). Thanks to the Department for Environment and Heritage for permission to sample at North Stromatolite and Old Man Lakes and to John Enright for granting access to Lake Amy. Big thanks to Karen Hulme and Angus MacGregor for their help collecting the sediment cores. Also, thanks to Doug Stewart for his gracious hospitality (and engineering prowess) during our time in the field.

Thanks to Dr. Erick Bestland, Dr. Peter Gell, Dr. John Tibby, Alan Brenchley and Bobbie Rice for their support and expertise in the early days of the project, and to Seamus Noone for his help in sub-sampling the cores. Thank you to the CSIRO lab crew: Dr. Jan Skjemstad, Dr. Matt Forbes, Mark Raven, Janine McGowan and Athina Massis for their assistance with sample preparation and analysis. Thanks also to Steve Cooke (The University of Waikato) for carbonate isotope analysis, to Dr. Frances Williams for running the optically stimulated luminescence dating samples and to Dr. Andrew Smith, Dr. Quan Hua and Dr. Ugo Zoppi (ANSTO) for radiocarbon dating under AINSE grant 04/172. Thanks to Dr. Richard Gillespie and Fred Leaney for helpful discussions on the radiocarbon reservoir effect and to Nathan Reid for vegetation sample identification.

Finally, to the all important support network… Thanks to Simon Carey for his wise words on a difficult day. Thanks to Dr. Stuart John Johnson and Dr. David McInerney for reminding me that it can actually be done. Thanks to Mattie Gray for his dry humour, technical expertise and continual encouragement; to Blonde Cat for much needed respite from it all. Mum, thank you ever so, ever so much for everything. It's all the little things along the way that make anything possible. And to Rhys; I couldn't have finished this off without you. Thanks for the cuddles, for the constant support, for the sapropel boogie and the science song, for hot drinks, for hometime, for holidays and for believing in me all along.

ABSTRACT

Many shallow, groundwater-fed lakes along the Coorong coastal plain of southeastern South Australia contain sapropelic sediments within their Holocene calcareous mudstone successions. The deposition of similarly organic-carbon-rich sediments in marine and deep-lake settings commonly has been linked to times of wetter regional climate. Increased precipitation boosted surface runoff and tributary flow, thereby increasing the input of terrestrial organic matter and nutrients to the depocentre and potentially causing stratification of its water column. The principal effect of increasing the nutrient supply is to promote aquatic productivity, which can in turn lead to oxygen-depletion of the bottom waters and enhanced preservation of sedimentary organic matter.

The three lakes of the present investigation, North Stromatolite Lake (NSL), Old Man Lake (OML) and Lake Amy (LA), are shallow and have become increasingly ephemeral over time, yet they have continued to accumulate sapropelic intervals with high concentrations of autochthonous algal and bacterial organic matter within their sedimentary successions. NSL and OML are charged by westward-flowing saline continental groundwater that is forced toward the land surface as it rises over an underlying wedge of denser, intruding seawater. In contrast, the more elevated LA is the surface expression of a local perched water table high in the Robe Range. No permanent streams enter these lakes, nor are there any present-day surface connections with the marine system. Therefore, they represent a distinctly different aquatic environment to those in which sapropels have previously been studied. This means that traditional models of sapropel formation cannot explain the Coorong lacustrine examples and this study adds a new perspective to the dynamics of sapropel genesis.

Lacustrine sedimentary sequences represent one of the most refined archives of environmental change presently available for investigation. While bulk sedimentary geochemistry has been successfully employed to document palaeoenvironmental changes in a broad range of settings across the globe, it has not yet been widely used in the study of shallow, ephemeral lakes in Australia. Nonetheless, the elemental, molecular and isotopic analysis of sedimentary organic matter and carbonate can greatly aid palaeoenvironmental reconstructions. The present study explores the extent to which the application of bulk geochemical analyses (TOC, C/N, ^{14}C, $\delta^{13}C_{org}$, $\delta^{15}N$, $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, ^{13}C-NMR) to the sediments of these coastal lakes reveals the Holocene environmental change that is already established for the region.

Radiocarbon dating (and correction for a local reservoir effect) indicates that sapropel deposition in NSL took place from ~6000 to ~4700 cal yr BP. Since this time the NSL basin has been accumulating organically-lean (TOC<1%) carbonate sediments. Episodic sapropel deposition recorded in the stratigraphic succession of OML ceased as recently as ~2200 cal yr BP and at LA ~1800 cal yr BP, thereby indicating that nutrient delivery or recycling continued to promote sapropel formation in these southern lakes for at least 2500 years longer than 200 km to the north, at NSL.

^{13}C-NMR analysis indicates that the sedimentary organic matter preserved in all three lakes is rich in carbohydrate and protein, and thus largely autochthonous. This agrees with the findings of previous biomarker studies of NSL and OML which indicated that their organic matter was derived mainly from lacustrine photoautotrophs, augmented by minor contributions from allochthonous terrestrial biomass. Therefore, the elemental and isotopic signatures of their organic matter, and that in LA, are considered to primarily reflect lacustrine conditions and processes, rather than alterations to the terrestrial ecosystem of their hinterland. Higher C/N ratios than those typical of algae and bacteria are interpreted as reflecting conditions of either nitrogen-deficiency or a nutrient abundance, the latter promoting primary productivity in the epilimnion and leading to oxygen depletion in the hypolimnion and preferential degradation of nitrogen-rich proteinaceous organic matter. $\delta^{13}C_{org}$ values around –20‰ reflect the photosynthetic use of bicarbonate by these aquatic biota and indicate variations in the extent of lacustrine productivity and respiration. A contribution from aquatic macrophytes, such as *Ruppia* sp., may account for some of the mixed source affinity suggested by the $\delta^{13}C_{org}$ values of these lakes. $\delta^{15}N$ values provide information on shifts in the phytoplankton and heterotroph assemblages that may be related to changes in the trophic state of the lake waters. $\delta^{13}C_{carb}$ values indicate periods of enhanced microbial contribution to the sedimentary biomass thus aiding the interpretation of secular $\delta^{13}C_{org}$ changes. $\delta^{18}O_{carb}$ values tend to increase up section in line with evaporation of shallowing lake waters in a progressively drier late Holocene regional environment.

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"..a scientist must also be absolutely like a child. If he sees a thing, he must say that he sees it, whether it was what he expected to see or not. See first, think later, then test. But always see first. Otherwise you will only see what you were expecting."

DOUGLAS ADAMS

CHAPTER 1: INTRODUCTION AND AIMS

1.1 Overview

Lacustrine sedimentary sequences represent one of the most refined archives of environmental change presently available to investigation. In fact, an increasing number of palaeoenvironmental studies on Holocene lacustrine sediments show comparable variability to that which is recorded within polar ice cores (e.g. Barnola et al., 1987; Jouzel et al., 1987; Petit et al., 1999) and marine cores (e.g. Cramp and Sullivan, 1999; Moss and Kershaw, 2000; Gallagher et al., 2003). However, as lacustrine sediments tend to accumulate at a faster rate than either polar ice or marine sediments (Ariztegui et al., 2001) and lakes often respond very rapidly to changing climatic and environmental conditions, the analysis of lacustrine sedimentary sequences has the potential to reveal information on the extent of local to regional scale Holocene environmental change at a high-temporal resolution.

Across the globe, lacustrine sedimentary sequences have been investigated using a multitude of techniques over a wide range of environmental settings and conditions. The techniques range from palaeoshoreline reconstruction, lacustrine sediment texture and trace element analysis, which aim to determine secular changes in water depth and composition, to palynology and the reconstruction of past biotic assemblages from both within and around the lake. Whilst palynology is concerned with long-term changes in the entire lake catchment (and even beyond), not directly with the water body itself, the types of aquatic and terrestrial plants that existed within both the lake and its catchment throughout the lake's history may be estimated from the elemental and isotopic composition of lacustrine sedimentary organic matter. Secular variations in these biotic assemblages reflect both short and long-term changes to a variety of internal and external conditions and processes. Thus, elemental and isotopic geochemistry has the potential to aid palaeoenvironmental investigations.

All fossil records are incomplete. Indeed, the different degrees of degradation to variably resistant organic matter components during settling through the water column and burial can introduce bias to the information that is eventually preserved within lacustrine sedimentary records. Although this means there is a potential skewing of the original source information provided by organic geochemical data, by evaluating the type and extent of active degradation processes one may provide further information on the lacustrine conditions (e.g. oxic state) and thus aid palaeoenvironmental reconstruction.

This chapter provides the necessary background to set the aims of the present investigation into context. It begins by describing the Late Quaternary environmental variability that has been established by a great many authors through a wide range of palaeoclimatic analyses (section 1.2). The broad picture of global glacial-interglacial cycles is summarised before detailing the smaller scale fluctuations that have occurred across Australia during the last 50 ka. Much of the evidence for small-scale changes in terrestrial environmental conditions at the regional scale has come from long and continuous lacustrine sedimentary sequences. Therefore, it is instructive to outline some of the basic aspects of lake sedimentology (section 1.3). Particular emphasis is placed on the formation and deposition of carbonate sediments as the present study is located in an area underlain by thick marine deposits and the three lakes of the present study comprise carbonate-rich sedimentary successions (section 1.4). Also, as the present research involves analysis of lacustrine sedimentary organic matter, the mechanisms of organic matter production and degradation are described (section 1.5). The factors that directly influence the actual elemental and isotopic composition of lacustrine organic matter and co-deposited sedimentary carbonate form the basis of Chapter 2. However, in section 1.6 of this chapter, some examples of research that have made use of these parameters are summarised to illustrate the unique nature of the present research. Finally, the aims of the present investigation are given.

1.2 Late Quaternary Environmental Variability

1.2.1 Glacial-Interglacial Cycles

The Quaternary epoch (1.8 Ma to present) is characterised by numerous sea-level oscillations and fluctuating global climatic conditions. Long and continuous records derived from ice-cores, deep-sea cores, and deep terrestrial lake and swamp sequences show that long glacial periods, characterised by cool temperatures, expanded icecaps and reduced global precipitation, have regularly been interspersed by brief (c. 10% of time) interglacial periods, with both sea-level and global climatic conditions somewhat similar to the present day (Figure 1.1) (McGlone et al., 1996; Petit et al., 1999). These glacial-interglacial cycles had a duration of ~40 thousand years between 1.8 and 0.7 Ma, and ~100 thousand years since 0.7 Ma (Williams, 1998). Both of these periods are consistent with the Milankovitch cycles of fluctuating Northern Hemisphere solar insolation due to slow variations in the earth's orbit that result from its 96 thousand year orbit eccentricity, 41 thousand year axial tilt and 22 thousand year equinoxial precession (Lowe and Walker, 1984; Williams et al., 1998). Milankovitch theory proposes that weaker high latitude insolation in northern summers triggers ice sheet formation and glacial conditions, and stronger insolation causes ice sheet retreat and interglacial warming (McGlone et al., 1996). This theory is fundamental to present day explanation of Quaternary climate change.

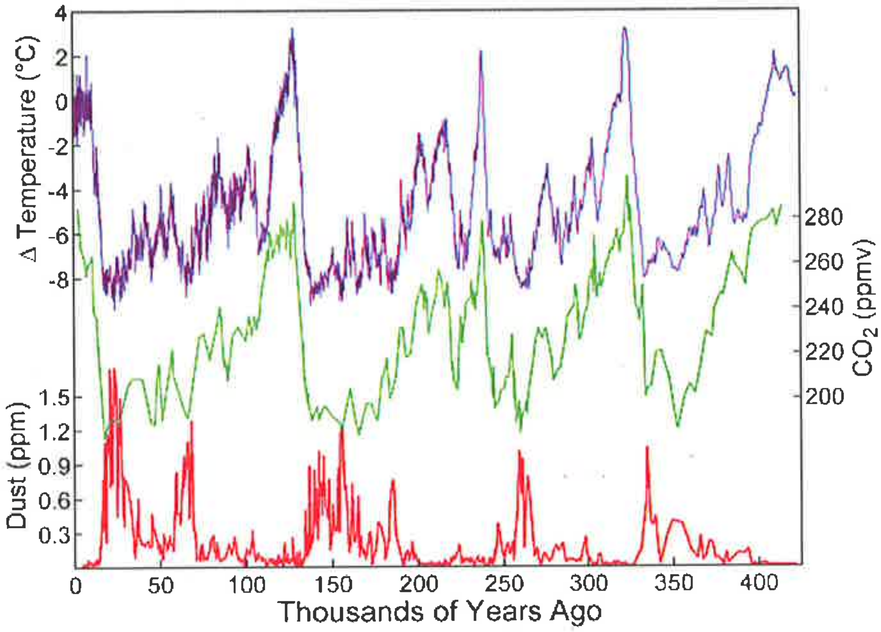

Figure 1.1: The repetition of glacial-interglacial cycles over the last 400 thousand years is shown by the patterns of changing atmospheric carbon dioxide and dust concentrations within air bubbles trapped in the Vostok ice core, plus the fluctuations in local temperature inferred from the deuterium isotope composition of the ice (Petit et al., 1999).

The last complete glacial-interglacial cycle is typical of the climate change resulting from Milankovitch forcing. The interglacial period (~120 to 140 ka) was the warmest and wettest phase of the cycle (Jouzel et al., 1987; Petit et al, 1999). This was followed by a 'saw-toothed' decline in global air temperatures toward maximum glaciation between 20 and 15 ka. At the peak of the last glacial maximum (LGM ~18 ka) sea level was ~130 m lower and glacier ice covered ~17% more of the earth's land surface than during the present interglacial (Chappell and Shackelton, 1986; Anderson and Borns, 1997). Land surface air temperatures were 5° to 10° colder, global precipitation was substantially lower and the concentration of atmospheric CO_2 and CH_4 was at a minimum (Barnola et al., 1987; Petit et al., 1999).

1.2.2 Smaller Scale Variability

Many variations of a smaller scale in both extent and magnitude are superimposed on these long-term global glacial-interglacial cycles. In demonstrating this, the small-scale climatic fluctuations that have occurred across Australia over the last 50 ka[1] are considered in detail. The localities discussed in the following text are shown in Figure 1.2.

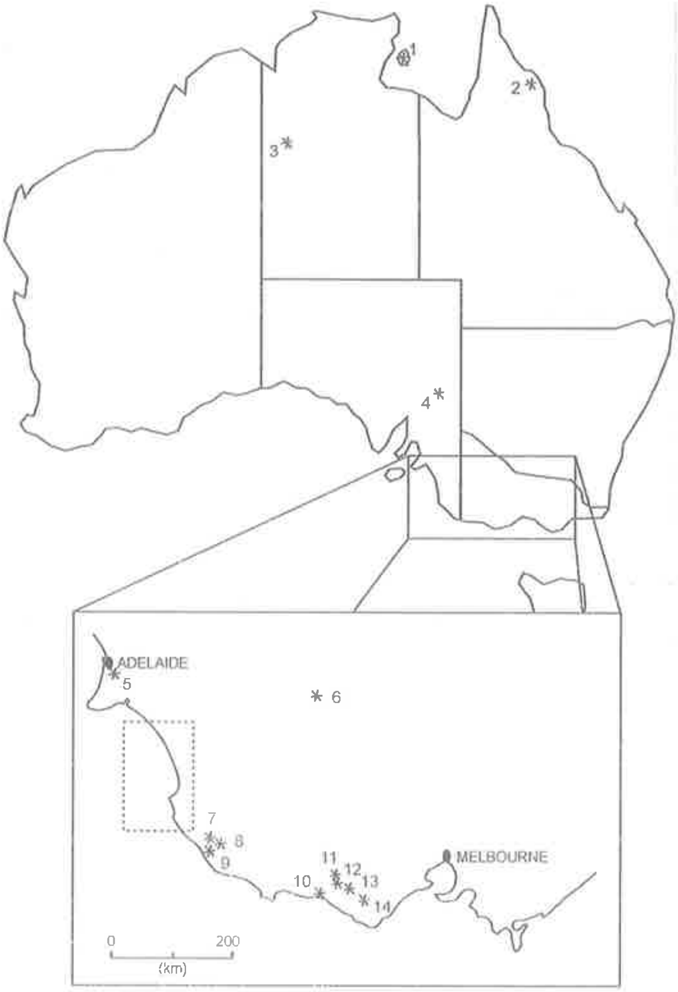

Figure 1.2: Locations of the studied sites mentioned in the text: 1 – Groote Eylandte, 2 – Atherton Tablelands, 3 – Lake Gregory, 4 – Lake Frome, 5 – Boat Harbour Creek, 6 – Lake Tyrrell, 7 – Marshes Swamp, 8 – Wyrie Swamp, 9 – Lake Leake, 10 – Lake Keilambete, 11 – Lake Terang, 12 – Lake Bullenmerri, 13 – Lake Wangoom, 14 – Chapple Vale Swamp.

Although the reliability of radiocarbon dating towards its limit (~40-50,000 years – Gillespie, 1986; Björck and Wohlfarth, 2001) remains questionable, a number of studies have used the technique to help establish chronologies for palaeoenvironmental

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[1] All ages discussed in this review are radiocarbon years before present, as opposed to calendar years, unless otherwise indicated.

reconstruction throughout this time period. D'Costa and Kershaw (1995) extrapolate Holocene radiocarbon dates to establish a basal age for sediments from Lake Terang, Western Victoria, of ~51 ka and set the transition from *Eucalyptus* to *Casuarina* dominated vegetation at ~48 ka. This transition reflects the termination of a local warm/wet phase that is recorded in a number of lakes and swamps in southern Australia. High lake levels and a dominance of woody taxa at nearby Lake Wangoom are evident around 50 ka (Figure 1.3), although again uncertainties associated with radiocarbon dating preclude an accurate definition of the subsequent shift to cooler and drier conditions (Edney et al., 1990). The slight increase in forest cover at ~40 ka reflects a temporary return to wetter conditions before the gradual descent toward glacial conditions around Lake Wangoom.

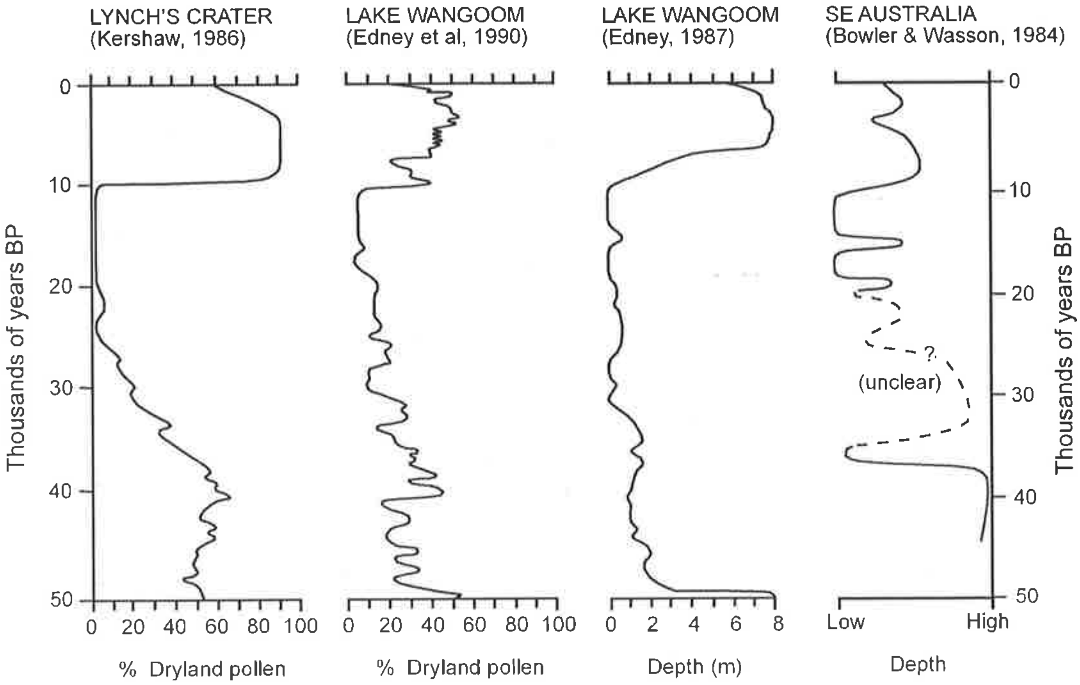


Figure 1.3: A comparison of the long, continuous vegetation records from Lynch's Crater and Lake Wangoom, along with the lake level record from Lake Wangoom and a generalised lake level record compiled for southeastern Australia (primarily from the Willandra Lakes and Lake Keilambete records). For the palynological records the x-axis represents the percentage of tree and shrub species out of the total dryland pollen. Lake depths have been derived from sedimentary texture and microfossil analysis (modified from Kershaw, 1989 and Edney et al., 1990).

Uncertainties in dating beyond 30,000 years at the Willandra Lakes, southwestern New South Wales, are recognised but it seems that lake levels remained high here until ~37 ka (Bowler and Wasson, 1984). At Lake Leake, southeastern South Australia, Dodson (1975) documents the period from 39 to 35 ka as a shallow water lacustrine phase bracketed by drier conditions. Similarly, nearby Wyrie Swamp records a shallow water phase from 40 to 30 ka, followed by gradual drying (Dodson, 1977). Regardless of the uncertainties associated with some of these examples of radiocarbon dated sediments the period of approximately 50-30 ka is thought to be a major wet phase, with a large expansion of lakes across the globe (Bowler, 1981). This phase seems to coincide with the occurrence of an interstadial period with slightly elevated global temperatures as suggested by deuterium data from Vostok ice core analysis, Antarctica (Jouzel et al., 1987).

From 30 ka the climate began to cool and become more arid in the lead up to the LGM. In southeastern Australia a general temperature decrease is suggested by the transition from Eucalyptus forest with a scrubby understory to more open woodland surrounding Lake Leake at ~26 ka (Dodson, 1975). The pollen study of Wyrie Swamp suggests that the driest period of last 50 ka occurred from 26 to 11 ka (Dodson, 1977). The onset of dry conditions at the Willandra Lakes is also dated at ~25 ka and widespread aeolian landforms were produced between 18-16 ka (Bowler, 1976). The transition to cooler climatic conditions seems to have occurred earlier in northeastern than southeastern Australia. At Lynch's Crater on the Atherton Tableland, northern Queensland, the transition is evident in the coincident reduction of rainforest and expansion of sclerophyll vegetation that is recorded at ~38 ka (Kershaw, 1986). This difference exemplifies the variable timing and extent of palaeoclimatic changes recorded across the Australian continent, which result from regional wind regimes (proximity to monsoonal or high-latitude storm tracks) and other local influences, such as vegetative cover and the effects of altitude and humidity on cloud formation.

During the height of the LGM low atmospheric CO_2 concentrations disadvantaged C3 plants and trees were excluded from 85% of the Australian continent (Hope and Kilpatrick, 1988). Lake levels at this time were generally low (Harrison and Dodson, 1993). As evaporation is reduced under the cool temperatures of glacial periods these low lake levels result primarily from reduced precipitation during this time.

At approximately 15 ka there was a sustained rise in both sea level and mean annual temperatures (McGlone et al., 1996). However, much evidence points toward maintenance of relatively dry continental conditions during the early stage of this transgression. Between 15-10 ka Lake Bullenmerri, Western Victoria, was at its lowest levels of the last 16,000 years (Dodson, 1979). Nearby, Lake Wangoom records extremely dry conditions between 19 and 10 ka (Edney et al., 1990). In general, lake level data from across Australia indicate that aridity reached its maximum at approximately 12 ka (Harrison and Dodson, 1993), and that lake levels began to rise earlier in the south (Tasmania ~11 ka – Harrison, 1993) than in more northern parts of the continent.

Radiocarbon dating of gastropods in a sedimentary study of Lake Gregory, northwestern Australia, suggests that the Australian monsoon, which all but ceased operation during the LGM, reactivated around 14 ka (Wywroll and Miller, 2001). An increase in the delivery of summer rains to the interior of the continent through monsoonal activity at this time is also suggested by a palynological study at Lake Frome, South Australia, which shows the first appearance of subtropical/tropical taxon at 13 ka (Singh and Luly, 1991). Indeed, an increase in the influence of monsoonal rains across the Australian continent seems a probable component of the regional climatic amelioration leading out of the LGM.

1.2.3 The Holocene in Australia

By 10 ka precipitation levels were not yet at those of today, however there is much evidence for a general climatic amelioration from the beginning of the Holocene. Summer insolation in the northern hemisphere was at a maximum around 12 ka (Berger and Loutre, 1991). The resulting atmospheric warming and glacial retreat caused eustatic sea-level rise and flooding of continental shelves that had been exposed during the LGM. Seas had begun to enter the gulfs of South Australia by ~9 ka (Belperio, 1995). In a marine core taken off the coast of northern Queensland an increase in rainforest and mangrove vegetation and decrease in herbaceous taxa between 9 and 5 ka exemplifies the positive relationship between sea-level and precipitation during this transgression (Moss and Kershaw, 2000). Ash and elemental data from a peat record at Lynch's Crater also suggest that the climate in northern Queensland was relatively wet during the early Holocene (Muller et al., 2006).

The expansion of woody taxa (Kershaw et al., 1991) and rising lake levels (e.g. Dodson, 1977; Bowler, 1981; Edney et al., 1990) in southeastern Australia indicate an increase in absolute precipitation beginning at around 10 ka. These studies are evidence for a transition from the semi-arid conditions that followed the LGM to more humid conditions during the early Holocene. This climatic amelioration incorporated a shift to less extreme temperature variations and weaker wind regimes across the continent.

A period of the early to mid-Holocene (8-6 ka) is considered by numerous authors (e.g. Chivas et al., 1993; Dodson and Ono, 1997) to be a prolonged warming event with rainfall in southeastern Australia possibly 5-10% higher and temperatures 1-2°C warmer than today (McGlone et al., 1996). In western Victoria there was a major rise in lake level from 10-7.5 ka at Lake Keilambete and this raised level was maintained until ~6.5 ka (Bowler, 1981). Pollen studies at nearby Lakes Terang and Bullenmerri indicate the development of wetter conditions between 8-6.2 ka (D'Costa and Kershaw, 1995) and 8-5.5 ka (Dodson, 1979), respectively. In South Australia, Lake Leake was at its deepest water phase of the last 50 ka from 8 to 3 ka (Dodson, 1974). High levels of peat formation at Boat Harbour Creek suggest that wet conditions also prevailed in the Mount Lofty Ranges of South Australia from around 8 to 5 ka (Bickford and Gell, 2005).

In southern Australia, the peak of the Holocene marine transgression was reached at ~6 ka (Belperio, 1995). Since this time there has been a change to generally cooler and drier conditions across the region. Vegetation change recorded in the sediments of Lake Frome suggests that summer precipitation in this part of South Australia had significantly decreased by ~4.5 ka (Singh and Luly, 1991). Playa conditions were re-established at Lake Frome by 3 ka (Bowler and Teller, 1986). A similar two-phase drying is recorded at Chapple Vale Swamp, in the Otway Region of Victoria, where pollen analysis suggests that a reduction in effective precipitation began at 4.6 ka and was further accentuated around 3.8 ka (McKenzie and Kershaw, 1997). Also at ~3.8 ka, a shift to drier conditions in the Mount Lofty Ranges is implied by a reduction in organic content and humification of the Boat Harbour Creek sediments (Bickford and Gell, 2005). Minimum effective precipitation seems to have been slightly later at Lake Keilambete, which was at its lowest Holocene level from ~3.5 to 2.5 ka and has returned to slightly wetter conditions since then (Bowler, 1981). There has been no such return to wetter conditions in semi-arid northwestern Victoria, where permanent Lake Tyrrell dried to a playa environment at around 2.2 ka (Luly, 1993).

Whilst there is much evidence for reduced effective precipitation in southern Australia during the late Holocene, in northern Australia the transition seems to be manifested not so much as a simple shift to drier conditions but as the change to a more variable climate system. At least three phases of dune activation across northern Australia are thought to represent periodic climatic fluctuations during the late Holocene (Lees, 1992) and a number of studies on plunge-pool and alluvial sedimentology suggest a reduction in monsoonal intensity during this time period (Wywroll and Miller, 2001). A sharp reduction in the organic content of sediments from Four Mile Billabong on Groote Eylandt, Arnhem Land, suggests that there was a significant decrease in effective precipitation at around 3.7 ka (Shulmeister, 1992). A similar decrease is also evident in the pollen record from Lynch's Crater at around this time (Kershaw, 1976). Pollen evidence then implies a precipitation increase at ~1 ka in Arnhem Land and at 1.4 ka on the Atherton Tablelands, respectively (Shulmeister and Lees, 1995).

The different timing that is suggested by Harrison and Dodson (1993) and Shulmeister and Lees (1995) for changing Holocene climatic conditions across Australia may be an artefact of the uneven spatial study site distribution considered within the two reviews. However, the theory of a mid-Holocene 'palaeoclimatic optimum' is well accepted and it was during the early to mid-Holocene (~8 to 5 ka) that there was both maximum expansion of tropical rainforest in northern Queensland (De Deckker et al., 1988) and in southeastern Australia effective precipitation was at a maximum (e.g. Chappell, 1991; McKenzie and Kershaw, 1997).

Although much of the above outlined data provides comparable information on Holocene climate change there are often discrepancies between sites in the timing and extent of changes in effective precipitation as implied through palynology. These differences reflect the influences of factors such as study site proximity to refuge areas for particular vegetation types during the LGM and different expansion rates for various vegetation types after the LGM.

The information on local to regional scale palaeoclimatic change across Australia that is summarised above has predominantly been determined through the use of palynology, trace element analysis, and through studies that infer past lake levels from palaeoshorelines and secular variations in lacustrine sediment textures. However, there are other methods of approach to palaeoenvironmental reconstruction through the investigation of lacustrine systems. The use of elemental and isotopic geochemical analysis is one such approach (outlined in Chapter 2) that can yield significant information on past biotic assemblages, and therefore environmental conditions, within the lake and its catchment.

1.3 Lake Sedimentology

The accumulation of lacustrine sediments is affected by a wide variety of processes both within and around the lake basin. In effect, lake sediments are natural archives that reflect the history of these natural processes and, therefore, record changes to the environmental conditions within the lake and its surrounding catchment (refer to four volume set: W.M. Last & J.P. Smol (Eds.), 2001. 'Tracking Environmental Change Using Lake Sediments'). This section discusses the processes that influence the formation/delivery of lacustrine sediments and which may therefore be evaluated through sedimentary analysis.

Whilst material that was actually produced within the lake will hold information about internal lake conditions, sediments that originated from beyond the lake will integrate information about processes acting within the entire lake catchment and even beyond. The importance of either sediment group varies depending on each individual lake setting. Lakes that are fed by numerous tributaries receive a greater proportion of externally derived sediments than lakes that are groundwater-fed, which are dominated by internal sediment formation and receive only minor contributions via local runoff and aeolian delivery (Figure 1.4).

Water depth influences the nature of lacustrine sedimentation in a number of ways. For example, under stratified conditions a variety of different ecological niches will exist at different water depths. The absence of benthic fauna under conditions of hypolimnic anoxia will reduce bioturbation at the sediment-water interface and therefore enhance preservation of sedimentary laminations. Depth dependent sedimentation effects still exist in the absence of stratification. For sediments delivered from beyond the lake, the rapid settling velocity of coarse particles results in deep-water sediments being finer than shallow-water sediments. This hydrodynamic sorting is also influenced by the proximity of any sedimentation point within a lake to the initial site of sediment delivery. A higher proportion of coarser particles will be deposited near a tributary mouth, although the actual point of particle deposition will depend on the tributary flow velocity. Wind induced surface water mixing causes settling sediments to remain in the water column for a longer time than would occur under still conditions. In shallow waters, where the wind-mixed layer is deep enough, this turbulence can promote resuspension of already settled sediments. A consistent prevailing wind direction will lead to the downwind accumulation of these sediments, plant and animal remains on the lakeshore.

In shallow ephemeral lakes, periodic drying of the lake waters can lead to aeolian reworking of the lake floor sediments and accumulation of these sediments on the leeward shore of the lake. Lunette formation eventually results from the repetition of this process and can subsequently influence the lakes hydrology. Lunettes and beach dune ridges that border or surround a lake can retain freshwater and may therefore act as a small local aquifer that contributes freshwater via seepage at the lake margin (De Deckker, 1988). The presence of these seepage zones can influence the nature of the lacustrine sediments by providing the environmental conditions in which particular biota will thrive and/or sediments may form.

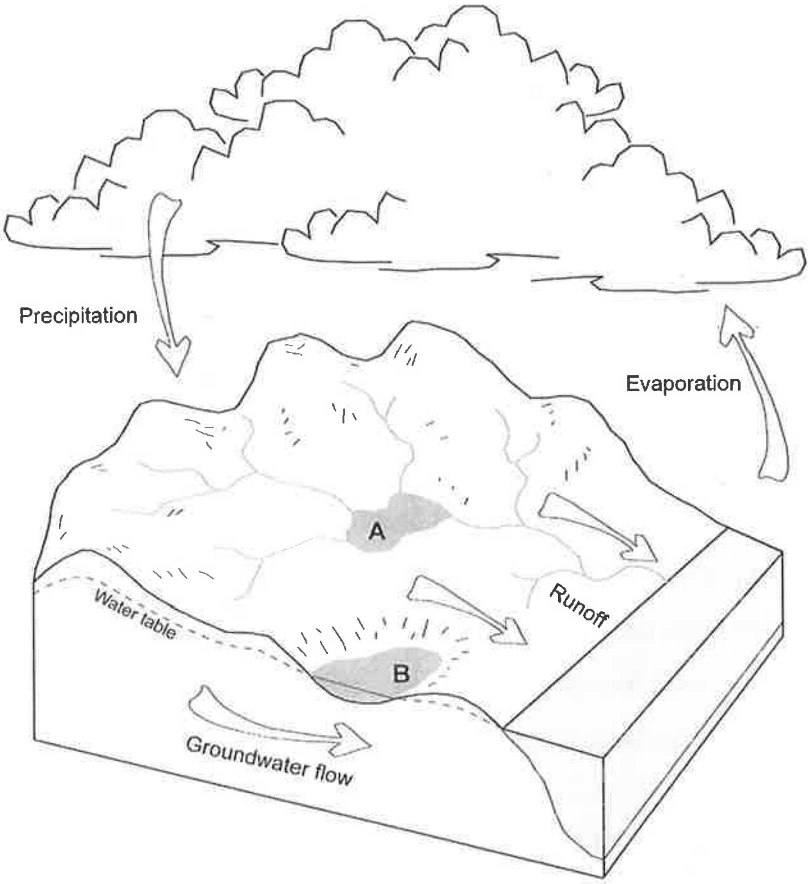


Figure 1.4: Schematic illustration comparing two lake types. As Lake A is fed by a system of tributaries, its sediments will incorporate information from the entire lake catchment. Lake B is groundwater-fed and its sediments will primarily reflect internal lake processes.

1.3.1 Allogenic Sediments

In a lacustrine setting, allogenic sediments are those derived from beyond the lake. These sediments are transported into a lake by aeolian and/or fluvial processes, and may therefore provide information on the local and regional mechanisms of atmospheric fallout, stream and surface flow and shore erosion (Håkanson and Jansson, 1983).

In arid areas, or during arid periods, aeolian processes dominate and are capable of shifting fine material over great distances (e.g. Hesse, 1994; Simonson, 1995; Zhao et al., 2003). Under arid conditions, sparse vegetation cover does little to stabilize the landscape and therefore irregular and occasionally extreme rainfall events can bring about significant fluvial transport of arid zone sediments (e.g. Jacob et al., 2004). In pluvial areas, or during pluvial phases, a denser cover of vegetation stabilizes the landscape and, therefore, sediments tend to be transported by fluvial rather than aeolian processes. Under these conditions it is generally the small regular rainfall events that are responsible for the majority of sediment transport. However, as in the arid landscape, large infrequent rainfall events can shift significant sediment loads.

1.3.2 Endogenic Sediments

Endogenic sediments are those that are formed within the lake, precipitating in the water column and accumulating on the lake floor. The nature of these sediments depends predominantly on the physiochemical nature and biological conditions of the water at the time of precipitation. Therefore, stratigraphic variations in the abundance and/or composition of endogenic sediments can hold information regarding temporal changes in lake water properties, such as salinity, alkalinity, temperature, chemical composition and nutrient loading (Håkanson and Jansson, 1983). Common examples of endogenic particulates are:

- Diatomaceous silica, which often occurs after a spring bloom of diatoms in temperate lakes (Engstrom and Wright, 1984; Ariztegui et al., 2001);
- Iron and manganese precipitates, which are influenced by changing pH and redox conditions (Davison, 1993; Boyle, 2001); and,
- $CaCO_3$ precipitates in calcareous lakes, which often result from a pH increase caused by algal photosynthesis (Stabel, 1986; Talbot and Kelts, 1990).

Formation of these precipitates in the epilimnion does not always lead to preservation within the lacustrine sediments. The possibility of dissolution in the hypolimnion or the upper sediment layers must be recognised when drawing any conclusions on the environmental history of a lake from the analysis of its endogenic sediments.

1.4 Lacustrine Carbonates

In lakes with calcareous bedrock, carbonates are often the markedly dominant sediment fraction. Not only does the erosion of calcareous rocks and soils from the lake surrounds contribute allogenic carbonates, but also, as the surface runoff, soil water and groundwater entering the lake are enriched with Ca^{2+} and HCO_3^- from weathering of the calcareous bedrock, the formation of endogenic carbonates can be significant under the appropriate physiochemical lake water conditions (Håkanson and Jansson, 1983).

Extreme loading of calcium and carbonates in lake waters of calcareous regions can have a negative effect on productivity through the physical interactions of carbonate precipitates with essential nutrients, which effectively reduce the photosynthetic availability of those nutrients (Wetzel, 1983). However, authigenic carbonates are commonly precipitated as a result of photosynthetic use of CO_2 inducing HCO_3^- supersaturation in the water column. Although carbonate precipitation can be brought about under specific physicochemical conditions (pH, temperature), metabolically induced carbonate precipitation is by far the most rapid and most important formation mechanism (Dean, 1981). Consequently, carbonate precipitation tends to coincide with periods of maximum phytoplankton productivity (Leng and Marshall, 2004). The photosynthetic removal of CO_2 produces disequilibrium in the bicarbonate-carbonate system, which causes a rise in pH (Figure 1.5). The solubility of calcite is pH dependent, decreasing with increasing pH; therefore, the photosynthetic removal of CO_2 induces carbonate precipitation. As the solubility of calcite also decreases with increasing temperature, warmer water temperatures will promote carbonate precipitation (Håkanson and Jansson, 1983). By the same token, carbonate precipitates can be redissolved during settling through the water column, as the deeper waters will be cooler and potentially have a lower pH resulting from CO_2 build-up during decomposition of settling organic matter. Indeed, this carbonate dissolution is the reason why the inverse relationship that often exists between the concentrations of carbonate and organic matter eventually preserved within lake sediments is not simply the dilution of one component by the other (Dean, 1999).

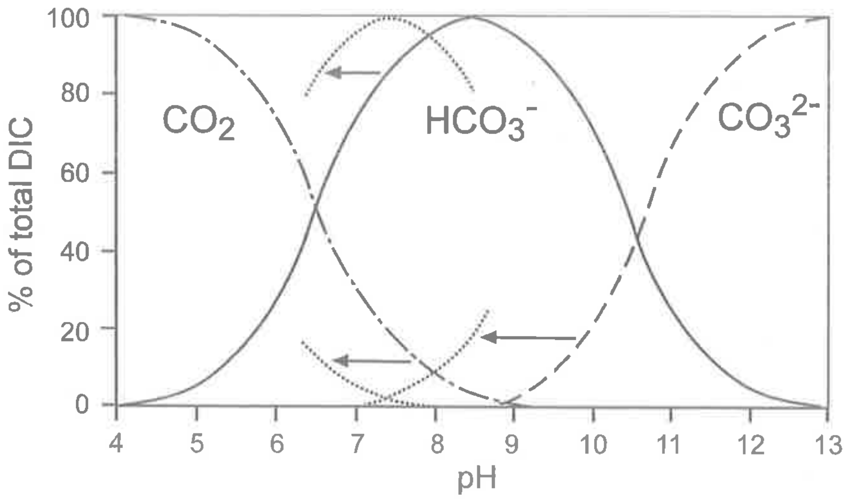


Figure 1.5: Relationship between solution pH and the proportions of dissolved inorganic carbon species for pure water (solid and dashed lines) and seawater with a salinity of 35‰ (dotted lines) at 1 atm pressure (Dean, 1981). Photosynthetic use of CO_2 produces a relative increase in the HCO_3^- and an increase in pH. Waters tend to resist changing pH as long as the $CO_2 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$ equilibria operates. Therefore, the use of CO_2 promotes $CaCO_3$ precipitation until equilibrium is re-established.

Photosynthetic activity is not the only mechanism that promotes carbonate precipitation through initiating adjustments to the $CO_2 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$ equilibria. Groundwater that flows through carbonate bedrock will become heavily enriched in HCO_3^-. Under reduced pressure upon surfacing much of this bicarbonate is released as CO_2 to the atmosphere, thus inducing carbonate precipitation (Wetzel, 1983). Similarly, the precipitation and cementation of carbonate plates often occurs as a result of rising carbonate-rich groundwaters mixing with fresh water seepage at a lake margin. This is most likely to occur in a region that experiences strong annual climatic contrasts, such as the Coorong, where fresh winter rains recharge aeolian or beach dune aquifers surrounding the lake and seepage subsequently mixes these freshwaters with saline carbonate groundwaters (De Deckker, 1988).

Authigenic carbonate mineralogy is to some extent determined by the Mg/Ca ratio of the lake waters; however, it may also be influenced by salinity, pH and dissolved sulphate and phosphate concentrations (Talbot and Kelts, 1990). As a broad generalisation, calcite tends to form in freshwaters, but with increasing evaporation other carbonate minerals, such as aragonite and dolomite, will precipitate from the water column (Talbot and Kelts, 1986). In this study it is not the mineralogy of the carbonate precipitates, but the isotopic composition, that is considered in most detail.

1.5 Organic Matter in Aquatic Environments

Much of the above discussion on sedimentology has focussed on lacustrine systems but could equally be related to the marine environment. The description of some elemental and isotopic studies on sedimentary organic matter in marine and deep-lake settings forms the final section of this chapter. Thus, although the present study is an investigation of lake sediments, it is nonetheless useful to point out some important differences between the sedimentary organic matter of lakes and oceans.

Lake basins receive proportionally more terrigenous sediment influx (clastic particles and nutrients) than deep ocean basins. Therefore, both sedimentation rates and aquatic productivity are significantly greater in lakes than in the oceans (Meyers, 1997). Organic matter preservation can be enhanced by these higher sedimentation rates, which cause more rapid burial of the organic matter that reaches the sediment-water interface. The high rates of sedimentation and the extent of organic matter preservation in lacustrine settings means that their sedimentary records provide information on short-term palaeoenvironmental processes of a local to regional scale at a high temporal resolution. Marine sediments are more suited to the investigation of long-term palaeoenvironmental changes at a regional to global scale.

Organic matter is generally a small, but important constituent of lake sediments. It is a mixture of biochemical fractions contributed from the (potentially wide) array of organisms formerly living both within the lake and its catchment, and derived from diagenetic alteration of these materials (Tyson, 1995). The composition and amount of organic matter preserved within lacustrine sediments varies in response to the types and abundance of organisms in and around a lake basin. As this biota varies with changing environmental conditions, lacustrine sedimentary organic matter has the potential to reveal information on secular variations in those relevant and influential conditions at the local to regional scale throughout the sedimentation period. There are a number of indicators, or proxies, that can be used to infer these environmental conditions and changes. As already indicated, the principles behind the application of proxies used in the present investigation are described in Chapter 2, whilst the remainder of this chapter is devoted to outlining the broad aspects of organic matter production and degradation within the aquatic environment.

As the more labile components of organic matter are preferentially degraded before the more stable components, diagenetic processes have the potential to alter the original composition of bulk organic matter and therefore mask the information that would be inferred from un-degraded organic matter. These alterations are also environmentally dependent and therefore a comprehensive grasp of organic matter diagenesis can enhance the researcher's understanding of past environmental systems.

1.5.1 Organic Matter Production

Although detritus from terrestrial plants can be an important contribution to the sedimentary organic matter of many lakes and coastal marine areas, phytoplankton produce the dominant proportion of primary organic matter that reaches the sediments of most aquatic systems (Meyers, 1997). Secondary organic matter derived from microbial and bacterial activity can also comprise a major portion of the organic matter that is preserved within the sedimentary record. The primary organic matter sources and processes of modification are shown in Figure 1.6.

Phytoplankton uses the energy available in sunlight to convert dissolved inorganic carbon into organic matter. This process is restricted to the waters that sunlight can penetrate, the photic zone, as it is sunlight that energizes aquatic photosynthesis. The photic zone can extend to depths of up to 200 m in exceedingly clear waters, though is typically only a few tens of meters in depth (Killops and Killops, 2005). In deeper waters, the chemical energy produced through oxidation of reduced substrates can be utilised in chemosynthesis, but this process is generally not a significant contributor to the overall aquatic organic matter pool.

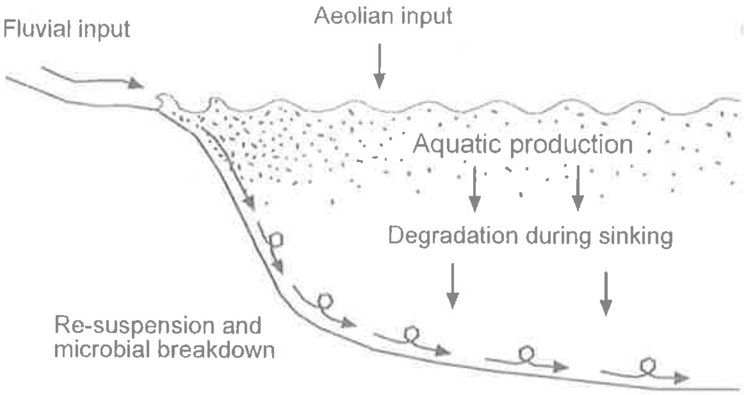


Figure 1.6: Schematic illustration of organic matter sources in an aquatic setting and the degradation that occurs prior to complete burial within the sediments. In most instances the aeolian contribution from beyond the lake catchment will be minor and the majority of sedimentary organic matter arrives via fluvial delivery from within the catchment and/or originates from algal production in the lake. Organic matter degradation occurs both within the water column and at the lake floor. (adapted from Meyers and Ishiwatari, 1993a).

Nutrient availability is also crucial to organic matter production. As nitrogen and phosphorous levels are often limited in natural waters, primary productivity in aquatic systems is often highly dependent on the terrestrial runoff that supplies these essential elements (Meyers, 1997). The dependence on nutrient supply makes lakes and coastal areas more productive than the open ocean, and has important implications in the field of palaeoenvironmental reconstruction. Periods of enhanced aquatic productivity evident in the sedimentary sequences of many marine and deep-lake settings have consistently been related to an influx of terrestrial nutrients during wetter climatic conditions (as discussed below, section 1.6).

Nutrients can be delivered to the photic zone not only from external terrestrial sources, but also through internal aquatic recycling. As biota utilize these nutrients in the formation of organic matter, the settling and deposition of organic matter removes these nutrients from the photic zone. Burial in the sediments subsequently removes these nutrients from the system. However, the decomposition of organic matter that occurs during settling through the water column and at the sediment-water interface re-releases nutrients to the hypolimnion. Recycling of these nutrients to the epilimnion can be brought about through turbulent mixing of the water column, which is enhanced during periods of strong winds (Meyers and Lallier-Vergès, 1999). For example, an increase in clastic particle delivery, which suggests a period of strong winds, coincides with an increase in the flux of diatom frustles to the sediments of Elk Lake, Minnesota, between 7.5 and 4 ka (Bradbury and Dieterich-Rurup, 1993). The authors interpret the apparent increase in diatom productivity to the occurrence of stronger winds enhancing turbulent mixing of the lake waters.

Although the maintenance of density stratification in many marine and deep-lake settings will inhibit the recycling of nutrients from deep waters (e.g. Luz, 1979; Rossignol-Strick, 1985; Nolet and Corliss, 1990), the increase in density of the surface-waters associated with either an increase in salinity or decrease in temperature can promote annual or semi-annual overturn, thereby mixing the water column, returning nutrient-rich waters to the photic zone and enhancing aquatic productivity (Meyers, 1997).

In strongly stratified water bodies, organic matter production from microbial and bacterial activity can be significant. However, microbes and bacteria are responsible for the secondary modification, rather than primary production of organic matter (Meyers and Ishiwatari, 1993a). Generally, bacteria do not create new biomass but instead catalyse the recycling of essential nutrients and compounds (Håkanson and Jansson, 1983). These processes of organic matter breakdown and diagenesis are discussed below.

1.5.2 Organic Matter Breakdown and Diagenesis

During the time between organic matter production in (or delivery to) the epilimnion and eventual burial in the underlying sediments, degradation processes can both decrease the amount, and modify the original structure/character of the organic matter. The extent of this degradation depends primarily on the nature of the water column (depth, oxic state). However, as degradation continues in the bottom sediments, conditions at the sediment-water interface and within the sediments themselves also influence the amount and type of organic matter that is finally preserved within subaqueous sediments. Microbes and benthic organisms preferentially utilize the more labile organic components; therefore degradation processes increase the relative proportion of recalcitrant components of lacustrine organic matter.

The carbon in organic matter is in a reduced state and therefore, organic matter is inherently unstable in oxidising environments (Tyson, 1995). The dissolved oxygen content of most natural waters is replenished through exchange with the atmosphere at a greater rate than it is removed through the respiration and oxidation of organic matter (Meyers, 1997). Therefore, in marine and deep-lake settings where sinking organic matter is exposed to an oxygenated water column for extended periods of time, typically only a small amount of the originally produced organic matter will actually be buried in the sediments (e.g. Suess, 1980; Eadie et al., 1984; Emerson and Hedges, 1988). The remainder is remineralized and recycled through the water column. In shallower lakes, shorter sinking times for the settling organic matter reduce the length of exposure to oxidation in the water column. Consequently, the extent of diagenetic alteration during sinking is limited, which enhances the phenomenon of shallower lakes sediments usually being organically richer than those of marine or deep-lake settings (Meyers and Ishiwatari, 1993b).

Organic matter degradation continues at the sediment-water interface, where resuspension of the surface sediments and bioturbation re-expose the organic matter to oxidation. The extent of these two processes varies depending on lake conditions (resuspension is more significant in large, well-mixed lakes than in smaller lakes), but can be significant. For example, in Lake Michigan, the resuspension of sedimented organic matter into the hypolimnion is nearly ten times the rate of sedimentation through the water column (Meyers and Eadie, 1993). Further to extending the oxidation of sedimented organic matter through re-exposure at the sediment-water interface, bioturbation also indicates the presence of benthic micro-organisms, which degrade organic matter through nutritional consumption. Many benthic fauna require oxygen for respiration (Håkanson and Jansson, 1983); therefore, the abundance of benthic fauna is more substantial, and bioturbation more significant, in oxic waters. Indeed, the absence of bioturbation recorded by the preservation of finely laminated sediments is generally an indication of hypolimnic anoxia (e.g. Ariztegui et al., 2001; Lücke et al., 2003). So, not only will a higher proportion of aquatic organic matter survive sinking through anoxic waters, but also the reduced bioturbation under conditions of anoxia further aids organic matter preservation. Anoxia develops in strongly stratified water bodies or during periods where productivity is elevated to the extent that dissolved oxygen is being utilized more rapidly than it is replenished (Cramp and O'Sullivan, 1999). The preservation of organically rich sediments has often been associated with either, or both, of these circumstances.

Although the aerobic breakdown of organic matter will continue for as long as there is dissolved oxygen available, it is not the only possible oxidising agent and thus, diagenesis continues under anoxic conditions. Even in the absence of hypolimnic anoxia, the low rate of oxygen diffusion into saturated sediments and its rapid use within the sediments mean that the breakdown of organic matter within sediments follows anaerobic processes (Wetzel, 1983). Once the dissolved oxygen supply is exhausted, decomposition proceeds via a progression of alternative electron acceptors: nitrate (NO_3^-), manganese (IV) and iron (III) oxides, sulphate (SO_4^{2-}), and CO_2 (Håkanson and Jansson, 1983; Shultz et al., 1994). Nonetheless, below the zone of bioturbation organic matter is degraded at a much slower rate than it is through oxidation within the water column and at the sediment-water interface.

Regardless of the potential for breakdown and diagenesis to significantly reduce the actual amount of organic matter that is eventually incorporated into the sediments of aquatic systems, the original information that is retained by bulk geochemical parameters can be preserved (e.g. Meyers and Eadie, 1993). Thus, the geochemical analysis of lacustrine sedimentary organic matter has the potential to yield important information pertaining to the investigation and reconstruction of secular changes in environmental conditions within the lake and its catchment. As described below, the presence of particularly organic-rich intervals within marine and lacustrine sedimentary successions has often been interpreted as resulting from a combination of enhanced primary productivity in nutrient-rich surface waters and reduced organic matter breakdown in sub-oxic or anoxic bottom-waters.

1.6 Sapropels and Sapropelic Sediments

Distinct sedimentary layers that are enriched in organic carbon have been deposited and are preserved in numerous marine and deep-lake settings across the globe. In the Mediterranean Sea, repeated organically rich layers were first identified in cores collected during the 1947/1948 Swedish Deep-Sea Expedition (Kullenberg, 1952, as cited in Rohling and Thunell, 1999). Since that time much research has been devoted to the formation of these layers, which have been termed sapropels. The term sapropel originates from the Greek *sapros* (rotten) and *pelos* (soil) following the work of German chemist, Wasmund (Cramp and O'Sullivan, 1999) and has been widely applied to describe aquatic sedimentary deposits rich in organic matter. In 1978, Kidd et al. proposed the quantitative definition of sapropels as being: "A discrete layer, greater than 1 cm in thickness, set in open marine pelagic sediments containing greater than 2% organic carbon by weight." Furthermore, Kidd et al. (1978) defined sapropelic sediments as being similar marine deposits that contain between 0.5 and 2% organic carbon. In the past, the term sapropelic had been applied to a much broader array of organic rich sediments, including those from lacustrine settings (Livingston, 1984; Cramp and O'Sullivan, 1999). The terms sapropel and sapropelic have been interpreted differently by numerous authors. For example, Korde (1960) described sapropels as organic carbon rich deposits containing abundant recognizable remains of microscopic organisms. More recently, Hilgen (1991) proposed a much simpler definition of sapropels as being "brownish, often laminated interbeds." Although the 1978 definitions proposed by Kidd et al. have been widely adhered to in the study of marine sedimentary deposits, in lacustrine environments the terms sapropel and sapropelic continue to be used somewhat loosely to this day.

Regardless of continuing differences in the use of sapropel nomenclature, studies on a wide variety of organic rich sediments have consistently concluded that their deposition and preservation result from palaeoenvironmental conditions that promoted an increase in aquatic productivity (e.g. Calvert et al., 1987, 1992; Martinez-Ruiz et al., 2000) and/or a decrease in organic matter degradation (e.g. Rossignol-Strick, 1985; Tolun et al., 2002). In marine and lacustrine systems that receive fluvial input, periods of wetter climate will generally enhance aquatic productivity through an increase in the wash-in of soil nutrients. In Lake Carajas, Brazil, the influx of both terrestrial nutrients and materials (macroscopic plant fragments) causes organic carbon mass accumulation rates to be up to four times larger in times of wetter climate than during dry periods of the last 60 ka (Siffeddine et al., 1994 as cited in Meyers and Lallier-Vergès, 1999). This pattern extends even further into the past in Lake Biwa, Japan, where organic carbon mass accumulation rates are up to nine times larger in the interglacial than the glacial intervals over the last 340 ka (Meyers and Takemura, 1997). More recently, at Lake Bosumtwi, Ghana, a sapropelic interval deposited from ca. 9 to 3 ka corresponds to a relatively stable period of wet climate and high lake levels (Talbot and Johannessen, 1992), as does a sapropel deposited from ca. 5.3 to 3.9 ka in Swan Lake, Nebraska (Hassan et al., 1997).

The sapropels of the Mediterranean Sea exhibit 19-23 kyr cyclicity and have been associated with intensified monsoonal circulation and increased precipitation in the Mediterranean region during precessional minima (Rossignol-Strick, 1985; Hilgen, 1991; Bouloubassi et al., 1999). A comparison of marine and lacustrine sedimentary records in the Mediterranean region documents the coincident deposition of organic rich sediments in the both marine and terrestrial realm at the time of sapropel S1 formation (ca. 9 to 6.8 ka; Ariztegui et al., 2000). The authors suggest that an increase in freshwater discharge from tributaries across the region enhanced productivity in both the lacustrine and marine systems, and may have also led to stratification and deep-water anoxia in the latter, which impeded organic matter degradation and aided in preservation of the organic rich sedimentary layers. Evidence for an Early Holocene warm, wet climate in the Mediterranean is also found in the sediments of Lac du Bouchet, France, where a significant increase in organic carbon of both aquatic and terrestrial origin was deposited between 9 and 8 ka (Siffeddine et al., 1996). These sediments also contain a smaller proportion of clastic minerals than those sediments deposited during the preceding glacial period, which reflects the diminished erosion of lake catchment soils as the vegetation cover expanded. Indeed, the glacial age sediments of temperate lakes are generally poor in organic carbon and have accumulated rapidly (Meyers and Lallier-Vèrges, 1999).

In all of the examples described above, a climatically induced increase in the amount of nutrients delivered to the system caused an increase in aquatic productivity and has been recorded by the deposition of organically rich sediments. However, an increase in the rate of organic matter burial within sub-aqueous sediments is not always indicative of an increase in aquatic productivity. For example, agricultural use of river water diverts it away from reaching terminal lakes, and has caused a lowering of the water levels in Mono Lake, California (Jellison et al., 1996) and Pyramid Lake, Nevada (Meyers et al., 1998). This lowering of water levels increased the salinity and decreased algal productivity in the two lakes, yet contrary to expectations, increased the sedimentary organic carbon mass accumulation rates. The explanation for this observation is that the lower water levels exposed sediments at the lake margin to turbulent re-suspension by wave action. Re-deposition of these sediments increased the rate of organic matter accumulation in the deeper parts of the lake basin (Meyers et al., 1998). This gives the appearance of an apparent productivity increase even though algal productivity actually declined as a consequence of the increased water salinities at this time (Jellison et al., 1996). This is a prime example of the reason why palaeoenvironmental reconstructions from marine and lacustrine sedimentary sequences require the analysis and interpretation of multiple geochemical proxies.

1.7 Rationale

Many shallow, groundwater-fed lakes along the Coorong coastal plain of southeastern South Australia contain sapropelic sediments within their Holocene calcareous mudstone successions (e.g. von der Borch and Altmann, 1979; Rosen et al., 1988; Warren, 1988, 1990, 1994; Hayball et al., 1991; McKirdy et al., 1999, 2002; Mee et al., 2004, 2007; Edwards et al., 2006: Appendix I). As described above, the deposition of similarly organic carbon rich sediments in marine and deep-lake settings has predominantly been linked to times of wetter regional climates. During these times, increased precipitation boosted surface runoff and tributary flow, thereby increasing the input of terrestrial organic matter and nutrients to the aquatic systems and potentially causing stratification of the water column. The increased nutrient supply primarily has the effect of promoting aquatic productivity, which can in turn lead to oxygen-depletion of the bottom waters and enhanced preservation of organic matter.

The three coastal lakes of the present investigation represent a distinctly different aquatic environment to those in which sapropels have primarily been studied in the past. The lakes of the present study are shallow and have become increasingly ephemeral over time, yet also contain sapropelic intervals with high concentrations of autochthonous algal and bacterial organic matter within their sedimentary successions. Thus, this study adds a new perspective to the dynamics of sapropel genesis.

Sedimentation in these coastal Coorong lakes spanned the mid-Holocene transition from generally warmer and wetter to cooler and drier (or more seasonal) conditions that is documented in many Australian palynological and palaeolimnological studies. At a number of sites near Lake Albert, close to the mouth of the River Murray (Figure 3.A), sapropel deposition (5.8 - 6.9 yr BP; von der Borch and Altmann, 1979) coincides with this early to mid-Holocene palaeoclimatic optimum of generally warm, wet conditions. Similarly, sapropel in the carbonate mudstone successions of two unidentified alkaline lakes adjacent to the southern Coorong Lagoon were radiocarbon dated at 6.6 ± 0.2 and 8.0 ± 0.5 yr BP (von der Borch and Altmann, 1979). Indeed, it seems that sapropel deposition beneath an extensive freshwater lake system along the Coorong coastal plain was associated with a period of humid conditions in the region. Geochemical analysis of both the sapropel deposits and surrounding sediments in the three lakes of the present study should help elucidate the palaeoenvironmental conditions that existed during sapropel deposition.

While the use of bulk sedimentary geochemistry has been shown to record palaeoenvironmental changes over a wide range of settings across the globe it has little been applied to the study of shallow, ephemeral lakes in Australia. Nonetheless, the elemental, molecular and isotopic analysis of sedimentary organic matter and carbonate can greatly aid palaeoenvironmental reconstructions. The present study explores the extent to which the application of this geochemical approach to the sediments of these coastal lakes reveals the Holocene environmental change that is already established for the region.

1.8 Aims

There are a number of aspects to the present investigation on the Holocene carbonate successions of three shallow, ephemeral lakes from the Coorong coastal plain. These are most easily addressed as the following list of aims and questions:

- ➔ To determine the timing of the sapropel 'events' (deposition of the sapropel layers) in the three lakes. Naturally, this requires clarification of which sediments are actually considered sapropel within the present environmental setting. Was sapropel deposition continuous or punctuated (variable) in each lake?

➔ To determine the origin of the sapropelic organic matter and evaluate any changes in the nature of the organic matter (autochthonous, allochthonous) throughout deposition of these lacustrine sedimentary sequences. What do the presence and composition of the sapropels indicate about the evolution of each host lake?

➔ To establish whether sapropel deposition in these shallow, coastal lakes primarily reflects increased organic matter delivery to the sediments during periods of enhanced terrestrial input and/or aquatic productivity, or results predominantly from the existence of conditions that significantly improved organic matter preservation. This requires investigation and hypothesis of the possible triggers to shallow lacustrine sapropel formation. Are the triggers different to those in marine settings?

➔ To relate sapropel deposition in these three coastal lakes to both regional and global palaeoenvironment reconstructions. What does this study add to our present understanding of Holocene environmental conditions in Australia? Where does this study fit in a global context?

The overviews of Holocene environmental variability, lacustrine sedimentology, organic matter in aquatic environments, and sapropel deposition were included in this introductory chapter so as to give context to the aims of the present investigation. Chapter 2 outlines the principles behind the elemental and isotopic geochemical analyses that are primarily used to address these aims. Following this, chapter 3 describes the chronological techniques used in the present investigation and chapter 4 provides detail on the methods of fieldwork and geochemical analysis. The environmental setting of the study area and complete stratigraphic descriptions are included in Chapter 5. Chapter 6 reports the results of elemental, isotopic and spectroscopic analysis of the lacustrine organic matter and co-deposited sedimentary carbonate. The chronological framework for sedimentary deposition in the three lakes is discussed in chapter 7. The origin of the lacustrine organic matter is discussed in chapter 8. In chapter 9, discussion ensues on the evolution of each lake as suggested by isotope chemostratigraphy of carbonate and organic carbon. The implications of these findings on our current understanding of Holocene climate change are discussed in Chapter 10. Finally, conclusions are summarised and suggestions for future research made in Chapter 11.

CHAPTER 2: PRINCIPLES OF ORGANIC AND INORGANIC GEOCHEMISTRY

Elemental and isotopic geochemical analysis of lacustrine sediments has the potential to yield significant palaeoenvironmental information if used in combination with a thorough understanding of elemental cycling and the associated effects of isotope fractionation. For example, by recognising the difference in elemental composition and isotopic signature of organic matter synthesised from an aquatic or atmospheric inorganic carbon source, atomic C/N ratios and organic carbon isotope ($\delta^{13}C_{org}$) values aid in evaluating whether the organic matter preserved in a lacustrine sedimentary sequence originated from within the lake itself (aquatic) or externally (terrestrial). The identification of genetically different types of sedimentary organic matter is fundamental to interpreting the organic geochemical trends recorded in lacustrine successions. For example, in systems where primary production is a principal source of organic matter, secular variations in organic carbon isotope values can provide information regarding changes in past productivity rates and in palaeoenvironmental factors, such as water temperature and alkalinity.

This chapter outlines the principles that guide the application of the geochemical parameters employed in this study of lacustrine organic matter and sedimentary carbonate. The manner in which a wide variety of natural processes influence the record of these geochemical parameters have been generalized through numerous lacustrine investigations. The importance of using multiple proxies in palaeolimnologic studies is illustrated by describing the potential for bias and post-depositional alterations of each of the parameters. Such alterations can obscure the original environmental information and must therefore be taken into consideration in any palaeolimnologic investigations.

The first section of this chapter describes the elemental analysis of bulk organic matter. The geochemical uses of stable isotopic analysis of both organic matter and sedimentary carbonate are then considered. The final section of the chapter briefly details the principles behind ^{13}C - nuclear magnetic resonance spectroscopy, a technique that is used in the present study to reinforce inferences made via elemental and isotopic geochemical analysis.

2.1 Elemental Distribution

2.1.1 Total Organic Carbon

Total organic carbon (TOC) content is an essential parameter for evaluating and describing the abundance of organic matter preserved in sediments. Carbon comprises approximately 50% of the total elemental composition of typical organic matter, and thus the concentration of organic matter in any sample is approximately twice the measured TOC content (Meyers and Teranes, 2001). TOC concentration represents the amount of organic matter that has survived remineralization since sedimentation. Therefore, it is a function of both the initial production (or influx) of biomass to the system and the extent of its subsequent degradation.

Because TOC concentrations are expressed as weight ratios relative to the total sample mass they are influenced by variations in other sedimentary fractions. When the rate of supply of one fraction increases relative to that of the other fractions then its concentration increases whilst the others decrease (Boyle, 2001). For example, an influx of siliclastic mineral matter will be preserved as a TOC decrease even though the total amount of carbon within the system at that time may have remained constant. Conversely, the dissolution of carbonate minerals will be preserved as a relative increase in TOC (e.g. Dean, 1999).

Mass accumulation rates of organic carbon expressed as mass of TOC per unit of lake bottom area per unit time (typically on the order of mg cm-2 y^{-1}) are potentially a more useful measure of organic matter delivery and preservation than TOC concentrations (Meyers and Lallier-Vergès, 1999). However, accurately dated sediments are fundamental to determining truly representative accumulation rates. The interpolation that is often required between the (sometimes few) dated sample points can add unknown biases and result in accumulation rate data that is considerably less precise than the measured concentration data (Boyle, 2001). Further complexity if added by the calibration process when using radiocarbon dates in the calculation of accumulation rates. Calibration is required to convert radiocarbon years into calendar years, and produces age ranges, rather than specific dates, with levels of statistical uncertainty (see section 3.1.2). Also, as mass accumulation rates are area dependent their calculation requires knowledge of how the area of the lake floor has changed through time. This effect will be relatively more important for smaller than for larger lakes.

Although organic matter may have been subjected to various degrees of post-depositional degradation, even subtle changes in the initial supply of organic matter to sub-aqueous sediments can be recorded by TOC variations (Jasper and Gagosian, 1990; Meyers, 1997). In this study of lacustrine sediments, the abundance of organic matter is represented by TOC values, rather than carbon mass accumulation rates.

2.1.2 Carbon/Nitrogen Ratios

Many researchers have used atomic carbon/nitrogen (C/N) ratios to aid in characterising lacustrine sedimentary organic matter, in particular to distinguish organic matter of aquatic and terrestrial origin (e.g. Prahl et al., 1994; Silliman et al., 1996; Talbot and Lærdal, 2000; Tolun et al., 2002). This distinction is a result of the high lignin and cellulose contents of land plants, and the high protein and nucleic acid contents, but absence of cellulose, in non-vascular plants such as phytoplankton. Typically, organic matter of algal origin will have an atomic C/N ratio between 4 and 10, whereas vascular land plants produce organic matter with C/N ratios of 20 and greater (Meyers, 1994; Tyson, 1995). Exceptions to this include certain types of green algae (e.g. *Botryococcus braunii*) and some riparian and aquatic emergent plants which have higher C/N ratios and are therefore more similar to terrestrial organic matter (Lamb et al., 2004).

Comparing C/N data with these generalised ranges will not necessarily provide the researcher with a completely accurate indication of the source of organic matter in an aquatic setting. C/N ratios can be influenced by several environmental conditions, and these may need to be considered. For example, during times of abundant nutrient supply some algae synthesise particularly lipid-rich organic matter with C/N ratios that may be as high as 18 (Meyers, 1997). Also, algae grown in nitrogen deficient settings (e.g. Lake Victoria, Africa) will have higher C/N ratios than those grown where the nitrogen supply is not physiologically limiting (e.g. Healey and Hendzel, 1980; Hecky et al., 1993; Talbot and Lærdal, 2000). Nonetheless, in lakes that receive significant amounts of vascular plant debris from the surrounding watershed (e.g. Lake Bosumtwi and Lake Tilo), C/N ratios are higher than in lakes where the influx of terrestrial organic matter is small relative to that produced within the water-column (e.g. Walker Lake and Lake Biwa: Table 2.1).

Selective degradation of different components of organic matter has the potential to modify C/N ratios (Meyers, 1997). Microbial denitrification of abundant proteinaceous material increases the C/N ratios of aquatic organic matter during sedimentation and burial (Talbot and Lærdal, 2000; van Mooy et al., 2002). This suboxic microbial degradation can be brought about under conditions of high productivity (Meyers and Bernasconi, 2005). Conversely, the degradation of buried vascular plant material, such as wood, involves the breakdown of carbon-rich carbohydrates and lipids and will therefore decrease C/N ratios (Meyers and Teranes, 2001).

The C/N decrease that commonly occurs in the sediments of oligotrophic lakes and the oceans (e.g. Müller, 1977) is not simply an indication that carbon-rich components of organic matter are degrading, but rather results from the interaction of the sediments with the products of organic matter degradation. Ammonia that is released during decomposition is absorbed and remineralized, whilst carbon dioxide and methane can escape the sediments, which results in a relative increase in nitrogen and decrease in carbon (Meyers and Lallier-Vergès, 1999). Clay minerals have large negatively charged surface areas that readily adsorb ammonia. Therefore, the impact of inorganic nitrogen uptake on C/N ratios is accentuated in the fine sediment fraction (Meyers, 1997). On the other hand, the coarser fraction is likely to contain larger proportions of terrestrial plant debris (e.g. Dickens et al., 2006) and therefore have elevated C/N ratios. These factors highlight the influence of sediment grain size, and thus hydrodynamic sorting on C/N ratios.

Table 2.1: Some examples of representative atomic C/N values of bulk organic matter in Holocene lake sediments.

Location	Atomic C/N	Reference
Lake Bosumtwi, Ghana, Africa	14 - 34	Talbot and Johannessen (1992)
Lake Tilo, Ethiopia, Africa	12 - 29	Lamb et al. (2004)
Mono Lake, California, USA	8	Jellison et al. (1996)
Walker Lake, Nevada, USA	8	Meyers (1994)
Lake Biwa, Honshu, Japan	6	Meyers and Horie (1993)

Generally, post-depositional alteration of the elemental composition of sedimentary organic matter is not large enough to obscure the distinction between aquatic and terrestrial sources (Meyers, 2003). A more significant point of potentially misleading information in the use of C/N ratios comes from the procedure of measuring carbon and nitrogen contents after removal of sedimentary carbonate. This results in comparison of a nitrogen value that incorporates both organic and inorganic nitrogen with a carbon value representing only the organic fraction, thus systematically lowering apparent C/N values (Meyers and Lallier-Vergès, 1999). In most lake sediments organic carbon is >1% and organic nitrogen is much more abundant than inorganic nitrogen. Therefore use of bulk nitrogen measurements in C/N ratios produces a reliable indication of organic matter source (Meyers, 1997). However, more accurate information would be obtained from a C_{org}/N_{org} than a C_{org}/N_{bulk} ratio. The amount of inorganically bound nitrogen can also be approximated through a cross-plot of the TOC and TN values (Talbot, 2001). A positive intercept of the regression line along the TN axis implies that some of the total nitrogen is not associated with the organic carbon (Figure 2.1). The N-intercept value can then be used to correct the TN values so that they only reflect the organic component of the nitrogen and thus more accurately represent the C/N ratio of the organic matter source (Talbot, 2001).

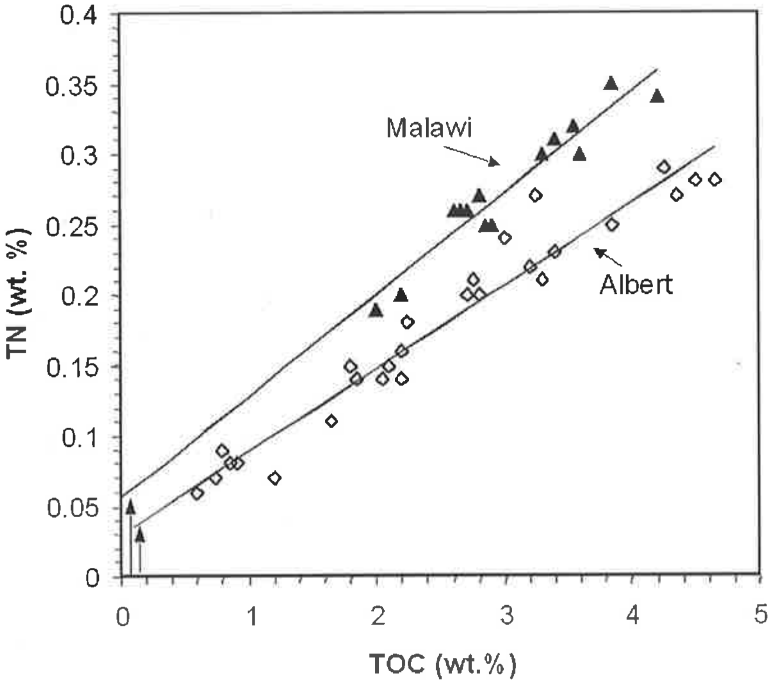


Figure 2.1: Total organic carbon (TOC) versus total nitrogen (TN) for core M98-2P from Lake Malawi and core F from Lake Albert. The positive intercept of the regression lines at the TN axis (indicated with arrows in the lower left hand corner of the plot) implies that some of the nitrogen is inorganically bound (Talbot, 2001).

2.2 Stable Isotope Geochemistry

The difference in mass between two stable isotopes of an element leads to fractionation effects during various natural processes. This fractionation produces small variations in the ratio of the two isotopes within different reservoirs of the element in question. Biochemical effects are responsible for the majority of observed isotopic variations, although physical effects associated with processes such as freezing/melting, evaporation/condensation, adsorption and diffusion can also influence isotopic ratios.

The fundamental cause for fractionation during all processes is the lower bond strength of the lighter isotopes, which makes them more biochemically reactive than the corresponding heavier isotopes and allows for more rapid diffusion and evaporation (Talbot, 2001).

To accurately determine isotopic composition requires highly precise measurement of the isotopic ratios using mass spectrometry. As the absolute amounts of each isotope are difficult to measure these results are most commonly expressed as delta (δ) values per mil (‰), calculated relative to the appropriate synchronously measured international standard as follows:

$$\delta^{B}X_{sample}(‰) = \left(\frac{{}^{B}X/{}^{A}X_{sample} - {}^{B}X/{}^{A}X_{std}}{{}^{B}X/{}^{A}X_{std}} \right) \times 1000$$

where X is the element in question and A and B are the mass numbers for the two isotopes, with ${}^{B}X$ being the heavier and less abundant isotope. For carbon and oxygen the standard is the Vienna Pee Dee Belemnite (V-PDB) and for nitrogen it is air.

The successful application of isotope geochemistry requires an understanding of elemental cycling and the extent of fractionation caused by processes within these cycles. In order to use the $\delta^{B}X$ values of lacustrine sediments as an indicator of palaeoenvironmental changes within the lake basin, catchment or region the effects that have the potential to modify or influence isotopic signals need to be identified and evaluated (Lücke et al., 2003).

The effects and processes that should be considered when interpreting results from isotopic analysis of sedimentary organic matter and carbonate form the basis of this section. The carbon cycle is the simplest and most easily understood of the cycles relevant to this study and is therefore addressed first. For the purposes of simplification the discussion herein is grouped into organic and inorganic carbon isotopic components. Following this, the factors that influence oxygen isotopes in sedimentary carbonates are described. Finally, nitrogen isotopic trends and effects are summarised. However, fractionations within the nitrogen cycle are numerous and complex and the interpretation of nitrogen isotopic data can be difficult.

2.2.1 Organic Carbon

There are two stable isotopes of carbon, ^{12}C and ^{13}C. In nature, the relative abundances of these two isotopes are approximately 98.89% and 1.11%, respectively (Boutton, 1996). The carbon isotopic composition of organic matter ($\delta^{13}C_{org}$) principally reflects the composition of the inorganic carbon source utilised during photosynthesis and the dynamics of carbon assimilation (Meyers, 1997). Autotrophic processes favour incorporation of the lighter isotope, which is more weakly bound and has a higher diffusion velocity than the heavier isotope (Deines, 1980; Killops and Killops, 2005). Consequently, surface CO_2 reservoirs (the ocean, the atmosphere) are relatively depleted in ^{12}C and have more positive $\delta^{13}C$ values than biologically produced material. The photosynthetic pathways used by C3, C4 and CAM (crassulacean acid metabolism) plants have different degrees of isotopic discrimination and therefore produce organic matter with different $\delta^{13}C$ values (Park and Epstein, 1961; Deines, 1980; Boutton, 1991).

Most plants incorporate carbon using the C3 Calvin-Benson photosynthetic pathway. In fact, approximately 85% of all known terrestrial plant species are classified as C3 (Ehleringer et al., 1991). The photosynthetic pathway used by these plants leads to an isotopic discrimination of approximately -20‰ with respect to the inorganic carbon source, although this can vary significantly in response to environmental factors, such as water stress (Farquhar et al., 1989; Tieszen, 1991) and soil salinity (Walker and Sinclair, 1992). For terrestrial plants using atmospheric CO_2, which has a $\delta^{13}C$ value of around –7‰, this leads to the production of organic matter with $\delta^{13}C$ values ranging from approximately –32 to –22, with a mean of –27‰ (O'Leary, 1981).

C4 plants (many, but not all grasses) make up approximately 5% of the current terrestrial plant population and are generally restricted to warm, arid or semi-arid environments (Ehleringer et al., 1991). These plants use the Hatch-Slack photosynthetic pathway, which creates an isotopic discrimination of –4 to –6‰ and therefore leads to the production of organic matter with $\delta^{13}C$ values of around –13‰ (O'Leary, 1988; Meyers and Lallier-Vergès, 1999).

The remaining 10% of the global population of plant species use the CAM pathway for photosynthesis. These are mostly desert plants and succulents (Winter and Smith, 1995), but also include some freshwater aquatic macrophyte species (Keeley, 1990). Freshwater macrophytes display a wide range of $\delta^{13}C$ values, predominantly between about –30 and –12‰ (Boutton, 1991). Obligate CAM species open their stomata to fix carbon at night using mechanisms similar to C4 plants and close their stomata during the day to minimise water loss (Boutton, 1996). These species produce organic matter with $\delta^{13}C$ values similar to those of C4 plants. Under particular environmental conditions facultative CAM species can switch to C3 photosynthesis in daytime, and can therefore produce organic matter with $\delta^{13}C$ values covering the full range between values typical for C3 and C4 plants (O'Leary, 1988; Boutton, 1991).

Although CAM plants are present in a wide array of ecosystems, they are generally only a minor component of the total biomass. Thus, the carbon isotopic distinction between C3 and C4 plants has often been used to aid in evaluating the proportional contribution of these plant types to soil organic matter (e.g. Arrouays et al., 1995; Boutton, 1996; Martinelli et al., 1996; Pessenda et al., 1996; Krull and Skjemsted, 2003).

In subaqueous settings, carbon isotope ratios can be used to distinguish between terrestrial and aquatic sources of organic matter. Freshwater phytoplankton (C3 algae) utilize dissolved CO_2. If this is in isotopic equilibrium with atmospheric CO_2 the organic matter produced will have $\delta^{13}C$ values of approximately –27‰ (Meyers, 1994). Thus, although these values are different from those of C4 plants, they will be indistinct from C3 vegetation of the surrounding watershed. The isotopic distinction between aquatic and terrestrial organic matter more clearly prevails in systems where dissolved CO_2 is in equilibrium with bicarbonate ions (HCO_3^-). These ions are ^{13}C-enriched by 7 to 12‰ in comparison to aqueous CO_2 (Keeley and Sandquist, 1992). Thus, typical $\delta^{13}C$ values for algal organic matter that has used dissolved HCO_3^- as its carbon source are between –20 and –22‰ (Meyers, 1994). The isotopic difference between this aquatic organic matter and that of continental plants has been widely used to assess organic matter sources in marine (e.g. Fontugne et al., 1989; Ariztegui et al., 2000) and lacustrine settings (e.g. Talbot and Johannessen, 1992; Qiu et al., 1993).

In systems dominated by autochthonous organic matter, $\delta^{13}C$ values primarily provide information on the dissolved inorganic carbon (DIC) reservoir. This can aid in reconstructing past productivity rates (e.g. Tolun et al., 2002) or suggest palaeolimnological conditions (e.g. Hassan et al., 1997). Consider the carbon cycle within a small lake (Figure 2.2). As phytoplankton preferentially remove ^{12}C from the DIC reservoir the remaining DIC becomes relatively ^{13}C-enriched. This is followed by a progressive increase in the $\delta^{13}C$ values of newly produced organic matter. Therefore, increased productivity is evident in an increase in $\delta^{13}C$ values of both the organic and carbonate carbon in lacustrine sediments (Meyers, 2003). During periods of extremely elevated productivity high rates of photosynthesis can reduce the availability of dissolved

CO_2 to the point where algae begin to utilize dissolved HCO_3^- as their main carbon source, thus producing significantly ^{13}C-enriched organic matter (Meyers and Lallier-Verges, 1999; Talbot and Lærdal, 2000). Similarly, the production of ^{13}C-enriched organic matter can occur in alkaline waters where the ratio of HCO_3^- to CO_2 is kept high (Hassan et al., 1997). In other systems, the influx of isotopically light soil-derived DIC ($\delta^{13}C \cong -12$‰) can lead to the production of ^{13}C-depleted organic matter (Meyers, 2003). Finally, because the isotopic discrimination that favours biogenic incorporation of ^{12}C increases when the concentration of CO_2 is high (Fogel and Cifuentes, 1993), δ^{13}C values can yield information regarding surface water temperatures during photosynthesis. The solubility of a gas in water increases with decreasing temperature. At 0°C the solubility of CO_2 is roughly 2.5 times greater than at 30°C (Nakai, 1972). As a result of increased isotopic discrimination under conditions of higher CO_2 availability the organic matter produced in cold waters will be ^{13}C-depleted in comparison to that produced similarly in warm waters (e.g. Rau et al., 1989).

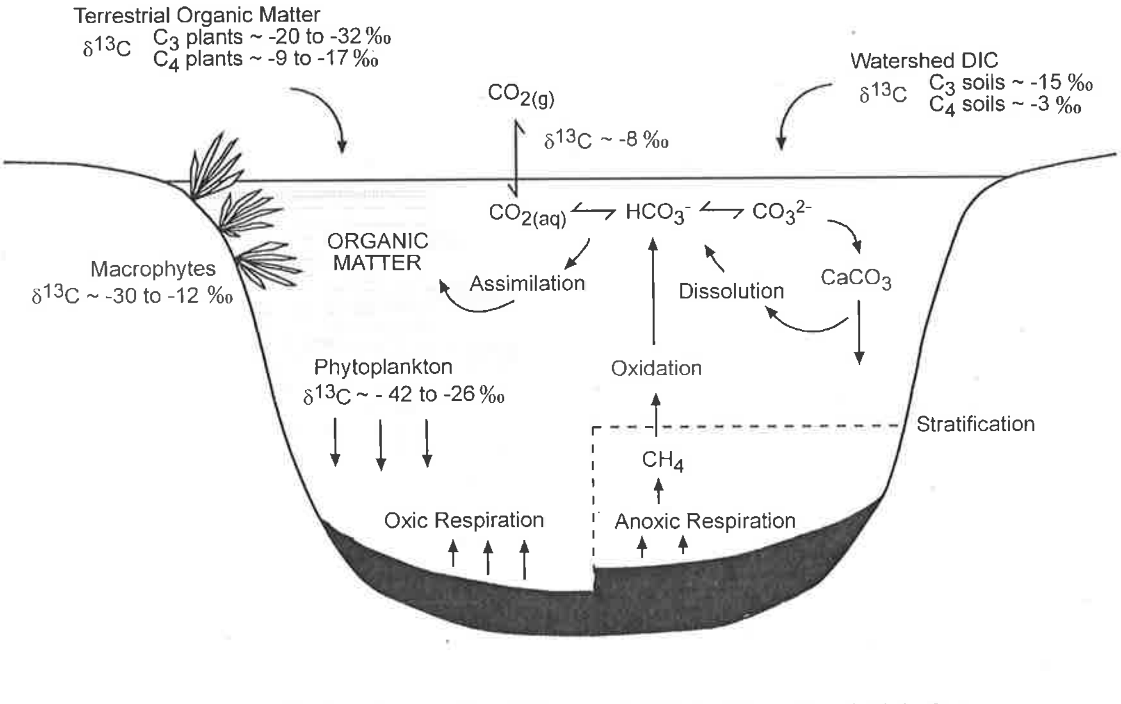


Figure 2.2: Idealized carbon cycle within a small lake showing the principle factors that control the isotopic composition of organic matter buried in the sediments. These factors are: the proportions of terrestrial and aquatic organic matter; the dissolved inorganic carbon isotopic composition; and, the amount of primary production and respiration in the water column. As inorganic carbonate precipitates in isotopic equilibrium with dissolved inorganic carbon its isotopic composition is also influenced by these factors (modified from Meyers and Teranes, 2001).

Photosynthetic carbon fixation tends to be the most important factor controlling the $\delta^{13}C$ values of organic matter within subaqueous sediments (Hodell and Schleske, 1998). However, organic matter is a mixture of variably resistant compounds that have different isotopic signatures (Figure 2.3). Selective degradation of specific organic compounds has the potential to modify bulk $\delta^{13}C$ values (Herczeg, 1988). Generally, diagenetic loss of the more labile components of sedimentary organic matter during sinking and sedimentation will produce a shift of <2‰ in bulk isotopic composition (Meyers, 1997; Prartono and Wolff, 1998).

During periods of significantly elevated primary productivity, such as that arising from increased nutrient availability, oxygen concentrations can reduce to the point of anoxia. Under these conditions microbially mediated carbon cycling can lead to distinct modification of $\delta^{13}C$ values (e.g. Hollander and Smith, 2001). The biogenic methane (CH_4) produced by anaerobic respiration of organic matter is markedly ^{13}C-depleted, as is the microbial biomass synthesised as a result of this diagenetic process (Herczeg, 1988). Therefore, eutrophic conditions and the subsequent development of water column anoxia can impart a significantly ^{13}C-depleted signature to the sedimentary organic matter.

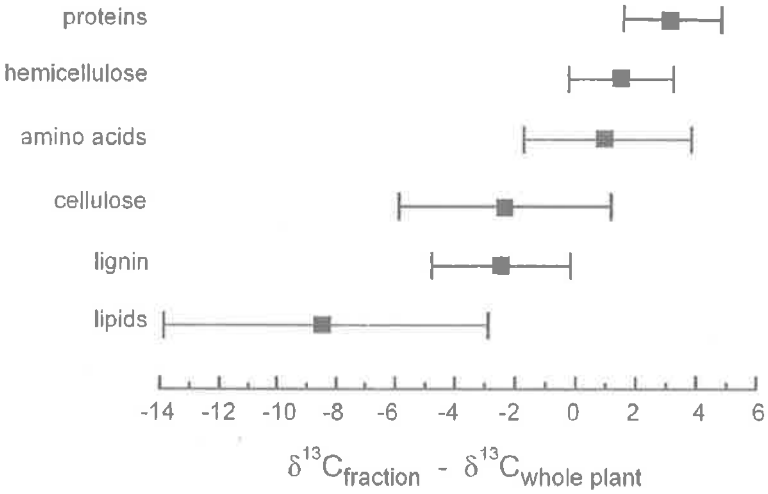


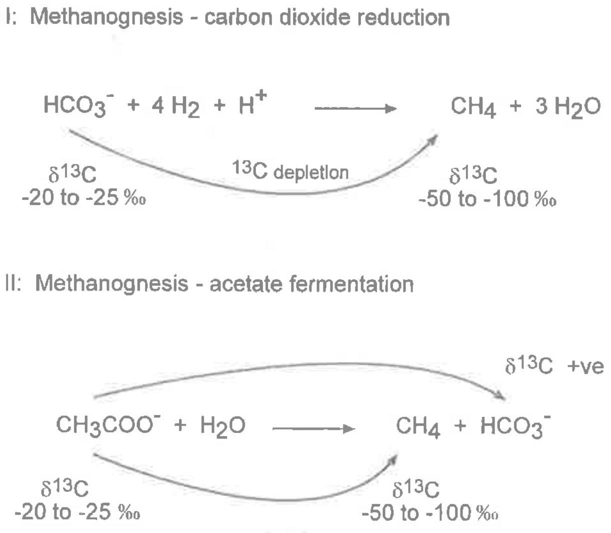
Figure 2.3: Carbon isotope values of isolated biochemical plant fractions relative to the carbon isotope values of the whole plant from which they were extracted (compiled and modified from Deines, 1980; Meyers, 1997; Krull and Skjemsted, 2003).

2.2.2 Inorganic Carbon

The stable isotopic ratio of inorganic carbon ($\delta^{13}C_{carb}$) in a lacustrine sedimentary sequence is a function of the lake's chemical and environmental history. As described above, the carbon cycle is complex and involves many inter-related processes. The major factors that may alter the isotopic composition of DIC, and therefore influence that which is recorded by primary carbonate precipitates, are water residence time, exchange with atmospheric CO_2, influx of isotopically different DIC, the rate of organic matter production and the extent of organic matter breakdown (Kelts and Talbot, 1990; Talbot and Kelts, 1990). These vary in relative importance in different environmental settings. For example, whilst the carbon isotopic signature of carbonate sediments is generally a key indicator of productivity rates in open water bodies (McKenzie, 1985), changes in productivity seem to have little impact on the DIC composition of closed water bodies with long-residence times (Talbot and Kelts, 1990). This relationship is discussed further when considering the oxygen isotopes of aquatic carbonates (section 2.3.3).

As described above with reference to organic carbon, the progressive removal of ^{12}C that accompanies elevated rates of photosynthesis and sedimentation of organic matter leads to an increase in ^{13}C content of the DIC pool. Similarly, ^{13}C-enrichment can occur when the lake productivity remains unchanged and elevated evaporation preferentially removes ^{12}C from the lake waters (Kelts and Talbot, 1990; Li and Ku, 1997). In both cases, ^{13}C-enrichment of the DIC pool causes the precipitation and deposition of increasingly ^{13}C-enriched carbonates over the period of intensified aquatic productivity and/or evaporation (e.g. Dean and Stuiver, 1993; Kolodny et al., 2005). The effects of evaporation and productivity are certainly closely linked. The increase in surface water salinity that results from either strong evaporation or decreased freshwater input can promote vertical mixing of the water column, which brings deep-water nutrients up into the photic zone and therefore enhances aquatic productivity (Li and Ku, 1997). Conversely, freshwater input to saline lakes suppresses vertical mixing through stabilising stratification, and yet, by increasing nutrient availability, freshwater inflow also promotes aquatic productivity.

Whilst the conditions of elevated aquatic productivity and/or evaporation are recorded by ^{13}C-enrichment in both the organic matter and the sedimentary carbonate, post-depositional breakdown of organic matter can cause opposing trends in the isotopic values of these two carbon pools (Hollander and Smith, 2001). Methanogenesis via acetate fermentation splits organic carbon into CH_4 and HCO_3^- (Figure 2.4). This reaction is accompanied by strong isotopic fractionation whereby biogenic methane is preferentially enriched in the lighter carbon isotope. Consequently, the HCO_3^- that is also produced is significantly ^{13}C-enriched. Therefore, conditions favourable for intense methanogensis can result in extreme ^{13}C-enrichment in the carbonates associated with organic-rich sediments (Talbot and Kelts, 1990).


I: Methanognesis - carbon dioxide reduction

II: Methanognesis - acetate fermentation

Figure 2.4: Carbon isotope fractionation during methanogenic breakdown of organic matter (modified from Talbot and Kelts, 1990).

2.2.3 Oxygen

The two isotopes of oxygen measured in stable isotope studies, ^{16}O and ^{18}O, exist at natural abundances of 99.76 and 0.20%, respectively (Hoefs, 1987). The δ^{18}O values of primary carbonates depend on the isotopic composition of the lake water and the temperature at which precipitation occurred (Talbot and Kelts, 1990). Variations in lake water δ^{18}O values are caused mainly by alterations in the composition and/or amounts of input water, or by changes in the balance between inflow and losses resulting from evaporation. Evaporative removal of the lighter oxygen isotope causes lake waters to become ^{18}O-enriched relative to the inflow waters (rainfall, surface runoff, river flow, groundwater seepage). The rate of evaporative removal of ^{16}O depends on environmental factors such as wind speed, temperature and relative humidity with windier and/or more arid conditions increasing evaporation rates (Ito, 2001).

As the oxygen isotopic composition of lake water is primarily a function of the hydrological balance between inflow and evaporative losses, isotopic analysis of sedimentary carbonates may be useful in evaluating the extent of these fluctuations in the past. Arid periods, during which evaporation exceeds freshwater input, are recorded by the deposition of progressively ^{18}O-enriched carbonates. Conversely, in fluvially active systems freshwater input is relatively more influential than evaporation on the isotopic composition of the lake waters. Under these conditions there is a shift toward lighter δ^{18}O values of the lake water and hence the deposition of relatively ^{18}O-depleted carbonates (Li and Ku, 1997). Indeed, numerous studies have used the δ^{18}O signatures of sedimentary carbonates to evaluate fluctuations in lake water volume, with decreasing δ^{18}O values interpreted to indicate rising lake levels and vice versa (e.g. Mayer and Schwark, 1999).

The isotopic evolution of lake waters through vapour exchange across the water-atmosphere interface causes the δ^{18}O values of lake water to be directly influenced by water residence times (Talbot, 1990). Lakes with short residence times have less opportunity to move towards isotopic equilibrium with the atmosphere and therefore differ little from the isotopic composition of the inflow. In humid environmental settings, some lakes with short water-residence times have δ^{18}O values matching that of local precipitation, although this is rare under most environmental conditions (Ito, 2001). Isotopic evolution proceeds further, principally through evaporation, in lakes that have longer residence times (Talbot and Kelts, 1990). Covariance of δ^{18}O and δ^{13}C values is common in these systems (e.g. Stuiver, 1970; McKenzie, 1985; Talbot and Kelts, 1986; Gasse et al., 1987) and is thought to indicate hydrologically closed conditions (Talbot and Kelts, 1990). The isotopic covariance observed in these lakes distinguishes them from hydrologically open lakes, which display relatively invariant δ^{18}O values (Talbot, 1990). Therefore, primary lacustrine carbonates have the potential to yield information on the past hydrologic status (open versus closed) of the lake in which they precipitated. However, when the CO_2 concentration in the lake water is high, the input of ^{18}O- and ^{13}C-depleted freshwaters leads to a smaller change in δ^{13}C than in δ^{18}O (Li and Ku, 1997). Therefore, isotopic covariance is reduced under hyper-alkaline conditions and the true hydrologic nature of the lake may be masked by this effect.

2.2.4 Nitrogen

The two stable isotopes of nitrogen, ^{14}N and ^{15}N, exist in abundances of 99.63 and 0.37%, respectively (Talbot, 2001). The isotopic composition of biologically fixed nitrogen depends on the composition of the inorganic nitrogen source and the metabolic assimilation pathway (Talbot and Lærdal, 2000). The difference between δ^{15}N values of the inorganic nitrogen reservoirs available to plants on land (atmospheric nitrogen, N_2: $\delta^{15}N \sim 0‰$) and in water (dissolved nitrate, NO_3^-: $\delta^{15}N \sim 7\text{-}10‰$) is generally preserved in the organic matter that is produced in each setting (C3 land plants: $\delta^{15}N \sim 1‰$, plankton: $\delta^{15}N \sim 8‰$) (Peterson and Howarth, 1987; Meyers and Lallier-Vergès, 1999). Thus, $\delta^{15}N$ values can help identify the source(s) of subaqueous sedimentary organic matter. However, the complex dynamics of nitrogen recycling and isotopic discrimination during biological assimilation can complicate the interpretation of $\delta^{15}N$ (Meyers, 1997; 2003).

In an aquatic setting, discrimination against ^{15}N during uptake of dissolved inorganic nitrogen (DIN) leads to the production of organic matter that is ^{15}N-depleted and a DIN reservoir that is consequently ^{15}N-enriched (Hassan et al., 1997). Similar to the trend in $\delta^{13}C$ during periods of enhanced primary productivity, the selective uptake of the lighter isotope, ^{14}N, is recorded as an increase in the $\delta^{15}N$ value of newly produced organic matter. In situations where the DIN concentration gradually decreases this isotopic fractionation effect is reduced and there is less discrimination against ^{15}N (Fogel and Cifuentes, 1993). On the other hand, during periods of enhanced nitrate availability there will be a greater isotopic discrimination against ^{15}N, which may lead to the production of organic matter with considerably lower $\delta^{15}N$ values than those typical of algal material (Calvert et al., 1992).

At very low DIN concentrations the nitrogen cycling process can shift from favouring plants that assimilate nitrate, nitrite or ammonium to those which are capable of fixing molecular nitrogen, such as cyanobacteria (Fogel and Cifuentes, 1993; Brenner et al., 1999). As the processes of both nitrogen dissolution and fixation involve minimal isotopic fractionation the assimilation of nitrogen via this metabolic pathway leads to the production of organic matter with $\delta^{15}N$ values close to those of atmospheric nitrogen (Talbot and Lærdal, 2000). Therefore, shifts in the phytoplankton and heterotroph species assemblage may influence the $\delta^{15}N$ values of organic matter preserved in sediments (Peterson and Fry, 1987). For example, as summer blooms of the species that use nitrogen-assimilating metabolic pathways deplete the DIN pool, species that are capable of molecular nitrogen fixation will become more important. The resultant bulk sedimentary organic matter may therefore be derived from nitrogen reservoirs that have very different isotopic compositions (Talbot, 2001).

The isotopic fractionation associated with changes in the composition and abundance of organic matter produced in an aquatic setting exemplifies the complex nature of the nitrogen cycle (Figure 2.5). Indeed, there are a many biogeochemical processes that complicate source identification through nitrogen isotope analysis and these must be considered during palaeolimnological studies. Delivery of isotopically heavy nitrate can be important in some cases where inputs from farm runoff and sewage are responsible for an increase in δ^{15}N values preserved in recent sediments (e.g. Teranes and Bernasconi, 2000). In most cases, however, diagenetic alteration of the original isotopic signature is a more important consideration during interpretation of δ^{15}N data. This is particularly true as nitrogen-rich proteins and lipids are more labile than carbon-rich cellulose and lignin.

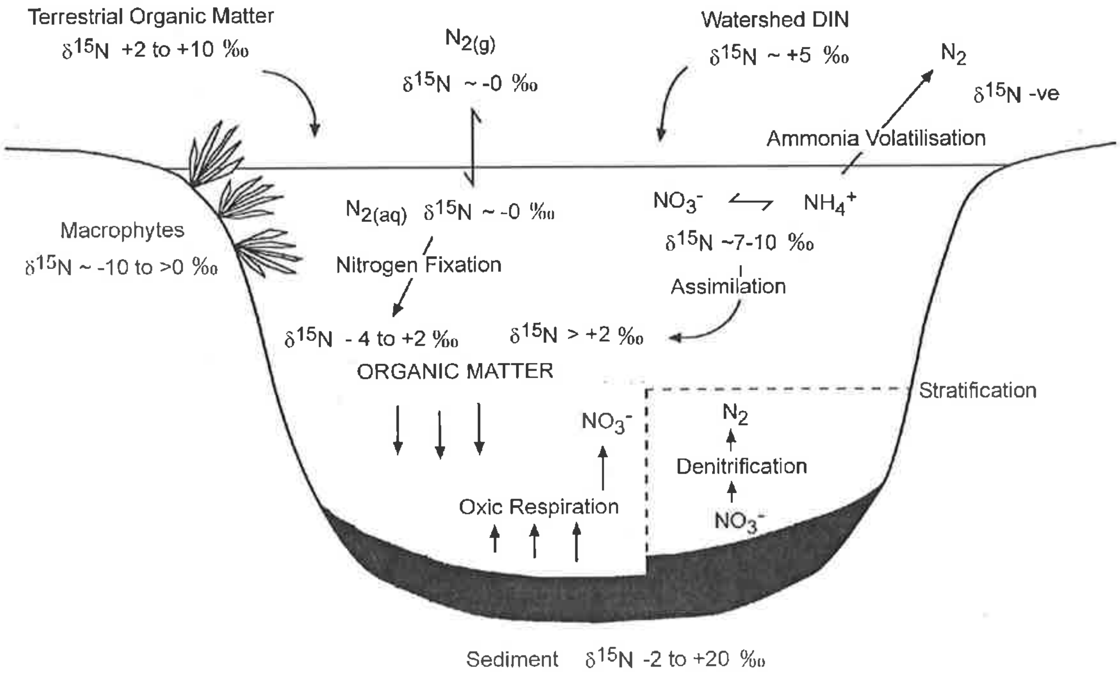


Figure 2.5: Idealized nitrogen cycle in a small lake showing the principle factors that control the isotopic composition of organic matter buried in the sediments. These factors are: the source of the nitrogen; the amount of primary production and respiration in the water column; and, denitrification. The importance of these factors can vary greatly between lakes (modified from Meyers and Teranes, 2001).

Larger fractionation effects result from microbial breakdown of organic matter through denitrification, nitrification and ammonia volatilisation than from the processes of nitrogen dissolution and fixation (Table 2.2). In oxygen-depleted waters bacterial denitrification of dissolved nitrate to gaseous nitrogen selectively releases the lighter isotope, which leaves the remaining DIN pool enriched in ^{15}N (Fogel and Cifuentes, 1993). Long periods of bottom-water anoxia resulting from seasonally increased lake productivity may consequently be recorded by an increase in the $\delta^{15}N$ values of organic matter preserved within the sediments (Macko et al., 1993; Hodell and Schelske, 1998). In alkaline lakes (pH>8.5), the preferential loss of ^{14}N through ammonia volatilisation may lead to strong ^{15}N-enrichment in the remaining DIN (Talbot and Johannessen, 1992).

Table 2.2: Isotopic fractionation factors (α) for important inorganic and biochemical nitrogen cycling processes in lacustrine systems. An α value of 1.02 for indicates that the reaction product is ^{15}N-depleted by ~20 ‰ with respect to the reactant (Talbot, 2001).

	Reactant → Product	Fractionation factor (α)
Inorganic Processes		
Nitrogen dissolution:	$N_{2\,(g)} \rightarrow N_{2\,(aq)}$	1.00085
Ammonia volatilisation:	$NH_4^+{}_{(aq)} \rightarrow NH_{3\,(g)}$	1.034
Biochemical Processes		
Nitrogen fixation:	$N_2 \rightarrow$ Cell-N	0.996-1.0024
Nitrate assimilation:	$NO_3^- \rightarrow$ Cell-N	1.011-1.023
Ammonium assimilation:	$NH_4^+ \rightarrow$ Cell-N	0.993-1.013
Remineralisation:	Cell-N $\rightarrow NH_4^+$	1.001
Nitrification:	$NH_4^+ \rightarrow NO_2^-$	1.02
Denitrification:	$NO_3^- \rightarrow N_2$	1.02

2.3 ^{13}C - Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) is a spectroscopic technique that provides information on the chemical structure of matter and is therefore a valuable aid in characterising organic matter (Kögel-Knabner, 1997; Mathers et al., 2000). The technique is based on the magnetic dipole and associated spin of an atoms nucleus, and the interaction of the magnetic fields produced by this spin on neighbouring nuclei (Veeman, 1997). These interactions produce a spectrum of resonance lines characteristic of chemical structure and can thus be used to determine the presence or absence and identity of specific molecules within a sample.

In studies of soil and sedimentary organic matter, ^{13}C-NMR is used to identify broad classes of organic chemical structure (e.g. alkyl, aromatic and carbonyl carbon) within a sample based on the specific frequencies or 'chemical shift' of the NMR resonances (Table 2.3). This has been used to investigate properties such as nutrient availability (e.g.

Randall et al., 1997) and soil structure (e.g. Skjemstad et al., 1996; Baldock and Skjemstad, 2000) as well as the analysis of chemical structural changes during organic matter degradation (e.g. Knicker et al., 1996) and burning (e.g. Krull et al., 2003). For example, the degradation and removal of carbohydrates is evident in a decreased signal intensity in the O-alkyl chemical shift region of increasingly degraded sedimentary organic matter (Knicker et al., 1996). Similarly, a loss of intensity in the carboxylic/amide chemical shift region reflects the degradation of labile proteins during decomposition.

Integration is used to determine the relative contributions of each carbon type to the total carbon pool (see section 4.2.6). Therefore, interpretation of the apparent increases and decreases of different functional groups must be made with care. For example, selective concentration, and the apparent increase, of aliphatic carbon results from the decrease in the carboxylic/amide chemical shift region associated with the degradation of labile proteins.

Table 2.3: Carbon structural type for the chemical shift (δ) ranges in solid state ^{13}C-NMR spectra (referenced to the methyl resonance of hexamethyl benzene – see section 4.2.6)

Chemical shift range (ppm)	Carbon assignment	
220 - 190	aldehyde/ketone C	
190 - 165	carbonyl C	
165 - 140	O-aryl C	aromatic C
140 - 110	aryl C	
110 - 45	O-alkyl C	
45 - 0	alkyl C	

Similarly to the manner in which organic carbon isotopes can be used to indicate the contribution of C3 and C4 plants to a soil profile, ^{13}C-NMR spectral data can be used to investigate the proportion of aquatic and terrestrially derived organic matter in the sediments of lacustrine and coastal environments (e.g. Dereppe et al., 1980; Golding et al., 2004; Dickens et al., 2006). Degradation-resistant compounds, such as lignin (Figure 2.6 A) and tannin, are characteristic of vascular plants. Thus, terrestrial organic matter is typically rich in aromatic carbon groups and poor in nitrogen-containing compounds, such as amino acids and proteins (Golding et al., 2004). In particular, charcoal (Figure 2.6 B) produces a single dominant broad resonance with a peak at ~130 ppm and a smaller resonance indicative of methylene groups in aliphatic rings and chains (45-25 ppm: Kögel-Knabner, 1997), with little else over the remainder of its ^{13}C-NMR spectrum.

On the contrary, aquatic organic matter is primarily bacterial and planktonic in origin (Figure 2.6 C, D). It is produced and recycled by nitrogen-rich micro-organisms and is, therefore, characteristically rich in nitrogen-containing compounds, which resonate at higher chemical shift fields (Hedges et al., 1997, 2002).

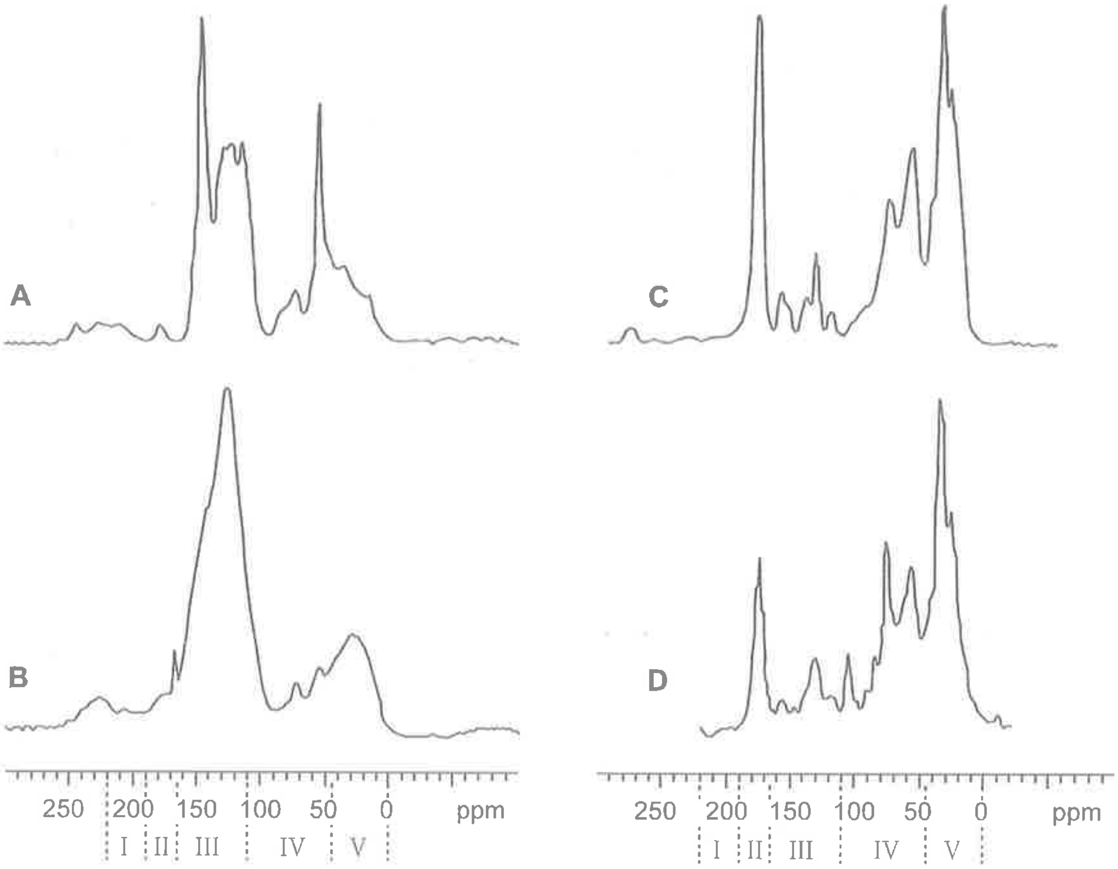


Figure 2.6: ^{13}C-NMR spectra for A) lignin, B) charcoal, C) marine bacteria and D) plankton from the Arabian Sea (modified from Hedges et al., 2002 and Dickens et al., 2006). Chemical shift ranges indicative of I) aldehyde/ketone, II) carboxyl, III) aromatic, IV) O-alkyl and V) alkyl carbon structures are labelled. A clear distinction is evident between the dominant functional groups present in the terrestrially (A, B) and aquatically (C, D) derived samples.

CHAPTER 3: CHRONOLOGICAL TECHNIQUES

In order to employ geochemical analyses, such as those described in the previous chapter, in palaeolimnologic investigations it is essential to establish a thorough understanding of the relevant lacustrine depositional history. A detailed chronological framework is fundamental to this endeavour. Although annually laminated (varved) sedimentary sequences are found in a wide range of environments (Lamoureux, 2001), more often than not Quaternary sediment age determinations are based on the systematic decay or accumulation of some sedimentary constituent. This chapter describes the principles of two techniques used to establish a sound chronological framework for the lacustrine successions of the present investigation: radiocarbon dating and optically stimulated luminescence dating. Radiocarbon dating is dealt with in considerably more detail, as it is widely applied to geological and archaeological materials over timescales in the order of thousands of years, and is the primary dating technique used in the present investigation.

3.1 Radiocarbon Dating

3.1.1 Principles

The radiogenic isotope of carbon, radiocarbon, ^{14}C, is produced in the upper atmosphere through the secondary neutron bombardment generated by cosmic ray flux that displaces protons from ^{14}N atoms (Björck and Wohlfarth, 2001). The oxidised isotope ($^{14}CO_2$) then diffused throughout the atmosphere and hydrosphere where it is integrated into living biomass. Whilst an organism is alive the carbon that it incorporates during growth is in isotopic equilibrium with the reservoir in which it exists (atmosphere, ocean or lake). Once the organism dies, uptake of this carbon stops and radioactive decay of ^{14}C shifts the ratio of ^{14}C to ^{12}C away from isotopic equilibrium with the surrounding reservoir.

Radiocarbon decays back to ^{14}N by β-emission with a half-life of 5730 ± 40 years (Polach and Golson, 1968; Williams et al., 1998). Because this radiogenic ^{14}N is indistinguishable from common nitrogen it is not possible to calculate the radiocarbon age of a material through measurement of the present day ratio between the parent and daughter product in that material. Instead, radiocarbon dating is founded on the principle that if the original ^{14}C concentration is known and the present concentration is measured, then the amount of time required for radioactive decay to have decreased the original concentration accordingly is the amount of time lapsed since carbon uptake ceased. The initial ^{14}C concentration used in radiocarbon age calculation is assumed to be that within a modern specimen of the same type of material (Williams et al., 1998).

Although the actual half-life of radiocarbon is now known to be 5730 years, the original estimate of 5568 years (Libby, 1952) has been the basis for so many radiocarbon dates that, to avoid confusing the results calculated from these two different values the Libby half-life is still internationally used in the geological and archaeological determination of 'conventional radiocarbon ages' (Mook, 1986). The length of the ^{14}C half-life allows for reasonable calculation of radiocarbon ages extending back to ~40,000-50,000 years (Gillespie, 1986). Samples older than this have already lost most of their original ^{14}C and therefore decay too slowly for reliable or meaningful measurement (Björck and Wohlfarth, 2001). On the other hand, younger samples may not have decayed sufficiently for a radiocarbon age to be apparent and will be defined simply as 'modern'. Also, anthropogenic alteration of the natural atmospheric concentration of ^{14}C prevents meaningful application of the radiocarbon dating technique for materials formed during the last 150 or so years. The release of large amounts of $^{12}CO_2$ through continual combustion of fossil fuel since 1850 AD effectively diluted natural ^{14}C concentrations; and massive increases of atmospheric ^{14}C resulted from nuclear weapons tests that commenced at 1950 AD (Williams et al., 1998).

In recognition of the huge perturbation to the natural ^{14}C system that resulted from nuclear weapons testing, radiocarbon dates are reported as years before 1950 (yr BP). Ages are generally reported with one standard deviation (σ) of statistical uncertainty, which implies that there is 68% chance that the true age of a sample falls within the interval bound by the upper and lower values of the reported age range (i.e. age $\pm \sigma$). At two σ this becomes the 95% confidence interval, and at three σ there is 99.5% confidence (Gillespie, 1986). These levels of statistical uncertainty must be taken into consideration during data analysis and interpretation. Attempts to fit age-depth curves through as many as possible, or all, of the reported or calibrated ages forget that at the one σ level only ~10 of any 15 dates must statistically fit the curve (Björck and Wohlfarth, 2001).

3.1.2 Calibration

The atmospheric concentration of ^{14}C has not always been stable. Natural variation results from both a long-term decrease in cosmonuclide production and century-scale fluctuations in solar magnetic activity (Bard, 1998). These variations are usually expressed as $\Delta^{14}C$ values, representing deviation from the present day ratio in ‰.

The natural variability in atmospheric ^{14}C production leads to differences between the true age of a sample and that calculated through radiocarbon dating. This must be corrected to obtain radiocarbon ages in calendar years, which can then be accurately compared with dates determined through other techniques or used to calculate meaningful rates of environmental change or sedimentary processes.

Past fluctuations in the atmospheric $^{14}C/^{12}C$ ratio have been reconstructed through measuring the ^{14}C concentrations of independently dated samples. This has been achieved with exceptionally high-resolution through dendrocalibration (comparison of ^{14}C levels and annual growth ring counts from age overlapping fossil pine and oak logs) for the period from 0 to nearly 12,000 yr BP (Stuiver et al., 1986; van der Plicht, 2004; Fairbanks et al., 2005). Coral samples analysed with paired uranium-thorium and ^{14}C age determination techniques have been used to extend the radiocarbon calibration curve beyond the Holocene to 50,000 yr BP (Bard et al., 1990; Fairbanks et al., 2005).

Calibration programs utilise this atmospheric ^{14}C curve derived from extensive analysis of tree and coral samples to convert measured radiocarbon ages into statistically likely calendar year time spans (Figure 3.1). Most calibration programs use a Bayesian statistical methodology to incorporate both the 'wiggles' in the calibration curve and the uncertainty in the measured radiocarbon age (Telford et al., 2004). The outcome of this complicated process is that any given radiocarbon age corresponds to multiple calendar age ranges with a variety of levels of statistical certainty. The results of the calibration procedure depend not only on the confidence intervals of the originally reported radiocarbon date and the confidence intervals of the data set for the relevant period of the calibration curve, but also the actual shape of the curve itself (Björck and Wohlfarth, 2001). For example, samples from periods of rapidly changing atmospheric ^{14}C concentrations will be more precisely calibrated than those from more stable periods.

Several calibration programs are available for downloading from the websites of radiocarbon dating laboratories, such as Oxford (OxCal) and Columbia (Fairbanks) Universities. Use of these programs is relatively simple, but should be done with care.

Some of the environmental considerations that may need to be taken into account prior to, or in combination with, calibration of radiocarbon-dated samples are described below.

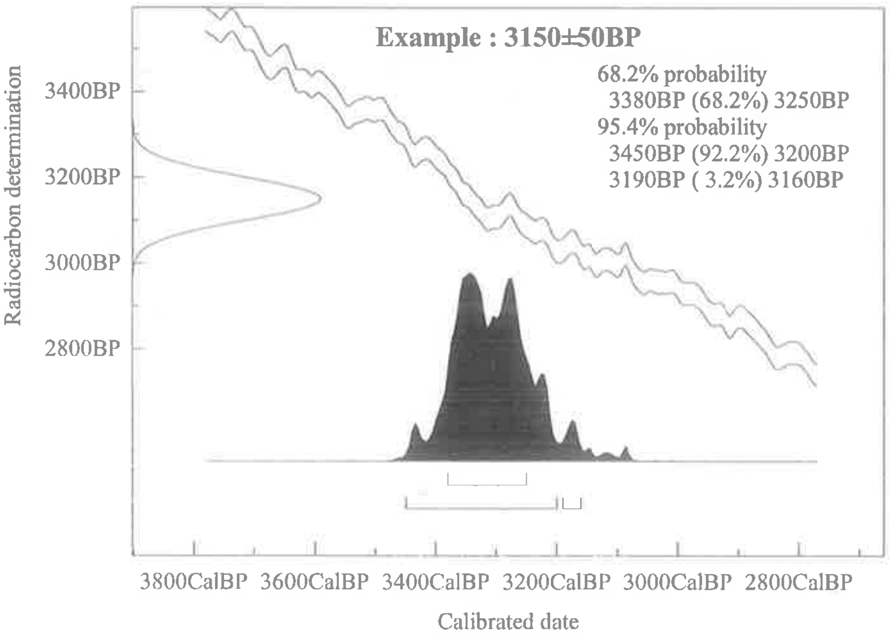


Figure 3.1: Calibration output for an example radiocarbon date (3150 ± 50 yr BP) using the OxCal calibration program (Bronk Ramsey, 1995, 2001) and Southern Hemisphere atmospheric data (McCormac et al., 2004), the relevant section of which is shown here as the blue 'wiggle'. The bell-shaped curve on the y-axis represents the conventional radiocarbon date and the solid, irregular curve on the x-axis represents the probability distribution of the calibrated date. The upper and lower bars below the probability distribution indicate the calibrated age ranges, which may be discontinuous, at 1 and 2σ levels of statistical certainty (or 68 and 95 % probability), respectively.

3.1.3 Considerations

The complex nature of the carbon cycle and the effects of numerous environmental conditions and processes influence, and have the potential to significantly hinder the accuracy of, radiocarbon dating in lacustrine settings. The isotopic fractionation processes that occur during photosynthesis and dissolution/volatilisation (as described above) naturally influence the ratio of ^{14}C to ^{12}C in the hydrosphere, atmosphere and biosphere. This effect is taken into account through normalising the ^{14}C concentration of a sample submitted for radiocarbon dating against the δ^{13}C value for that sample (Gillespie, 1986). The derivation of this fractionation coefficient allows a truly representative initial ^{14}C concentration to be determined, which is then used in calculating the radiocarbon date.

Addition of 'old' or 'young' carbon can occur through a variety of avenues and has the potential to be a significant source of error in radiocarbon dating. In a lacustrine setting, the addition of reworked charcoal, pollen or soil organic matter to the lake basin will act to increase the radiocarbon age of a bulk sediment sample. This effect will be most noticeable in lakes of low aquatic productivity that receive a significant contribution of allochthonous organic matter from the surrounding catchment. Younger carbon can be introduced by the respiration of roots that penetrate the sediments and through bioturbation by metazoan (Björck and Wohlfarth, 2001). Bacterial activity recycles in situ carbon atoms and therefore introduces little error to radiocarbon dating (Hedges, 1991).

Differences in the nature and source of the DIC in a water body can also introduce a significant error to the radiocarbon dating of samples from aquatic settings. Organic matter produced through photosynthetic utilization of a DIC reservoir that has a ^{14}C to ^{12}C ratio lower than that of the atmosphere at the time will appear older than its true age. This reservoir effect results from preferential partitioning of the lighter carbon isotope into the hydrosphere. Prior to atmospheric bomb testing, the concentration of ^{14}C in ocean waters was 5-10% less than in the atmosphere (Williams et al., 1998). This means that organic matter produced from the shallow marine DIC reservoir appeared older than organic matter produced from atmospheric CO_2 at the same time. As deep ocean waters are more isolated from the atmosphere than are shallow ocean waters, they have even lower ^{14}C to ^{12}C ratios and give rise to more pronounced reservoir effects. Upwelling of these deep ocean waters reduces the ^{14}C to ^{12}C ratio of the overlying surface waters and contributes to the global distribution of marine surface water reservoir effects that is incorporated into calibration programs for marine samples (Hughen et al., 2004).

Where groundwater flows into a lake basin through carbonate systems (limestone aquifers) it can carry in dissolved carbonates with no ^{14}C content ('dead' carbon). The photosynthetic incorporation of this, along with 'fresh' carbon, leads to older apparent radiocarbon ages being determined for the autochthonous organic matter preserved within the lake's sediments (e.g. Andrée et al., 1986, Törnqvist et al., 1992). This hard-water reservoir effect can introduce significant errors (in the order of 100s of years), which vary in magnitude throughout lacustrine sequences (e.g. Barnekow et al., 1998 as cited in Björck and Wohlfarth, 2001). For groundwater-fed lakes in which the mean water residence time is long, ^{14}C exchange between the dissolved HCO_3^- and atmospheric CO_2 shifts the ^{14}C activity of the dissolved HCO_3^- toward equilibrium with atmospheric CO_2, thus minimising the effect of ^{14}C dilution from 'dead' carbon (Leaney et al., 1995).

Conversely, for lakes with short mean water residence times, the ^{14}C activity is dominated by the groundwater HCO_3^- and the effect of ^{14}C dilution is maximised.

Parallel dating of bulk sediment and terrestrial macrofossils seems a reliable way of ascertaining the presence and magnitude of any hard water effect (Törnqvist et al., 1992; Geyh et al., 1998), but is limited in its application as terrestrial macrofossils are absent from many lacustrine sedimentary sequences. In the present study an attempt is made to quantify the possible hard water effect in two lakes through comparison of ^{14}C dates on the bulk organic matter with those obtained from optically stimulated luminescence dating of the quartz and fine grains.

3.2 Optically Stimulated Luminescence Dating

Luminescence dating, either optically or thermally stimulated, can be used to establish the amount of time that has passed since quartz or feldspar grains within wind-or water-borne sediments were last exposed to light or heat (Stokes, 1999). Exposure to sufficiently high temperatures (ca. 400 °C; Lian and Huntley, 2001) or sunlight empties electron traps within individual grains and irradiation after burial causes these electron traps to gradually become repopulated (Huntley et al., 1993a). Natural irradiation of the buried grains results from alpha, beta and gamma radiation emitted during decay of uranium, thorium, potassium, rubidium and their daughter products, plus cosmic ray activity.

Optically stimulated luminescence (OSL) dating uses infrared excitation of quartz grains in the laboratory to again empty these electron traps. This process yields luminescence, the intensity of which is a measure of the number of electrons trapped since burial. Providing that the natural radiation dose ('environmental dose rate') is accurately determined, the stimulated luminescence is a measure of the time elapsed since the sample was last exposed to sunlight (Prescott and Hutton, 1995). Calculation of the environmental dose rate requires that the concentration of radioactive elements within the mineral grains and the sample surroundings is accurately determined. The depth of sample burial is also required, as the intensity of cosmic ray activity decreases with depth. Finally, as water and organic matter absorb radiation differently to the mineral matter, the quantities of these substances must also be evaluated in dose rate calculations.

Luminescence dating is most applicable to quartz-rich samples deposited between ~1 to 150 ka (Lian and Huntley, 2001).

4.1 Fieldwork

4.1.1 Sliphammer Core Collection

In early December 2003 a single core was collected from each lake using the sliphammer technique (Figure 4.1). The act of manually driving the PVC pipe (50 mm internal diameter) into the sediment through repetitive hammering causes the sediment within the core to compact to varying degrees, depending on the initial sediment density. Once the PVC pipe has reached the basal unit or cannot further penetrate the sediment, the space between the internal compacted sediment-water interface and the upper end of the pipe was filled with water and sealed off using a rubber bung and gaffa tape so that the core could be extracted under vacuum.

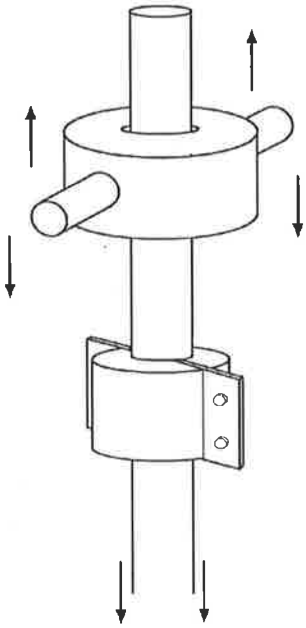


Figure 4.1: The sliphammer technique proceeds by repeatedly lifting the upper handled ring and 'hammering' it down onto the lower clamped ring, thus driving the PVC tube vertically into the lake sediment. The core is extracted manually using a levered set of handles (two persons required).

The cores were taken to depths of 130 cm (36% compaction), 144 cm (40% compaction) and 165 cm (21% compaction) in Old Man Lake, Lake Amy and North Stromatolite Lake respectively. Upon return from the field, the cores were split in half by using a circular saw to cut the PVC and then slicing the sediment through with a piece of wire. After removing approximately 2 mm of the freshly exposed sediment face by careful cross-core scraping, each complete core was photographed and its stratigraphy described in detail. Sediment colours were identified quickly upon removal of the surface layer so as to avoid the impact of oxidation on these stratigraphic descriptions. The halved cores were then individually wrapped in Alfoil, matching halves wrapped in thick clear plastic and stored at 4°C in the cold room of the School of Geographical and Environmental Studies, University of Adelaide.

4.1.2 D-Section Core Collection

Also in December 2003 a continuous and uncompacted half core (50 mm internal diameter) was taken from each of the three lakes using a modified Russian peat (D-section) corer (Figure 4.2). The core was taken in 50 cm sections to depths of 2.0, 2.5 and 3.0 m, respectively in Old Man Lake, Lake Amy and North Stromatolite Lake. Each 50 cm section was placed into a half-section of PVC pipe, covered in clingwrap and stacked between layers of cardboard in a large chilled esky for transportation out of the field. The cores were photographed and stored (prior to sampling for analysis) in the same manner as the sliphammer cores.

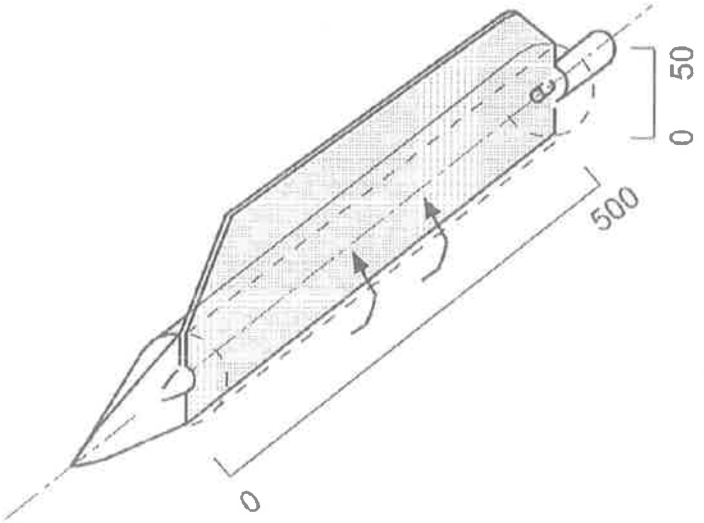


Figure 4.2: The D-section corer is driven into the lake sediment by using attachable control rods (1 m length). Once at the appropriate depth a handle at the lake surface is used to rotate the D-shaped chamber with respect to the plate (hatched). This captures the undisturbed sediment adjacent to the plate surface. Note: Image scale is in millimetres.

4.1.3 Vegetation and Water Sampling

In June 2005 a short trip to the field area was undertaken to photograph and sample the present-day vegetation surrounding each lake and to sample the modern lake waters for radiocarbon analysis. Twelve tree and shrub species were deemed representative of the vegetation around the three lakes. These were sampled using clean household secateurs and stored in loosely closed brown paper bags to minimise sweating during transport back to the University of Adelaide where Nathan Reid (School of Earth and Environmental Sciences) identified the species.

4.2 Analytical Procedures

This section details the sample preparation and analyses that were used to determine the elemental, isotopic and spectroscopic parameters described in Chapter 2, and for the dating techniques described in Chapter 3. All analyses were carried out on samples taken from the uncompacted D-section cores, with the lone exception of optically stimulated luminescence dating, for which the fully cylindrical cores that were collected using the sliphammer technique are better suited.

4.2.1 Mineralogy

Dried and crushed sediment samples were sent to CSIRO Land and Water (Waite) for X-Ray diffraction (XRD) analysis by Mark Raven. 1g sub-samples were ground for 10 minutes in a McCrone micronizing mill under ethanol. The resulting slurries were oven dried at 60°C then thoroughly mixed in an agate mortar and pestle before being lightly pressed into aluminium sample holders for analysis. XRD patterns were recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Co Kα radiation, variable divergence slit, post diffraction graphite monochromator and fast X'Cellerator Si strip detector. The diffraction patterns were recorded in steps of 0.05° 2θ with a 0.5 s counting time per step, and logged to data files for analysis. Quantitative analysis was performed on the XRD data using the commercial package SIROQUANT from Sietronics Pty Ltd. The results are normalised to 100%, and hence do not include estimates of unidentified or amorphous materials.

4.2.2 Total Organic Carbon (TOC)

Approximately 1g of each crushed sample was treated with 5% w/w sulphurous acid (H_2SO_3) to remove carbonate prior to analysis. Carbonate-free fractions were incinerated at 1300°C in a LECO C 144 carbon analyser. Duplicate analyses of one in five samples gave results differing by <0.5%. This technique determines percent total organic carbon (TOC) through measuring the amount of carbon dioxide released during incineration.

4.2.3 Isotopic Analysis of Organic Matter ($\delta^{13}C_{org}$, $\delta^{15}N$)

Sediment samples were dried at 50°C, finely ground and treated with 0.5 M HCl to remove carbonates. For each sample a mass estimated to contain 300-800 µg of organic carbon and 40-150 µg of nitrogen was measured into a tin capsule and sealed. These samples were combusted using a 20-20 Europa Scientific Automated Nitrogen Carbon Analysis – Mass Spectrometer (ANCA-MS) to determine their stable organic carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotope values and their percent total nitrogen (TN). The isotopic results are reported in the conventional δ notation, expressed in parts per mil (‰) relative to the standard Pee Dee Belemnite (PDB) for carbon and to air for nitrogen. Every fifth sample was analysed in duplicate yielding an average standard deviation of ± 0.19‰ for $\delta^{13}C_{org}$ and ± 1.1‰ for $\delta^{15}N$. Sample AMY 19 was an exception ($\delta^{13}C_{org}$ ± 1.31‰).

Vegetation samples were oven-dried at 40°C and crushed to a fine powder in a steel mill. Aliquots (1-1.5 mg) were weighed into tin capsules, sealed and analysed for $\delta^{13}C_{org}$ as above. Every sample was analysed twice with a precision of ± 0.1‰.

4.2.4 Isotopic Analysis of Carbonate ($\delta^{13}C_{carb}$, $\delta^{18}O$)

Dried and crushed bulk sediment samples were sent to Waikato Stable Isotope Laboratory (New Zealand) and analysed by Steve Cooke on a GEO 20-20 Dual Inlet Mass Isotope Ratio Spectrometer with an attached Carbonate Automated Preparation System. Samples were treated with H_2O_2 to remove organic matter prior to the isotopic analysis. Currently opinion within the scientific community is divided on whether organic matter present in sediment samples interacts with the CO_2 liberated via the reaction of $CaCO_3$ with orthophosphoric acid during the isotopic analysis procedure. Hence, an additional suite of untreated samples was analysed to assess the impact of the pre-treatment method on the isotope values obtained. Results are reported in conventional δ notation and expressed in parts per mil (‰) relative to the PDB standard.

4.2.5 Radiocarbon Dating

Radiocarbon dating of bulk organic matter (n = 25), one charcoal sample and two lake water samples was completed at the Australian Nuclear Science and Technology Organisation (ANSTO) Accelerator Mass Spectrometry (AMS) facility in 2005 (Fink et al. 2004). All conventional radiocarbon dates (1σ) received from ANSTO were converted to calendar years by calibration against the atmospheric ^{14}C curve for the Southern Hemisphere (McCormac et al., 2004) using the internationally ratified online calibration program, OxCal v.3.1 (Bronk Ramsey, 1995, 2001). Carbon isotopic values, $\delta^{13}C$, are reported in parts per mil (‰) relative to the PDB standard. Replicate analyses of laboratory standards typically showed a precision of ± 0.1‰.

4.2.6 Optically Stimulated Luminescence Dating

Seven samples (5 cm thickness) were collected under red light from the sliphammer cores. Frances Williams undertook sample preparation and OSL analysis in the School of Physics and Chemistry at the University of Adelaide: Samples were treated with 20% HCl to remove carbonate and then with H_2O_2 to remove organic matter and leave behind only the mineral fraction. This was split into two parts: quartz (90-125 μm), and 'fine grains' (4-11 μm), which consist of quartz and smaller quantities of other minerals (usually feldspars: F. Williams pers. comm.). OSL measurements were made using the single aliquot regeneration method (e.g. Murray and Roberts, 1997) and five to six aliquots of each sample were measured. Environmental dose rates were calculated from bulk sediment samples using uranium and thorium contents measured at AINSE by delayed neutron analysis and neutron activation analysis respectively; potassium content measured at Adelaide University by X-ray fluorescence analysis; water content determined by loss on weight upon drying at 110°C; and the cosmic ray contribution calculated by the procedure of Prescott and Hutton (1994).

4.2.7 ^{13}C - Nuclear Magnetic Resonance Spectroscopy

Wet sediment samples were treated with 1.0 M HCl to remove carbonates and then treated with 2% HF (5 x 1 hr treatments, 3 x overnight treatments, 1 x weekend treatment) to remove paramagnetics and increase the organic matter content. Acid-treated samples were then freeze-dried and finely ground prior to analysis. The 50.309 MHz cross-polarisation with magic angle spinning (CP/MAS) ^{13}C-NMR spectra were obtained on a Varian Unity 200 spectrometer with a 4.7 T wide-bore Oxford super-conducting magnet housed at CSIRO Land and Water, Urrbrae. Samples were spun at 5 kHz in 7 mm diameter zirconia rotors with Kel-F caps in a Doty Scientific MAS probe. All spectra were obtained using a contact time of 1 ms, a recycle delay time of 500 ms, 50 Hz Lorentzian line broadening and 0.01 s Gaussian broadening. Chemical shift assignments (δ) were externally referenced to the methyl resonance of hexamethyl benzene at 17.36 ppm. The proportional contribution of the following functional groups were calculated by integrating the signal intensities within each of the given chemical shift regions: ketonic/aldehyde (220-190 ppm), carbonyl (190-165 ppm), O-aryl (165-140 ppm), aryl (140-110 ppm), O-alkyl (110-45 ppm) and alkyl (45-0 ppm). Individual spectral regions were calculated by dropping vertical lines to a baseline defined by the Varian operating software between 300 and -100 ppm (Appendix II).

CHAPTER 5: THE STUDY AREA, SAPROPELS AND STRATIGRAPHY

The three shallow, coastal lakes that are the focus of the present study represent a distinctly different environmental setting to those in which similar geochemical studies have hitherto been carried out (i.e. marine and deep-lake settings). As for those studies on much deeper aquatic settings, a thorough understanding of the local lacustrine system is fundamental to the complete and accurate interpretation of results obtained through bulk geochemical analysis in the present investigation.

This chapter describes the Late Quaternary evolution of the study region and summarises the Holocene development of the three studied lakes as presently understood from the work of earlier researchers in the area. Summaries of the present-day climate and vegetation regimes are also provided. Following this, a sapropel nomenclature appropriate for the present investigation (as distinct from that previously used for marine settings) is defined, and then employed in the subsequent detailed descriptions of the stratigraphic successions in each lake.

5.1 Environmental Setting

5.1.1 Regional Landform Evolution

Numerous transgressions and regressions of the world's oceans associated with Quaternary climate change have resulted in the construction, destruction, and reworking of Pleistocene and Holocene beach-barrier complexes along exposed coastal areas of southeast South Australia (Figure 5.1: Cook et al., 1977; Belperio, 1995). Here uplift of the coastal plain has caused these phases of beach-dune accumulation to be physically separated and preserved as a sequence of sub-parallel NW-SE trending topographic ridges (Schwebel, 1983). There are thirteen stranded coastal ridges between Robe in the west and Naracoorte in the east, each of which has been related to specific Pleistocene sea-level high-stands (Huntley et al., 1993b; Belperio, 1995). The modern coastal Robe Range and the adjacent Woakwine Range, situated 10-15 km inland, are the youngest of this beach-dune ridge sequence. The Woakwine Range formed during the last interglacial period (~125 ka: Huntley et al., 1993b; Murray-Wallace, et al., 1999).

As described in section 1.2.1, sea-level during the Last Glacial Maximum (21 ± 3 ka) was up to 130 m lower than during the present interglacial. By ~7000 yr BP the post-glacial marine transgression had flooded the Robe-Woakwine corridor, resulting in the formation of a shallow back-barrier lagoon, which was open to the Southern Ocean near the present towns of Robe and Beachport (Cann et al., 1999). Sea-level stabilised close to its present position at ~6700 cal yr BP (Belperio, 1995). Since this time, sand transport associated with a combination of ocean swell, wave action and tidal movement has isolated the Robe-Woakwine back-barrier lagoon from the open ocean.

To the north lies the Coorong Lagoon (Figure 5.1). At the peak of the Holocene marine transgression, this water body extended continuously for more than 200 km from the Murray mouth to Kingston. Subsequent landward migration of the coastal dunes of the Younghusband Peninsula has broken the lagoon south of Salt Creek into a series of ephemeral lakes (Warren, 1990). Evidence of rapid change from marine to lacustrine conditions is evident within sediment cores retrieved from these modern lakes. For example, beds of fossil marine fauna, such as oysters, mark the base of the lacustrine sedimentary sequence within lakes Eliza (Burne and Ferguson, 1983) and Robe (Cann et al., 1991).

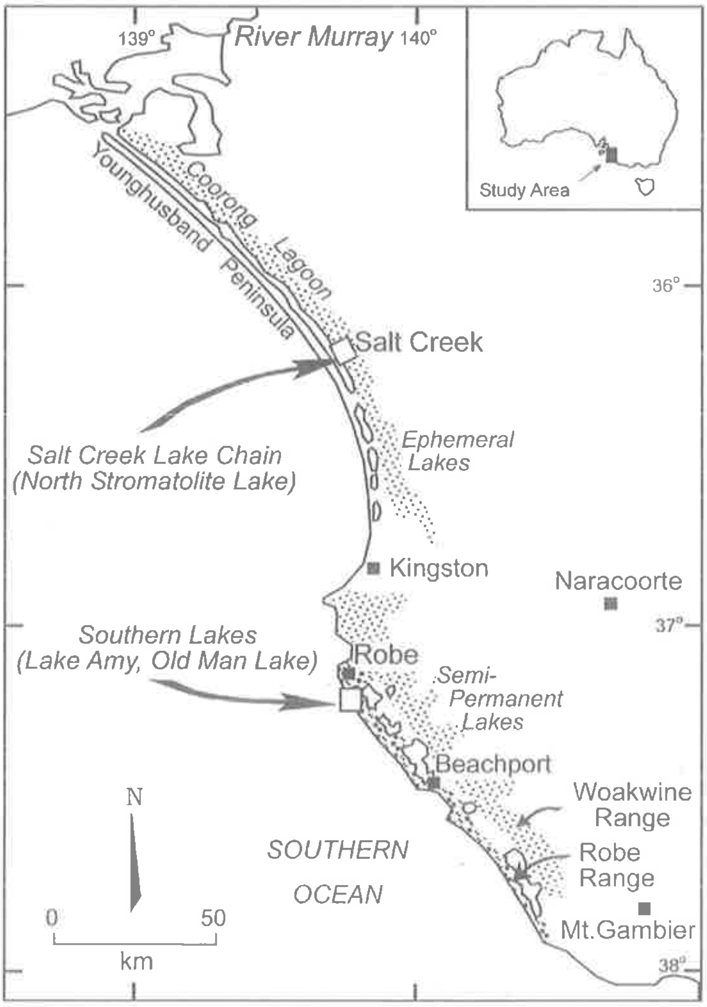


Figure 5.1: Map of southeastern South Australia indicating significant coastal features and the location of the northern and southern study areas.

5.1.2 The Three Lakes of the Present Study

North Stromatolite Lake (NSL), Old Man Lake (OML) and Lake Amy (LA) are three small, shallow coastal lakes found in southeastern South Australia. NSL and OML are charged by westward-flowing saline continental groundwater that is forced toward the land surface as it rises over an underlying wedge of dense, intruding seawater (Holmes & Waterhouse 1983; Warren 1990). In contrast, the more elevated LA is the surface expression of a local perched water table high in the Robe Range (A.J. Brenchley, pers. comm.). No permanent streams enter any of the lakes, nor are there any present-day surface connections with the marine system. Other than groundwater inflow, lake water levels are augmented by seasonal precipitation (section 5.1.3), surface runoff and vadose zone throughflow from the surrounding dunes. The Holocene evolution of each lake is unique and is described below.

NSL is part of the Salt Creek lake chain, situated at the northern end of the ephemeral Coorong Lagoon and within the Coorong National Park, approximately 230 km SSE of Adelaide (Figure 5.2). During the early Holocene this group of four lakes existed as a narrow extension of the Coorong Lagoon, connected via the southern end of NSL. Dune migration and sediment deposition eventually blocked this access corridor and isolated the embayment from the Coorong Lagoon. The resulting restriction of water movement led to the build up of sandy estuarine sediments within the interlake corridors effectively converting the water body from an estuarine/marine environment into the chain of isolated schizohaline lakes that exist today.

The Salt Creek lakes are designated Type 2 lakes by Warren (1990) to distinguish them from others like Milne Lake (Type 1) that were not initially connected to the Coorong Lagoon. The subsequent evolution of water chemistry and therefore sedimentology is unique to each lake and has been well documented by Rosen et al. (1988) and Warren (1990). Typically, the upward-shoaling calcareous mudstone succession of the Salt Creek lake chain contains three distinct Holocene lacustrine carbonate units (sapropelic mudstone; laminated pelletal mudstone; massive pelletal mudstone/packstone) that overlie Pleistocene siliciclastic-carbonate grainstone to wackestone and beach-dune sands. This textural transition from laminated to massive sedimentary units has been interpreted as a change from perennial to ephemeral lacustrine conditions in a setting of relatively low energy (Warren 1990). Analysis of the sedimentary sequence in North Stromatolite Lake carried out by Hayball (1990) showed it to represent a progression from estuarine, through density stratified lacustrine and perennial lacustrine, to ephemeral lacustrine settings (Hayball et al., 1991).

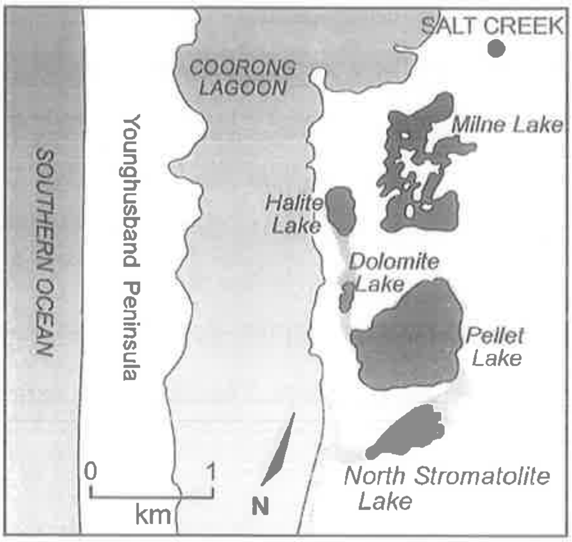


Figure 5.2: The Salt Creek lake chain. Shading indicates where the now infilled inter-lake corridors connected the modern lakes to each another and to the Coorong Lagoon during the Early Holocene (modified from Warren, 1994).

Both LA and OML are shallow (<4 m water depth) perennial lakes nestled within topographic lows of the Robe Range (Figure 5.3). These two lakes are located just south of the Robe township, approximately 100 km further south than NSL. As a result of differential neotectonic uplift, the coastal barrier deposits of the Last Glacial Maximum in this area are now ~2 m higher than those at Salt Creek (Murray-Wallace & Belperio, 1991). LA is situated on 'The Hermitage' (private property owned by Mr. John Enright) and OML within Little Dip Conservation Park.

OML has evolved in a manner similar to that described above for NSL. During the early Holocene, OML existed as a restricted embayment of the back-barrier lagoon that formed via transgressive flooding between the Robe and Woakwine ranges. Progressive landward migration of the dune sands of the Robe Range isolated the lagoon and eventually cut OML off from its surface connection to what is now known as Lake Eliza. This transition of environmental settings is recorded in the sediments of OML. A siliciclastic-carbonate lagoonal unit containing humic organic matter is associated with the rising groundwater table that preceded the early Holocene transgressive marine flooding and was deposited unconformably on the basal Pleistocene aeolianite. The upward-shoaling transition from marine to lacustrine conditions is apparent in the three subsequent and distinct carbonate units: lagoonal silts and muds with abundant remains of shallow marine fauna, laminated lacustrine mudstone with sapropel intervals, and massive pelletal mud with abundant remains of the gastropod *Coxiella striata* (McKirdy et al., 1999).

LA was never directly connected to the marine system. Thus, its sediments are an expression of changes in the local perched groundwater table. A massive bioturbated pelletal carbonate mudstone overlies a laminated lacustrine mudstone with sapropel intervals, hardpans and variable amounts of ostracod and gastropod remains. This sequence represents an upward shoaling lacustrine system analogous to the Type 1 lakes near Salt Creek. In the absence of an estuarine connection to the ocean there is no lagoonal unit. A humic unit, similar to that observed in OML, formed as a result of rising local groundwaters in association with the marine transgression and unconformably overlies the basal Pleistocene aeolianite.

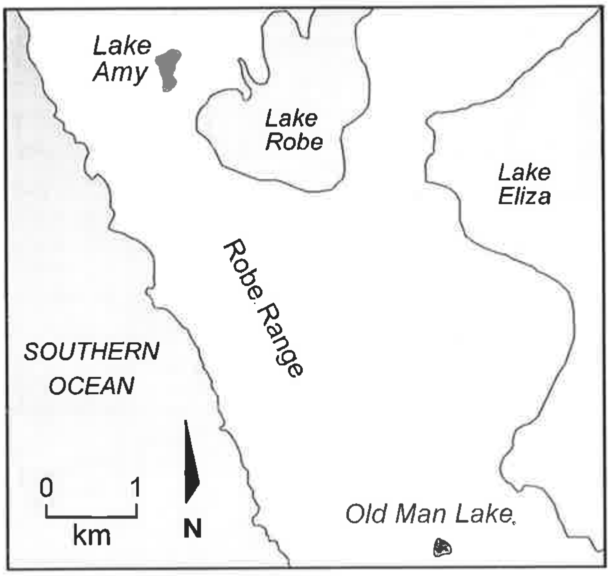


Figure 5.3: The southern study area showing the locations of Lake Amy and Old Man Lake within the modern Robe Range.

5.1.3 Present Day Climate

Today southeastern South Australia has a cool temperate, mesothermal climate with cool, wet winters (June – September) and warm, dry summers (December – March). The prevailing winds in the area are westerlies and southerlies that result from the west to east passage of anticyclones (high pressure systems), which are stronger in summer, and the winter influence of mid-latitude depressions (low pressure systems). The latitude of the anticyclone tracks varies seasonally, from 37-38°S in summer to 27-32° in winter (Short and Hesp, 1980). Afternoon seabreezes tend to reach <100 km inland and are strongest in January and February (Gentilli, 1971). Evaporation rates estimated from measured pan evaporation rates rise from ~2 mm/day in winter to ~7 mm/day in summer (Short and Hesp, 1980). A strong latitudinal variation in the annual distribution of rainfall in southeastern South Australia exists (Figure 5.4). This is a result of the increasingly oceanic origin of the southern rain-bearing airmasses, which are less affected by land to the northwest (Kangaroo Island, Yorke and Eyre Peninsulas: Penney, 1983). In general, annual rainfall is 700 mm in the far southeast and decreases to 500 mm in the northwest. Thus, evaporation exceeds precipitation for all but a few weeks of the year near Salt Creek (June-July) increasing to a few months in the far southeast (May-August) (Warren, 1990).

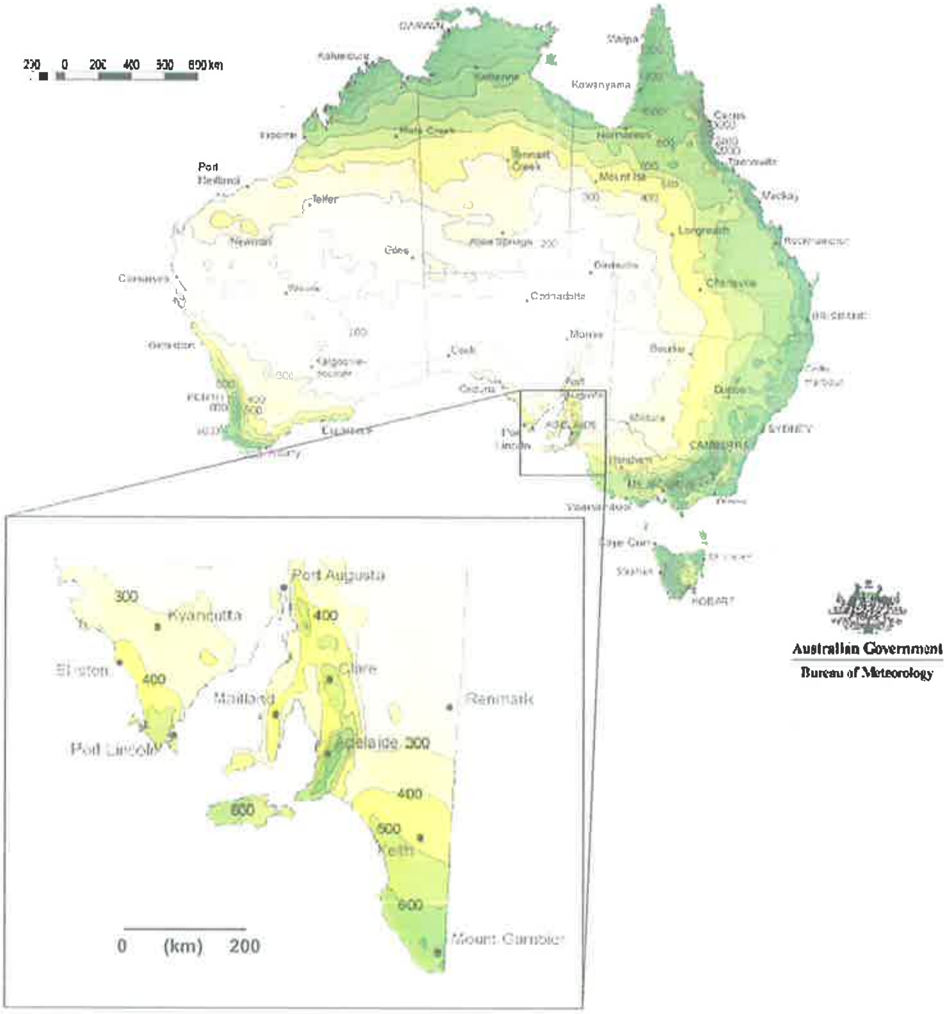


Figure 5.4: Average annual rainfall (mm) in southern South Australia (Australian Bureau of Meteorology public data, based on standard 30 year climatology, 1961-1990). In the southeast region a strong latitudinal effect is evident. This results from the increased oceanic influence on its rain-bearing air masses.

5.1.4 Vegetation

The flora in southeastern South Australia are limited to those types that thrive in a temperate Mediterranean-like climate on a flat, low-elevation landscape with minimal exposed bedrock, and nutrient-poor sandy, clayey and calcareous, often poorly drained soils (Lange, 1983). Accordingly, much of this flora seems to have migrated from central, inland Australia since the Southern Ocean withdrew from the ancient Murravian Gulf. The modern assemblage of native vegetation in the study area is described below. This has been collated from Lange (1983) and Bonney (1988) and supplemented by new field observations and sample identifications.

A coastal scrub environment dominates the Coorong region and the present-day shorelines of calcareous sand dunes and dunefront beaches. *Spinifex hirsutus* (spring rolling grass) binds the coastal dunes, aiding the proliferation of *Atriplex cinerea* (coastal saltbush), *Calocephalus brownii* (cushion bush) and a variety of rushes (e.g. *Typha domingensis* – bulrush) and sedges (e.g. *Gahnia trifida* – cutting grass, *Isolepis nodosa* – knobby club rush). Grasses of both C3 and C4 varieties grow sparsely, rather than as savannah, and include genera such as *Stipa stipoides* (coastal spear grass), *Distichlis* (salt grass), *Phragmites australis* (common reed). Succulents are well expressed in association with salty places: *Salicornia quinqueflora, Suaeda australis, Halosarcia halocnemoides, Rhagodia candolleana* and *Carpobrotus rossii* (pig-face). *Samolus repens* (creeping brookweed) is found near the fringes of coastal swamps, brackish saline swamps and lagoon areas. Inland of the coastal dunes is an abrupt transition into a dense scrub of *Leucopogon parviflorus, Olearia axillaris, Acacia longifolia, Acacia sophorae*, and *Melaleuca halmaturorum* with minor *Pimelia serpyllifolia, Thomasia petalocalyx, Tetragonia implexicoma, Banksia marginata*. The limestone bedrock supports some shrub and tree species closer to the coast than other bedrock is able (e.g. *Eucalyptus diversifolia, Melaleuca lanceolata, Acacia ligulata, Casuarina stricta*).

Prior to the extensive drainage and clearing of the southeast since the introduction of agriculture to the region, much of the coastal landscape existed as an alkaline freshwater peat swamp, or fen. Little of this swampy habitat remains nowadays. However, the three lakes of the present investigation may have existed as such an environment prior to European settling of the area. Therefore, the description of fen at Eight Mile Swamp, a trough parallel to the coast and just inland in the extreme southeast, by Eardley (1943) is outlined here as a possible palaeoenvironment for the three studied lakes. Eardley documented a concentric series of vegetation communities, progressing outwards from those of permanent open waters (watermat) to shallow waters (reed-swamp) and swamp margins (sedge meadow). The watermat that choked the open waters included aquatics such as *Chara, Nitella, Hydrocotyle verticillate, Lepilaena elatinoides* and freshwater algae. The reed-swamp surrounding this stood mostly clear of the water (*Phragmites australis, Typha angustifolia, Gahnia clarkei, Scirpus pungens, Juncus* sp.) but also included some submerged species (*Triglochin procerum* – water ribbons). The shallower waters supported a thick sedge meadow of *Machaerina* sp. The damp-decay product of the plants in this habitat, a peat that varied from coarse and fibrous beneath the swampy waters to fine beneath the tea-tree thicket at the fen margins, was on average over 1.5 m deep (Lange, 1983).

5.2 Sapropel Nomenclature

The terms sapropel and sapropelic have been widely applied to describe aquatic sedimentary deposits rich in organic matter. Specific definitions of these terms have been used somewhat inconsistently, both within and between marine and lacustrine settings. For example, although Taylor et al. (1998) state that the term sapropel can be used for deep-water and shallow-water lacustrine and marine deposits rich in aquatic organic matter, the commonly used definition proposed by Kidd et al. (1978)[2] applies exclusively to open marine pelagic sediments. To strip the latter definition of its marine aspect and define the terms purely on the basis of TOC values would render some lacustrine successions entirely sapropel. Thus, before describing the stratigraphy of the lacustrine sediment cores collected in the present study, it is important to define how and why the terms sapropel and sapropelic are used herein.

The North Stromatolite Lake core contains the most distinct sapropel. In this core the boundary between the organic-rich interval (TOC > 2%) and the overlying laminated interval (TOC < 1%) is marked by an abrupt transition from the lower dark olive grey to brown, gelatinous textured sediments into light olive brown to grey, pelletal textured sediments. Whilst this change in sediment colour and texture clearly marks the halt in sapropel deposition within NSL, the sapropel interval would be equally defined using the TOC value proposed by Kidd et al. (1978). However, the cores from both Old Man Lake and Lake Amy contain >2% TOC throughout their entire lacustrine successions. Therefore, within the present study, the definition of sapropel is not based on TOC values alone, but requires consideration of sediment colour and texture.

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[2] "A discrete layer, greater than 1 cm in thickness, set in open marine pelagic sediments containing greater than 2% organic carbon by weight."

For the present study, sapropels are defined as: 'dark olive grey-brown to black lacustrine sediments with a gelatinous 'cheesecake'-like texture, variable granular to platy calcitic structure and containing >2% TOC wt/wt' (Table 5.1). In OML, a sapropelic interval is defined on the basis of containing intermittent bands of 'sapropel' as per this definition whilst the mottled intervals in both OML and AMY contain similarly darkly coloured and gelatinous sediment in patches rather than distinct bands or layers. Although these latter definitions are somewhat arbitrary, they are considered sufficient for the present investigation in that they adequately distinguish between lacustrine sedimentary intervals that would otherwise be grouped entirely under the term 'sapropel'.

Table 5.1: Summary of definition of stratigraphic terms as used in the present investigation.

Terminology	Definition
Sapropel	Dark olive grey-brown to black lacustrine sediments with a gelatinous 'cheesecake'-like texture, variable granular to platy calcitic structure and containing >2% wt/wt.
Sapropelic interval	Sedimentary interval containing intermittent bands of sapropel.
Mottled interval	Sedimentary interval containing patches of darkly coloured, organic-rich, gelatinous sediment.

5.3 Stratigraphic Descriptions

Core details and the general sedimentology of each lake are summarised below. The sliphammer cores underwent 21-40% compaction during collection. Compaction may not have been uniform for each sedimentary unit in a given core and so thicknesses calculated from the compacted sections retrieved in the sliphammer cores may be unrepresentative of the true sediment thickness. Therefore, all depths and thicknesses reported in this chapter are from the uncompacted D-section cores. Detailed stratigraphic sections of each core are included below. Complete results of XRD mineralogical analysis can be found in Appendix III.

North Stromatolite Lake

Both the D-section and sliphammer cores were taken from the lake axis centre and southern end of NSL (36° 10'05" S, 139° 39'43" E; Figure 5.5). Water depth at the time of collection was ~12 cm. The D-section core (NSL1) retrieved 300 cm of the lacustrine sediments (Figure 5.6). The sliphammer core (NSL2) reached a depth of 209 cm. However, only 165 cm of sediment was retrieved indicating 21% compaction.

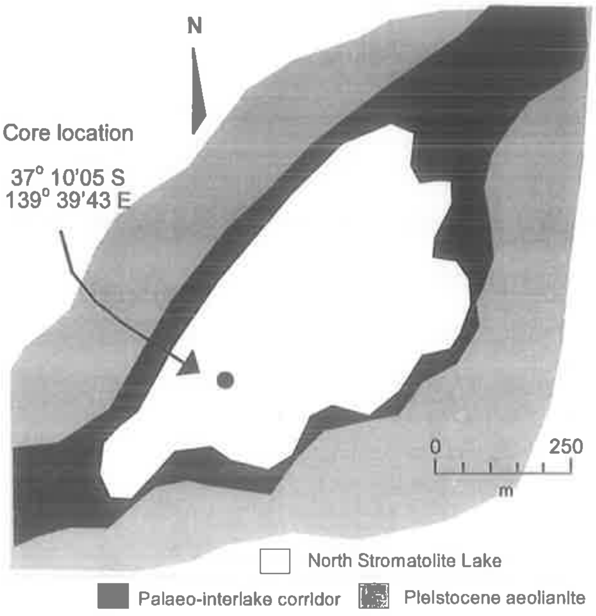

Figure 5.5: Map of North Stromatolite Lake showing the position of the core site.

The stratigraphy of the Salt Creek lake chain is described in detail by Warren (1988, 1990, 1994) and is summarised here with reference to the cores collected in the present study. The upward-shoaling calcareous mudstone succession of these lakes typically contains three distinct Holocene carbonate units: sapropelic mudstone, laminated pelletal mudstone and massive pelletal mudstone/packstone.

The basal unit of Warren's Type 2 lakes (such as the Salt Creek lake chain) is an olive grey siliciclastic-carbonate grainstone to wackestone that was deposited during the early Holocene connection to the open Coorong lagoon. Mineralogy is predominantly quartz with minor dolomite and Mg-calcite. Preserved macrofauna are marine-type molluscs and gastropods. This organically lean unit is thicker (up to 2-3 m) in the interdunal corridors of the Salt Creek lake chain and thins in the lake centres. In the D-section core of the present study (NSL1) the basal unit is intersected at a depth of 286 cm.

The overlying sapropelic mudstone can be divided into two sub-units (Hayball, 1990). In NSL1 the lower sub-unit (Sapropel A) is 102 cm thick, dark olive grey and has a gelatinous, 'cheesecake'-like consistency. The upper sub-unit (Sapropel B) is 34 cm thick, olive to dark yellowish brown and has a more clayey texture than the preceding unit. Gastropods preserved within the entire sapropel unit are indicative of the restricted saline conditions produced by isolation of the lake chain from the open Coorong lagoon. In Sapropel A the gastropods are white (i.e. bleached during reworking), whereas in Sapropel B the gastropods retain their natural colour. Filamentous cyanobacterial remnants are preserved throughout the whole sapropel interval.

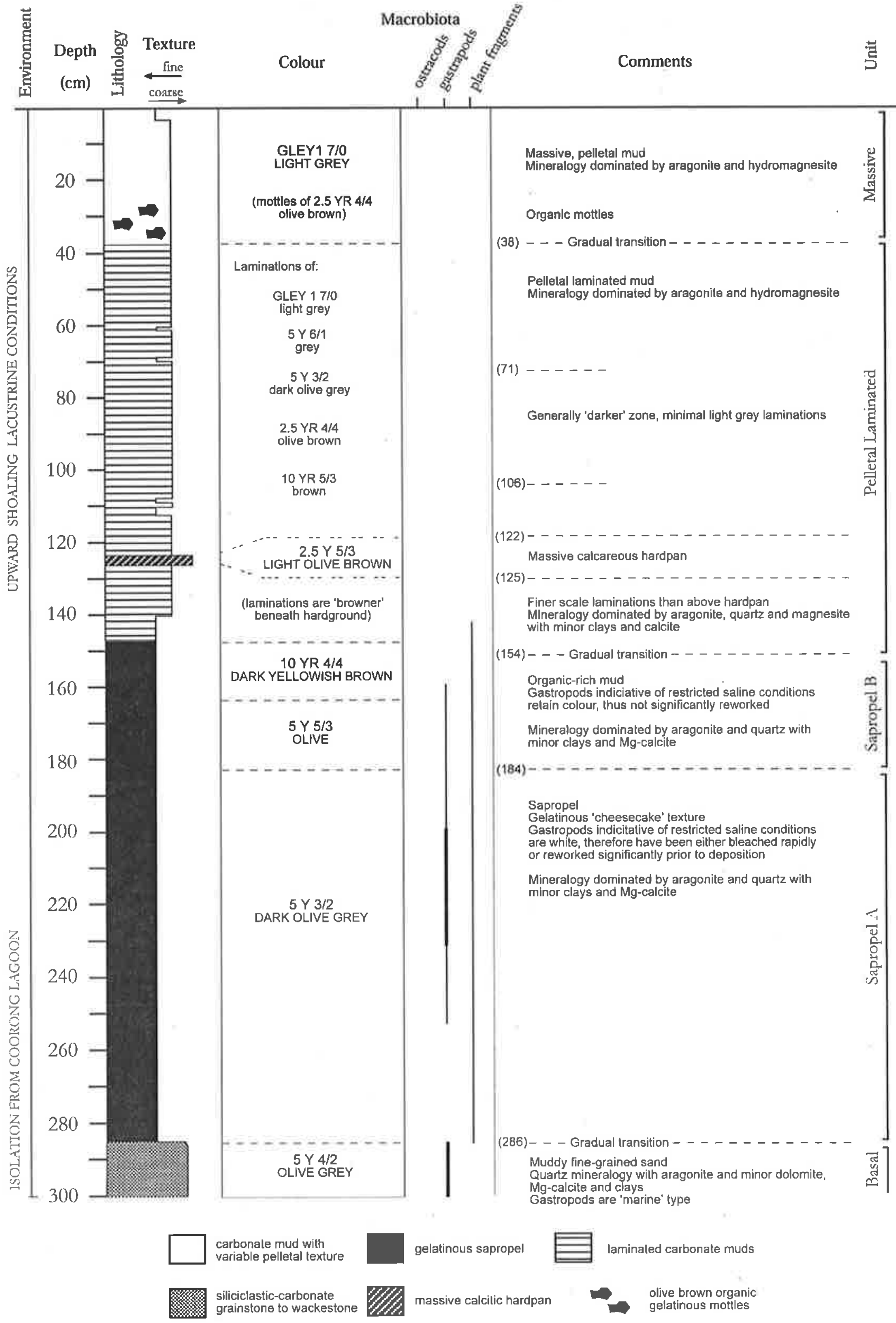

Figure 5.6: Stratigraphic log of the D-section core from North Stromatolite Lake (NSL1). Vertical line thicknesses indicate the relative abundance of macrobiota present through core depth.

The organically-lean pelletal laminated unit overlying the sapropel is 112 cm thick in NSL1 and is volumetrically the most important sedimentary unit in most Type 1 and 2a lakes (Warren, 1990). Its mineralogy is dominated by aragonite, magnesite and hydromagnesite. Organic content is low (TOC < 1%) and no significant macrofauna are preserved. Laminae are up to 1 cm thick and their colours range across the grey scale but beneath the 3 mm-thick calcitic hardpan[3] at 124 cm depth there are more browns and greens.

The transition into the overlying massive unit is gradual and comprises an indistinctly laminated zone of olive brown mottles. This textural transition from laminated to massive sedimentary units is typical of a change from perennial to ephemeral aquatic conditions in a relatively low energy setting (Warren, 1990). The massive unit is an organic-poor pelletal mudstone, light grey in colour and makes up the surficial 38 cm of the NSL1 core (including the 10 cm thick mottled transition zone). This unit has predominantly aragonite and hydromagnesite mineralogy, although dolomite also presently forms on the lake margins (von der Borch and Lock, 1979).

Old Man Lake

Cores were taken from the eastern side of the OML, just south of the carpark and west of the widest area of lake beach (37° 15'40" S, 139° 49'16" E; Figure 5.7). Water depth was ~50 cm. The D-section core (OML1) reached 200 cm depth (Figure 5.8). The sliphammer core (OML2) compressed 211 cm of sediment to 130 cm (36% compaction).

The stratigraphy of OML as described by Mazzoleni (1993) and McKirdy et al. (1999) is observed in the cores of the present study although neither reaches the basal sandy unit or overlying humic unit reported by previous researchers. A siliciclastic-carbonate lagoonal unit containing humic organic matter is associated with the rising groundwater table that accompanied the early Holocene marine transgression. This unit was deposited unconformably on the basal Pleistocene aeolianite. The subsequent progression from marine to upward-shoaling lacustrine conditions is apparent in three distinct carbonate units: lagoonal silts and muds, laminated lacustrine mudstone with sapropelic intervals, and massive gastropod-rich pelletal mud (McKirdy et al., 1999).

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[3] In the present investigation the term 'hardpan' is used to describe an accumulation of either variably consolidated calcareous nodules or well-consolidated calcareous laminae.

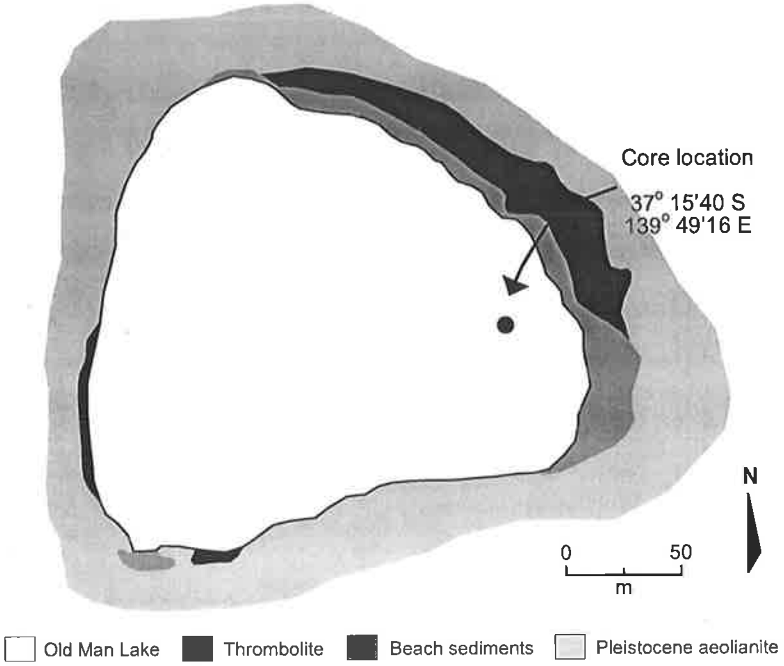

Figure 5.7: Map of Old Man Lake showing the position of the core site.

The lagoonal unit is a dark greyish brown silty mud containing abundant molluscan remains (whole and fragmented) characteristic of a shallow marine setting. The major contribution of shelly fauna to the sediment is also evident in the calcite and aragonite dominated mineralogy of the unit. Quartz content is minor and decreases toward the top of the unit, which may reflect the reducing marine influence as connection with the local back-barrier lagoon became restricted and eventually ceased. In OML1 the transition between the lagoonal unit and the overlying lacustrine unit occurs abruptly at 106 cm depth.

The laminated lacustrine unit can be separated into three sub-units. The lowest unit is an olive brown mud that has a gritty texture arising from the presence of abundant nodules of fine-medium grain size carbonate. Gastropods and ostracods are absent. The unit contains three distinct thin (<3 cm) bands of dark brown sapropel. Filamentous algal and/or cyanobacterial remains appear within the first sapropel band and are present over the remainder of the laminated lacustrine unit. Transition into the middle sub-unit occurs gradually at a depth of ~86 cm. This 35 cm-thick very dark brown sapropel has a gelatinous consistency that is interrupted by variable amounts of carbonate nodules and the presence of two fragmented calcitic hardpan layers. These calcitic features are attributed to supersaturation of the lake waters with respect to calcium that results from the uptake of dissolved CO_2 by aquatic flora and fauna (McKirdy et al., 1999). Ostracods are preserved only in this sub-unit, between 55 and 73 cm depth. An abrupt colour

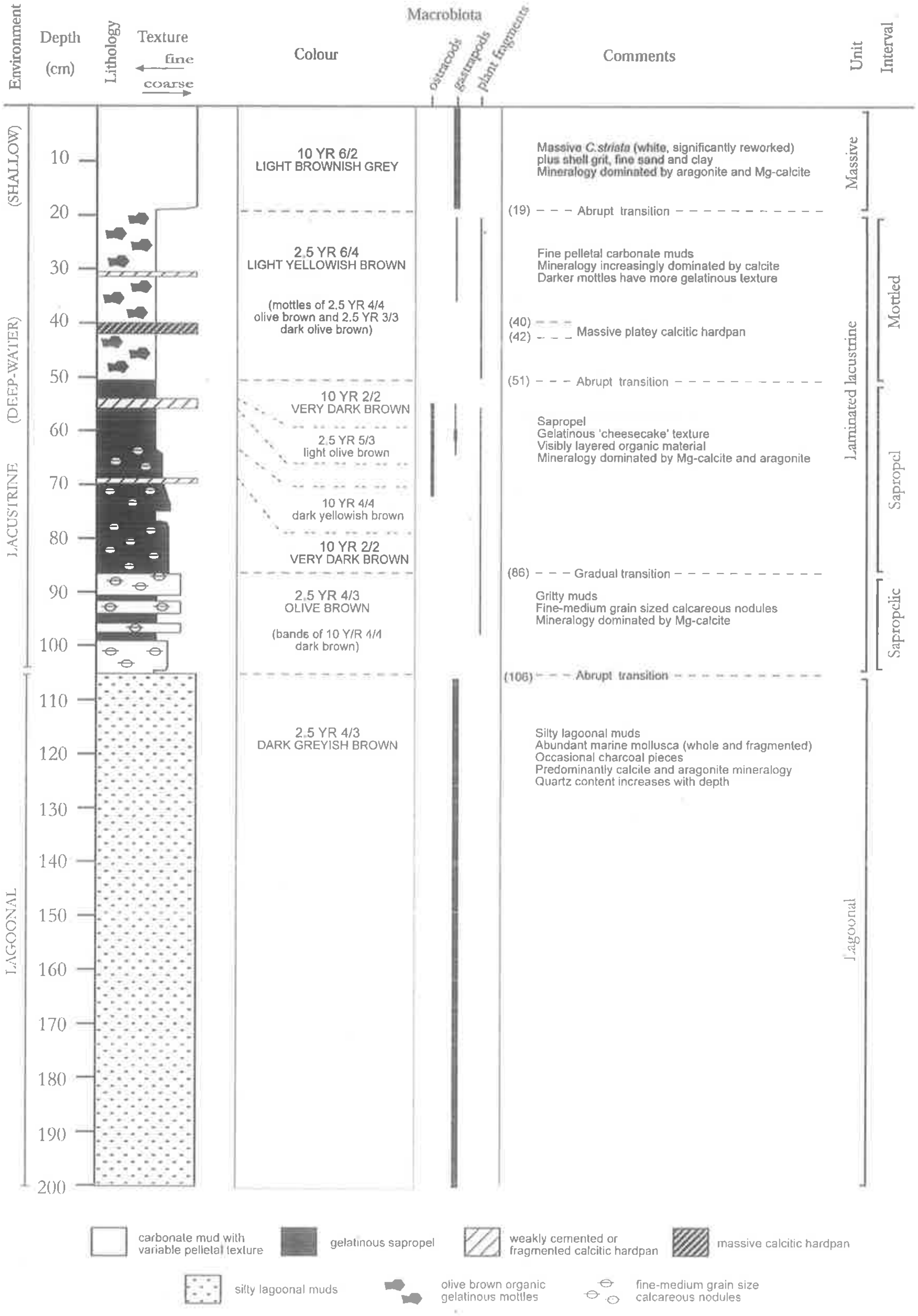

Figure 5.8: Stratigraphic log of the D-section core from Old Man Lake (OML1). Vertical line thicknesses indicate the relative abundance of macrobiota present through core depth.

change at 51 cm marks the transition into the uppermost sub-unit of the laminated lacustrine mudstone. These light yellowish brown fine pelletal carbonate muds feature dark olive brown gelatinous organic-rich mottles. There is a 2 cm-thick massive platey hardpan at 41 cm and a thin fragmented hardpan at 31 cm depth.

The surficial unit of OML is 19 cm thick and comprises light brownish grey massive pelletal mud with abundant remains of the gastropod *Coxiella striata*, indicative of restricted saline conditions. Its mineralogy is dominated by aragonite with minor calcite. Gastropod remains are white indicating that they have been subject to bleaching and reworking since deposition. This unit represents the shallow water lacustrine phase.

Lake Amy

Both cores were taken from the southern end of Lake Amy, approximately 5 m out from the lake beach, at a water depth of ~72 cm (37° 12'51" S, 139° 47'05" E; Figure 5.9). The D-section technique retrieved 250 cm of sediments (LA1; Figure 5.10). The sliphammer technique could not break through a massive hardpan near the base of these sediments and therefore sampled only 240 cm (LA2). These sediments underwent 40% compaction during the coring process.

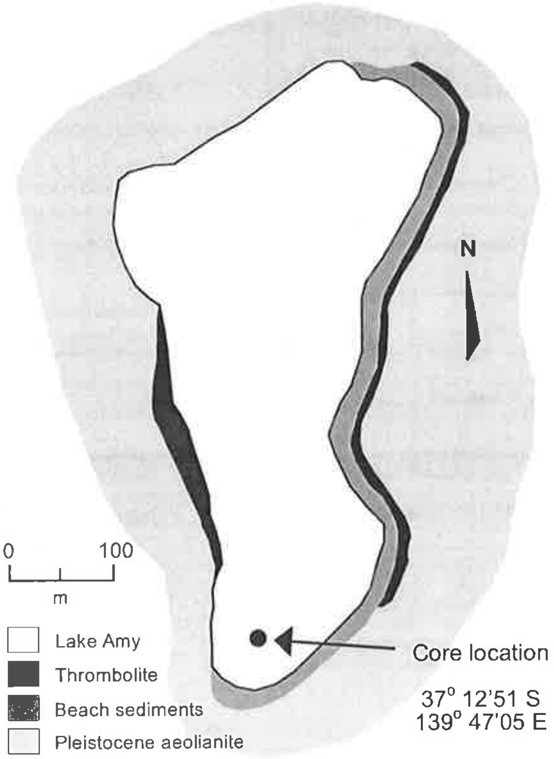

Figure 5.9: Map of Lake Amy indicating the site of sediment core collection.

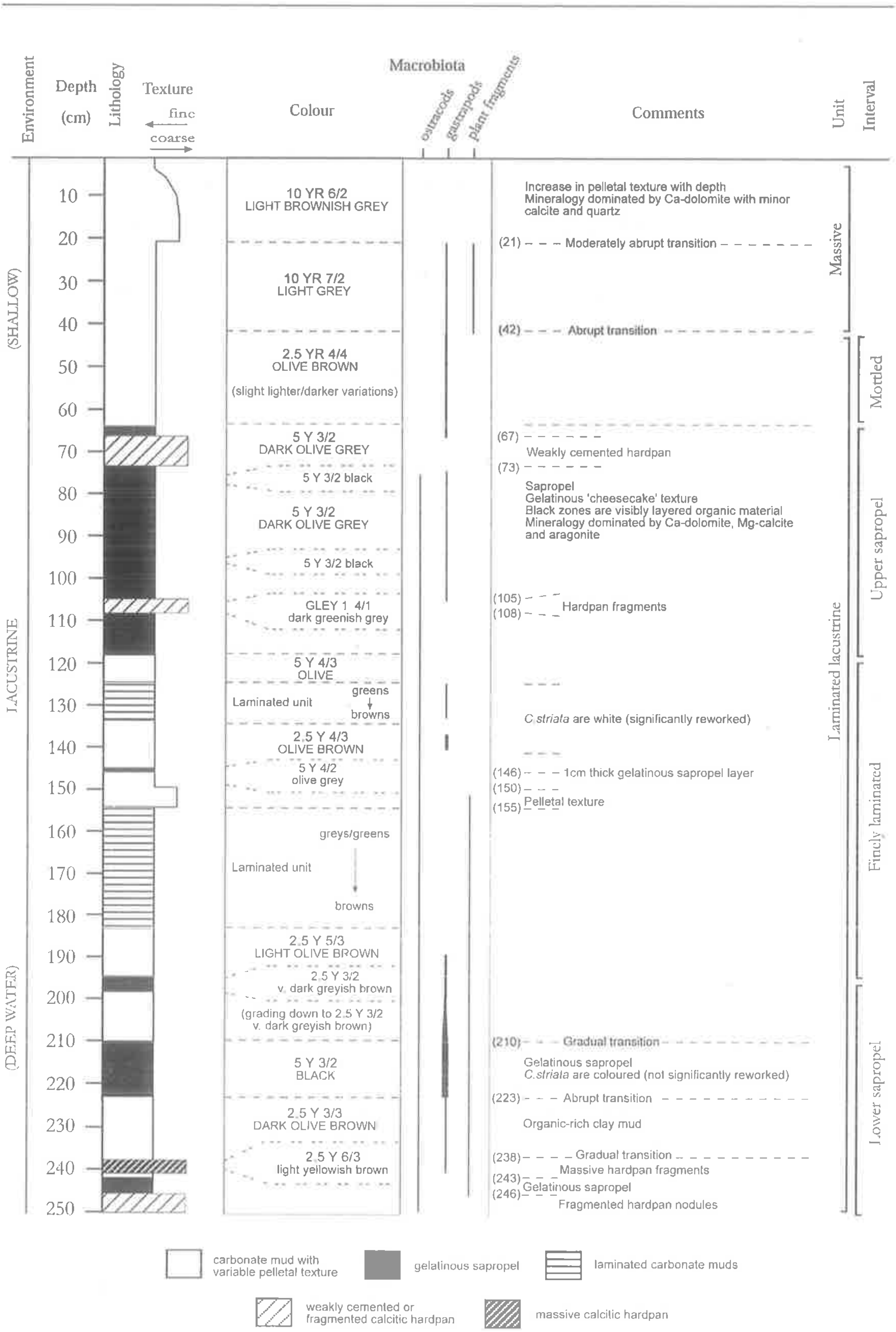

Figure 5.10: Stratigraphic log of the D-section core from Lake Amy (LA1). Vertical line thicknesses indicate the relative abundance of macrobiota present through core depth.

Lake Amy was never directly connected to an open marine system and is therefore analogous to the Type 1 lakes near Salt Creek (Warren, 1990). Its sedimentary sequence represents an upward-shoaling lacustrine system and consists of a massive bioturbated pelletal carbonate mudstone overlying a laminated mudstone with sapropel intervals, hardpans and variable amounts of ostracod and gastropod remains. Previous workers have observed a humic transgressive unit, similar to that in OML, overlying the basal Pleistocene aeolianite (McKirdy et al., 2005). However, in the present study the coring did not reach these older units.

The laminated mudstone unit makes up the majority of the lacustrine sedimentary succession in LA1. Its mineralogy is predominantly aragonite and variably Mg-rich calcite. The unit varies in colour from light olive grey and brown through to dark olive grey and brown. There are five distinct intervals of very dark brown to black gelatinous sapropel. The oldest sits at 243-246 cm depth beneath the fragmented massive calcitic hardpan that halts at 241 cm depth. Above this is a 15 cm-thick interval of organic-rich mud with minor *Coxiella striata*, which at 223 cm depth passes abrubtly into the overlying 12 cm thick sapropel. This transition is coincident with a large increase in the amount of gastropod remains, which are abundant within the sapropel and peter out gradually over the following 24 cm. This interval includes the third sapropel at 195-199 cm depth. Above this is a more finely laminated zone of mudstone that includes a 1 cm thick sapropel at 146 cm depth. The thickest sapropel (64-119 cm depth) overlies this laminated zone and includes two weakly cemented hardpan intervals (67-73 and 105-108 cm depth). Minor *C. striata* are present between the hardpans. Ostracods that have been present through the entire sequence thus far disappear at the base of the upper hardpan. A 22 cm thick-mottled zone with moderately abundant *C. striata* overlies the uppermost sapropel and makes up the remainder of the laminated lacustrine mudstone unit.

A massive mudstone comprises the upper 42 cm of LA1 and, as with both NSL and OML, represents a shallower phase of the lake than the underlying laminated unit. The massive unit has two zones, each 21 cm thick. The lower zone is light grey and contains minor gastropods and filamentous organic remains, whereas the upper one is light brownish grey and has a pelletal texture that decreases moving up-section. Throughout the entire massive unit the proportion of high-Mg calcite increases upwards toward the present-day sediment-water interface.

CHAPTER 6: ORGANIC AND INORGANIC GEOCHEMICAL DATA

This chapter presents and summarises the geochemical data obtained from analysis of lacustrine organic matter and co-deposited sedimentary carbonate in the cores from North Stromatolite Lake, Old Man Lake and Lake Amy described in Chapter 5. Discussion of the resulting data is kept to a minimum herein, and focuses primarily on the potential sources of error within specific analyses. Integration and interpretation of the geochemical results presented herein follows in the subsequent chapters where detailed discussion focuses on addressing the aims of this study.

6.1 Total Organic Carbon

The TOC data for all three lakes are listed in Table 6.1 and plotted against the core stratigraphy in Figure 6.1.

The basal estuarine unit of NSL has a TOC content of less than 1%. In the overlying sapropelic mudstone, TOC values range from 6 to 16% in sapropel A and are ~4% in sapropel B. These values then decrease to less than 1% in the pelletal laminated and massive units that comprise the remainder of the lake's sedimentary succession.

The lagoonal unit in the lower section of the OML core has a TOC content of less than 0.5%. In the overlying lacustrine unit TOC content varies widely between 3 and 17%, the lower values coinciding with the presence of various carbonate accumulations (ostracods, gastropods and calcitic nodules and hardpans). Similarly, the massive unit, with its abundant remains of *C. striata*, is relatively organic-poor at only 2-3% TOC.

In the LA core, TOC contents remain above 10% (max. 21.5%) throughout the lacustrine laminated mudstone unit. As described in the previous chapter this mudstone comprises four intervals. The TOC contents are as follows: lower sapropel, 14-20%; laminated interval, 10-13%; upper sapropel, 18-21.5%; and mottled interval, 7.8%. The sediments of the overlying massive unit contain just 2-3% TOC and are thus similar to the equivalent unit in OML.

Table 6.1: Results of geochemical analyses (percent CO3, TOC and TN, C/N and stable isotopes of nitrogen and organic carbon) for samples from North Stromatolite Lake, Old Man Lake and Lake Amy. Note that although the TN values are listed for Lake Amy these have been reduced by the amount of inorganic nitrogen present prior to calculation of the listed C/N ratios (see section 6.2).

Lake	**Sample**	**Depth**	**CO3**	**TOC**		**TN**		**C/N**		**δ^{15}N**		**$\delta^{13}C_{vpdb}$**	
		cm	**%**	**%**	***Std Dev***	**%**	***Std Dev***	**(mass)**	**(atomic)**	**‰**	***Std Dev***	**‰**	***Std Dev***
NSL	NS1	7	86.1	0.5	*0.07*	0.03		16.9	19.8	10.99		-22.26	
	NS2	40	90.3	0.6		0.02	*0.001*	23.3	27.2	16.17	*1.32*	-19.61	*0.28*
	NS3	52	89.2	0.8		0.03		30.5	35.6	13.50		-19.93	
	NS4	76	81.8	0.5		0.02		23.5	27.4	13.44		-19.39	
	NS5	95	74.5	0.4		0.01	*0.0004*	25.3	29.5	13.76	*0.14*	-18.36	*0.07*
	NS6	124	77.1	0.7		0.04		18.2	21.3	10.20		-19.61	
	NS7	143	69	0.8		0.04		19.2	22.4	11.67		-19.20	
	NS8	155	73	3.9	*0.07*	0.32	*0.02*	12.1	14.1	4.44	*1.46*	-17.01	*0.27*
	NS9	166	74.3	4.2		0.29		14.2	16.5	6.88		-16.39	
	NS10	179	77.8	4.1		0.30		13.7	16.0	6.51		-17.53	
	NS11	190	48.1	10.9		0.77		14.2	16.6	6.81		-18.05	
	NS12	214	59.9	5.9	*0.05*	0.46		12.9	15.0	6.36		-18.60	
	NS13	238	43.6	16.4		1.11		14.8	17.3	1.48		-18.59	
	NS14	260	34.5	15.4		1.13		13.7	15.9	1.89		-18.96	
	NS15	283	48.9	9.5		0.56	*0.41*	16.9	19.8	3.39	*0.16*	-18.42	*0.19*
	NS16	293	29.6	0.74		0.06	*0.02*	12.6	14.7	2.42	*3.87*	-19.14	*0.51*
OML	OM1	4.5	96.4	2.4		0.15		15.6	18.2	-3.55			
	OM2	19.5	89.4	3.4		0.41		8.2	9.5	0.54		-17.49	
	OM3	28	77.7	16.7		0.91	*0.04*	18.4	21.5	1.25	*0.23*	-18.41	*0.37*
	OM4	39	93.4	2.5	*0.03*	0.22		11.2	13.1	3.03		-18.82	
	OM5	52.5	55.8	4.0		1.71	*0.07*	2.3	2.7	4.99	*0.09*	-22.58	*0.02*
	OM6	59.5	53.1	16.0		1.96		8.2	9.6	1.98		-21.08	
	OM7	65	62.2	13.4		1.68	*0.02*	8.0	9.3	1.35	*1.77*	-19.19	*0.18*
	OM8	74.5	58.2	4.6		1.68		2.7	3.2	1.59		-20.42	
	OM9	84.5	64.9	15.9		1.03		15.4	18.0	3.88		-19.95	
	OM10	88	92.6	2.8	*0.07*	0.17	*0.001*	16.8	19.5	4.25	*0.26*	-19.89	*0.12*
	OM11	94.5	64.6	9.1		1.25		7.3	8.5	3.63		-21.28	
	OM12	101.5	78	5.8		0.44		13.3	15.6	5.95		-22.20	
	OM13	105.5	67.2	3.1		0.47		6.6	7.7	4.39		-21.00	
	OM14	123.5	63.2	0.3		0.04		7.3	8.5	1.85		-18.94	
	OM15	182.5	65.2	0.4	*0.002*	0.02	*0.003*	17.2	20.1	2.10	*2.65*	-19.72	*0.002*
LA	A1	12.5	93.7	2.6	*0.18*	0.20		20.7	24.2	5.67		-19.17	
	A2	32	88.1	3.4		0.32		13.5	15.7	4.72		-18.31	
	A3	54	75.1	6.9		0.55		14.3	16.7	0.80		-17.44	
	A4	70.5	80.6	8.1	*0.31*	0.91		9.7	11.3	1.62		-17.14	
	A5	85.5	61.5	21.5		1.76		12.7	14.8	3.30		-15.91	
	A6	97	54.4	18.4		1.52	*0.14*	12.6	14.7	3.14	*1.04*	-18.19	*0.10*
	A7	103.5	62	16.8		1.64		10.7	12.5	2.26		-17.35	
	A8	109.5	74.5	16.4		1.08	*0.04*	16.2	18.9	1.62	*1.30*	-17.88	*0.07*
	A9	120.5	66.3	18.7		1.35		14.6	17.0	3.36		-16.20	
	A10	136.5	79	13.2		0.77	*0.03*	18.8	22.0	-0.32	*0.75*	-18.68	*0.25*
	A11	152.5	73.1	10.4		1.09		10.2	11.9	-0.34		-17.13	
	A12	173	72.5	11.5		0.89		13.9	16.2	1.50		-17.24	
	A13	187.5	79.8	11.2		0.66		18.9	22.1	1.78		-17.53	
	A14	201.5	72.7	10.5		0.94		12.0	14.0	3.36		-17.40	
	A15	210.5	60	14.3		1.37	*0.01*	11.0	12.8	2.88	*0.54*	-19.13	*0.25*
	A16	222	58.1	20.6		1.49		14.5	16.9	4.72		-20.51	
	A17	225	60	17.7		1.32	*0.07*	14.1	16.4	3.88	*1.68*	-19.56	*0.08*
	A18	236.5	57	16.4		1.25	*0.06*	13.9	16.2	3.00	*1.18*	-20.31	*0.23*
	A19	244	48.6	17.4		1.77		10.2	11.9	3.67	*1.25*	-22.11	*1.31*
	A20	249	78.7	7.8	*0.11*	0.65	*0.02*	13.3	15.6	3.61	*0.62*	-23.18	*0.15*

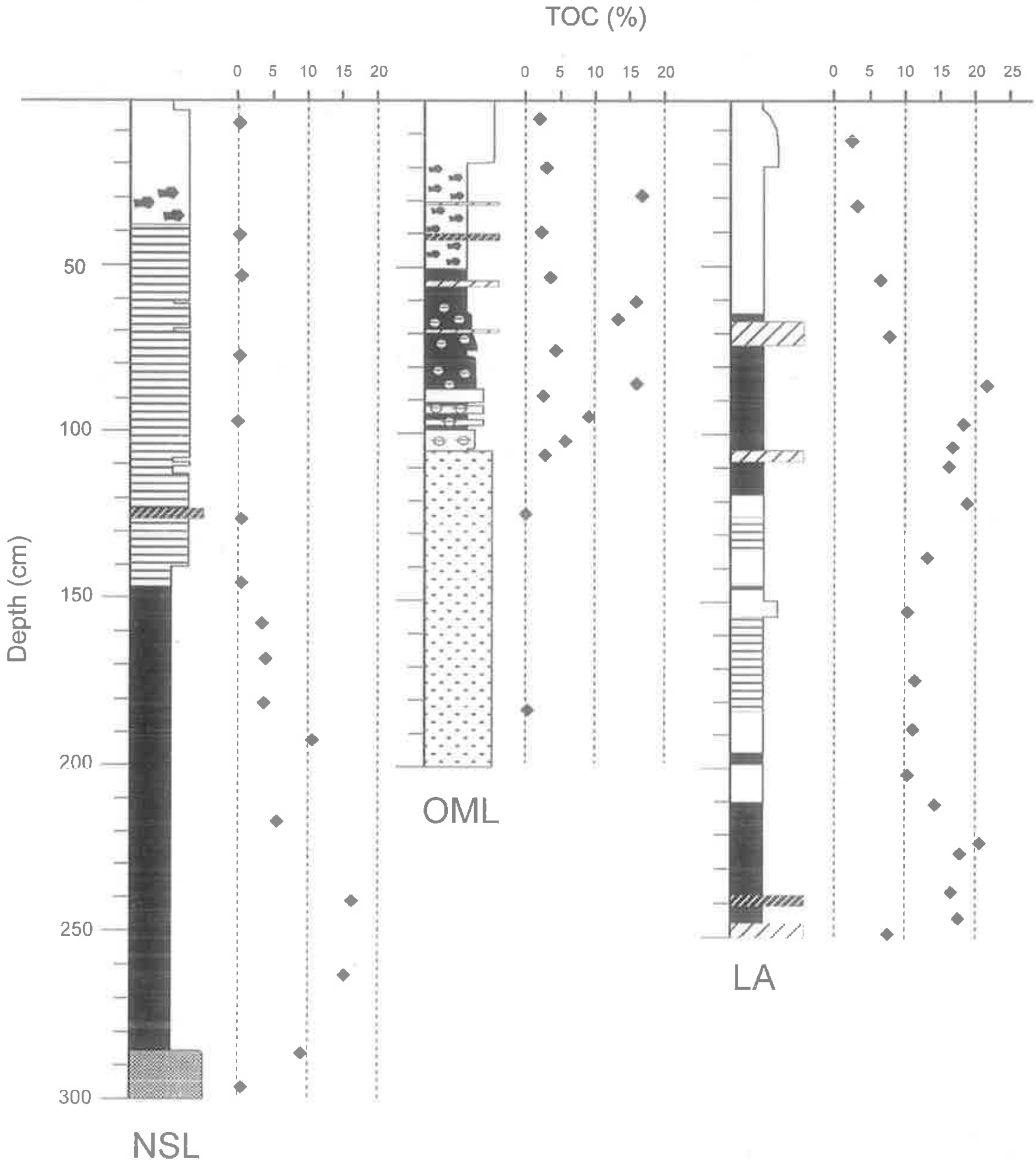

Figure 6.1: Depth profiles of total organic carbon (TOC) concentrations (%) in the sediments from NSL, OML and LA.

6.2 Carbon/Nitrogen Ratios

Sediment samples, especially those with an organic carbon content <1%, can produce misleading C/N ratios because their organic carbon value is compared with a value that incorporates both organic and inorganic nitrogen (Meyers, 1997). However, as described in section 2.1.2, the amount of inorganically bound nitrogen can be approximated through a cross-plot of sedimentary TOC and TN values (Talbot, 2001). All lacustrine sediment samples from the present investigation, with the exception of the laminated and massive units of NSL, contain TOC contents >1% and can thus be presumed to provide meaningful C/N ratios. The TOC vs. TN cross-plot approach was used to determine whether the organically poor sedimentary units of NSL (TOC<1%) contained significant proportions of inorganically bound nitrogen (Figure 6.2). The significant correlation (R^2=0.99) between TOC and TN, and an N-intercept value of approximately zero suggests that inorganic nitrogen is negligible. Therefore, regardless of the low organic content of these NSL sediments, C/N ratios have been calculated.

C/N ratios have not been calculated for the lagoonal unit of OML as the TOC contents are <1% and there are not enough samples from within this organically poor unit to validate a cross-plot approximation of inorganic nitrogen.

All C/N mass ratios were multiplied by 1.167 to convert them to atomic C/N ratios[4] for direct comparison with other published atomic C/N data (e.g. Table 2.1). Both sets of ratios are listed in Table 6.1 and the atomic C/N ratios are plotted against the lacustrine stratigraphy in Figure 6.3. All values discussed within the text are atomic C/N ratios unless otherwise specified.

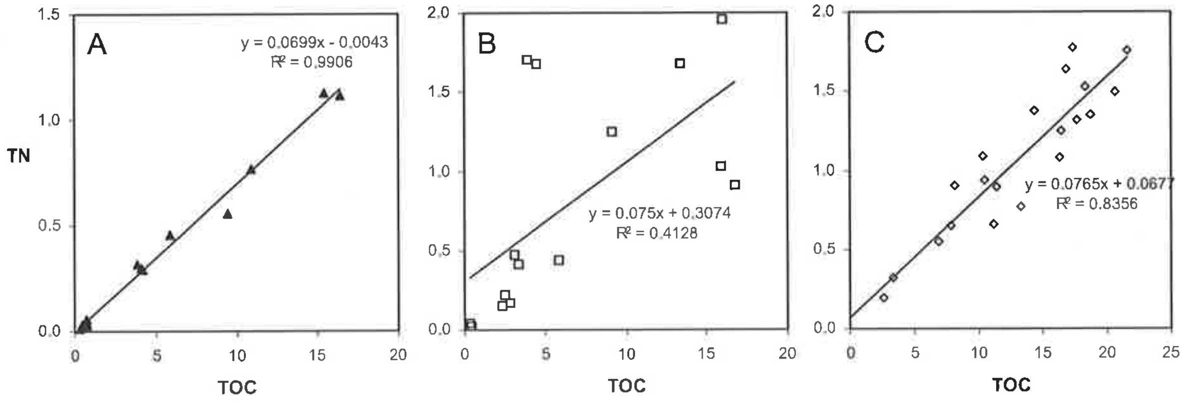

Figure 6.2: Total organic carbon (TOC) versus total nitrogen (TN) for A) NSL, B) OML and C) LA. The positive intercept of the regression line at the TN axis is the implied amount of nitrogen that is inorganically bound in the Lake Amy sediments.

In NSL, the basal unit has a C/N ratio of 14.7. In Sapropel A, C/N ratios (n=5) range from 19.8 at 283 cm depth to 15.0 at 214 cm and in Sapropel B (n=3) from 16.0 at 179 cm depth to 14.1 at 155 cm. The entire sapropelic mudstone interval has a mean C/N ratio of 16.4 ± 1.7. There is a marked increase in C/N through the overlying laminated unit (mean = 27.2 ± 5.2), and a further decrease in the massive unit (19.8).

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[4] Mass numbers: C = 12, N = 14 Therefore, conversion from mass to atomic ratios requires multiplication by 14/12 = 1.167 (Meyers and Teranes, 2001).

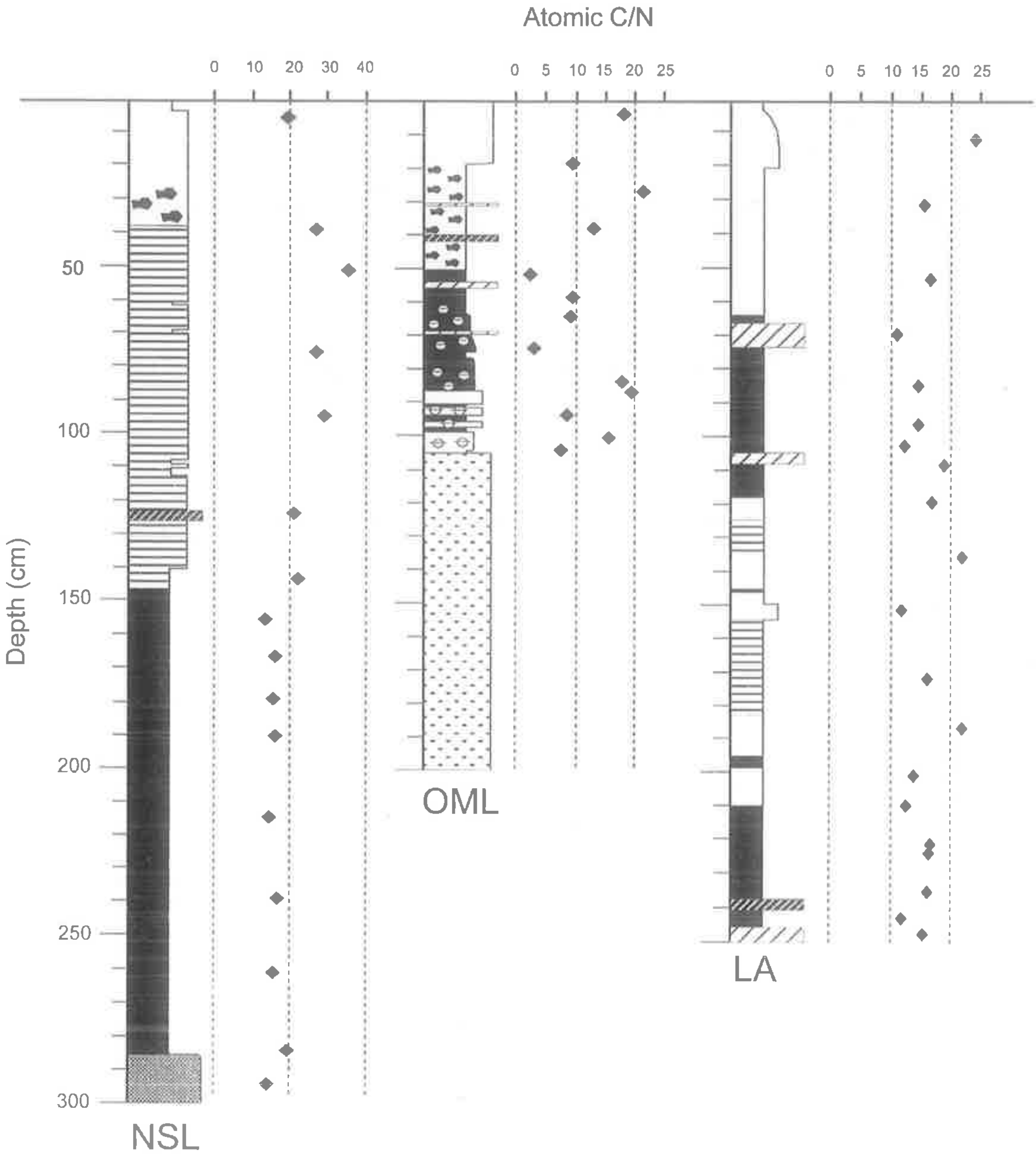

Figure 6.3: Depth profiles of atomic C/N ratios in the sediments of NSL, OML and LA.

The lagoonal unit of OML is too lean to calculate meaningful C/N ratios. Throughout the remainder of the sedimentary succession C/N values (n=12) fluctuate dramatically (maximum 21.5 at 28 cm; minimum 2.7 at 52 cm). However, lower values (2.7-9.6) are consistently evident in sapropelic sediments, particularly the 35 cm-thick sapropel that dominates the laminated lacustrine unit.

TOC is greater than 1% over the entire LA core and therefore C/N ratios can be calculated and presumed meaningful for all samples (n=20). However, the linear correlation (R^2 = 0.84: Figure 6.2 C) of these samples on a TOC versus TN cross-plot has a positive intercept (y = 0.068). This implies that this proportion of the TN is inorganically bound and should be corrected for prior to calculation of atomic C/N. The corrected C/N values fluctuate throughout the sedimentary succession, although mostly within the range 11-17. Notable excursions are those of samples A10 and A13 (22.0 at 136 cm and 22.2 at 187 cm, respectively) located immediately below finely laminated zones of the lacustrine mudstone. The mean C/N values calculated for the two sapropel intervals (upper, 14.4 ± 2.9: lower, 14.7 ± 2.1) are notably lower than those of the intervening laminated interval (17.8 ± 4.3). Sample A1, from the massive unit, also has a relatively elevated C/N ratio of 24.2, thus precluding calculation of an average C/N ratio for the relatively organic-poor sediments of the mottled interval and massive unit.

6.3 $\delta^{13}C$ and $\delta^{15}N$ of Organic Matter

Stable carbon isotope analysis of the sedimentary organic matter returned a similar range of $\delta^{13}C_{org}$ values for each lake: NSL –22.3 to –16.4‰, OML –22.6 to –17.5‰, LA –23.2 to –15.9‰ (Table 6.1). These values are plotted against the core stratigraphy in Figure 6.4.

In NSL, $\delta^{13}C_{org}$ displays a clear variation with stratigraphy. The basal unit is markedly more ^{13}C-depleted ($\delta^{13}C_{org}$ = –20.9‰) than the overlying sapropelic mudstone (A_{avg} = –18.5 ± 0.3‰; B_{avg} = –17.0 ± 0.6‰). An abrupt shift to more ^{13}C-depleted values occurs at the transition into the laminated unit ($\delta^{13}C$ average = –19.4 ± 0.5‰), followed by a further negative offset in the massive unit ($\delta^{13}C$ = –22.3‰).

Stratigraphic distinctions are also evident in OML. However, $\delta^{13}C_{org}$ shows a greater degree of variability within the sapropelic sediments in OML (range: 3.4‰) than in NSL (range: 2.6‰). The lagoonal unit of OML has a mean $\delta^{13}C_{org}$ value of –19.3 ± 0.6‰, whereas the overlying sapropel-rich zone of the laminated lacustrine mudstone is isotopically lighter (mean $\delta^{13}C_{org}$ = –20.8 ± 1.1‰). There is no correlation between $\delta^{13}C_{org}$ and TOC in the laminated lacustrine mudstone unit (R^2 = 0.11), which incorporates the sapropel-rich zone and the overlying moderately ^{13}C-enriched mottled zone (mean $\delta^{13}C_{org}$ = –18.2 ± 0.7‰). Complete carbonate removal was difficult for the organically-lean massive unit of OML (carbonate mud with abundant *C. striata*) and was not achieved during initial and repeated sample treatment with 0.5M HCl. As the use of any stronger acid has potential to also remove some of the labile organic matter and therefore produce an inaccurate result (Midwood and Boutton, 1998) no $\delta^{13}C$ data are reported for the massive unit of OML.

The $\delta^{13}C$ profile of the laminated mudstone unit in LA exhibits a well-defined positive excursion. Through the lower sapropel values climb from –23.1 to –17.4‰. The remainder of sedimentary succession is comparatively ^{13}C-enriched with an average $\delta^{13}C_{org}$ of –17.6 ± 0.9‰. The laminated interval between the two sapropels is relatively uniform (–17.4 ± 0.9‰), as is the upper sapropel (–17.3 ± 0.9‰). $\delta^{13}C_{org}$ then gradually declines through the mottled interval and into the massive unit (–18.7 ± 0.6‰).

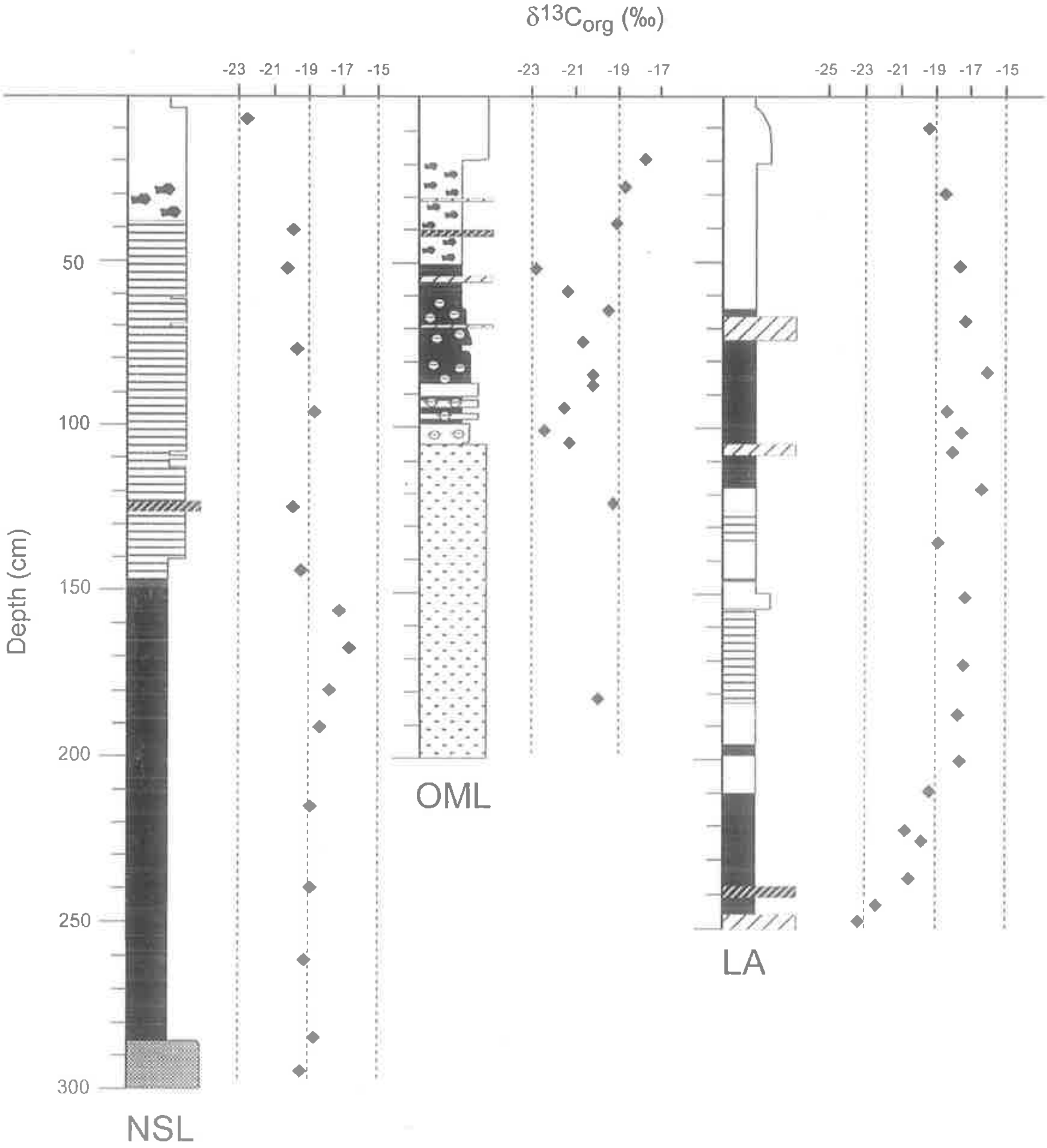

Figure 6.4: Depth profiles of organic carbon isotopes ($\delta^{13}C_{org}$, ‰) in the sediments from NSL, OML and LA.

The results of nitrogen isotope analysis are presented in Table 6.1 and plotted in Figure 6.5. $\delta^{15}N$ falls in the range of ~0 to 6‰ for both OML and LA, but extends to considerably higher values in NSL (maximum: 16.2‰). In NSL, the organic matter in the basal unit has a $\delta^{15}N$ value of ~2.4 ± 3.9‰[5]. Above this, $\delta^{15}N$ progressively increases from 2.3 ± 1.0‰ in the lower half of Sapropel A, through 6.2 ± 1.0‰ across the upper half of Sapropel A plus Sapropel B, to 10.9 ± 1.0‰ in the pelletal laminated unit beneath the hardpan at 125 cm depth and 13.6 ± 0.2‰ in the remainder of that unit. The mottled zone of the massive unit and the massive unit have single $\delta^{15}N$ values of 16.2 and 11.0‰, respectively.

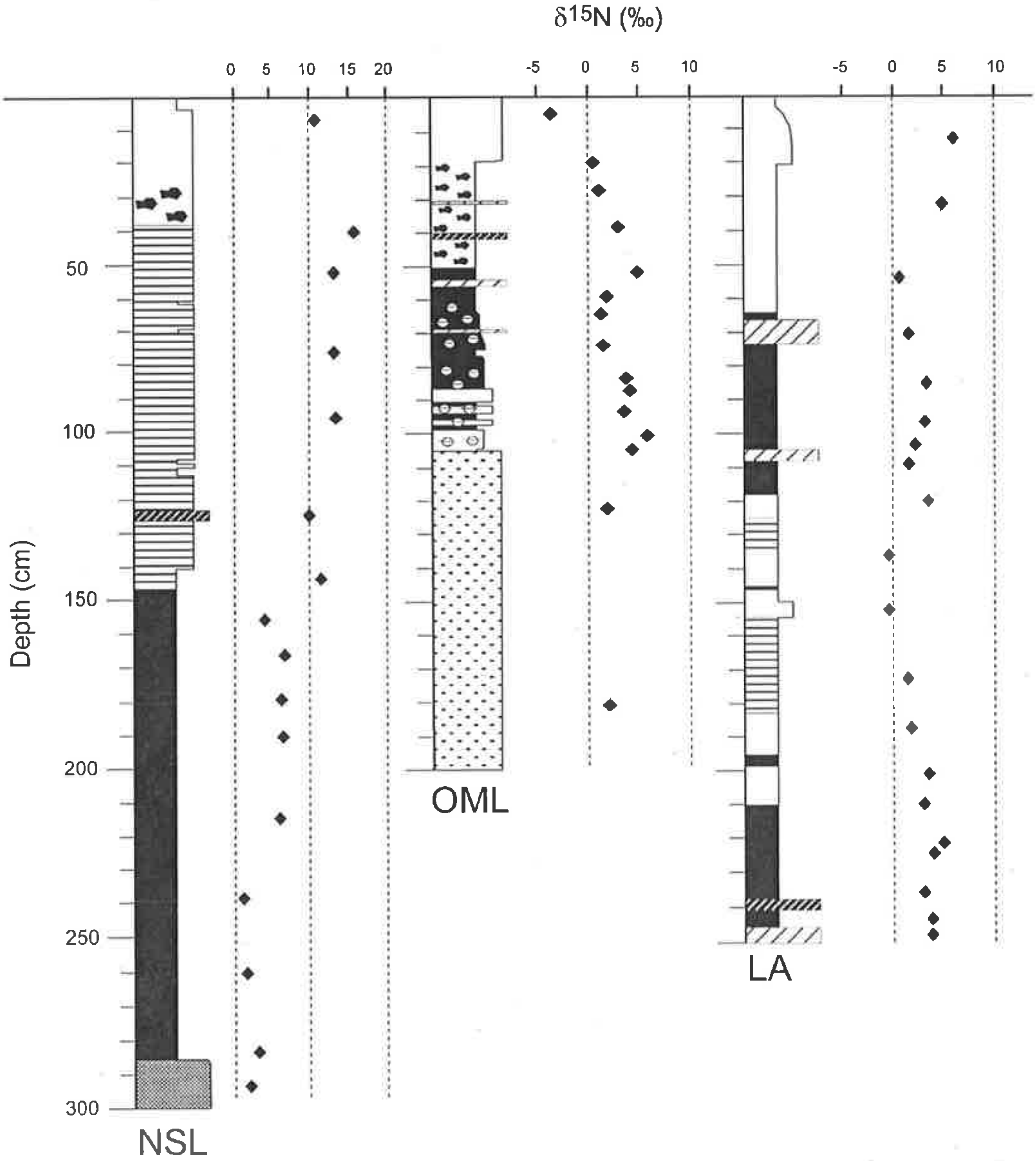

Figure 6.5: Depth profiles of nitrogen isotopes ($\delta^{15}N$, ‰) in the sediments from NSL, OML and LA.

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[5] This value is quoted cautiously as it is calculated from only two duplicates and those differed by ~5‰.

Organic matter in the lagoonal unit of OML has $\delta^{15}N$ values of 2.0 ± 0.2‰. In the overlying lacustrine unit, organic matter is relatively ^{15}N-enriched in the sapropelic interval (4.4 ± 0.9‰), and ^{15}N-depleted through the overlying 35 cm-thick sapropel (1.64 ± 0.3‰). A $\delta^{15}N$ value of 5.0‰ marks the upper boundary of this sapropel. Thereafter, $\delta^{15}N$ steadily declines to ~0‰ at the top of the mottled interval, and –3.5‰ in the massive unit.

The three lower intervals of the laminated lacustrine mudstone in the LA core can be distinguished by their $\delta^{15}N$ profiles. The lower sapropel interval has $\delta^{15}N$ values of 3.6 ± 0.6‰. $\delta^{15}N$ then gradually decreases (toward ~0‰) through the laminated interval. The upper sapropel makes a return to heavier $\delta^{15}N$ values of 2.6 ± 0.8‰, a trend that continues until ~87 cm depth. Thereafter, $\delta^{15}N$ drops to 0.8‰ at 54 cm depth in the mottled interval before rising again in the shallower sediments of the overlying massive unit (5.2 ± 0.7‰).

6.4 $\delta^{13}C$ and $\delta^{18}O$ of Carbonate

Two sets of results from the isotopic analysis of the bulk carbonate fraction of the cored sequences are displayed in Table 6.2. The first data set is from sediment samples that were treated with H_2O_2 to remove organic matter prior to isotopic analysis. The second set of results is from an untreated portion of the same samples. A comparison of the two data sets is shown in Figure 6.6.

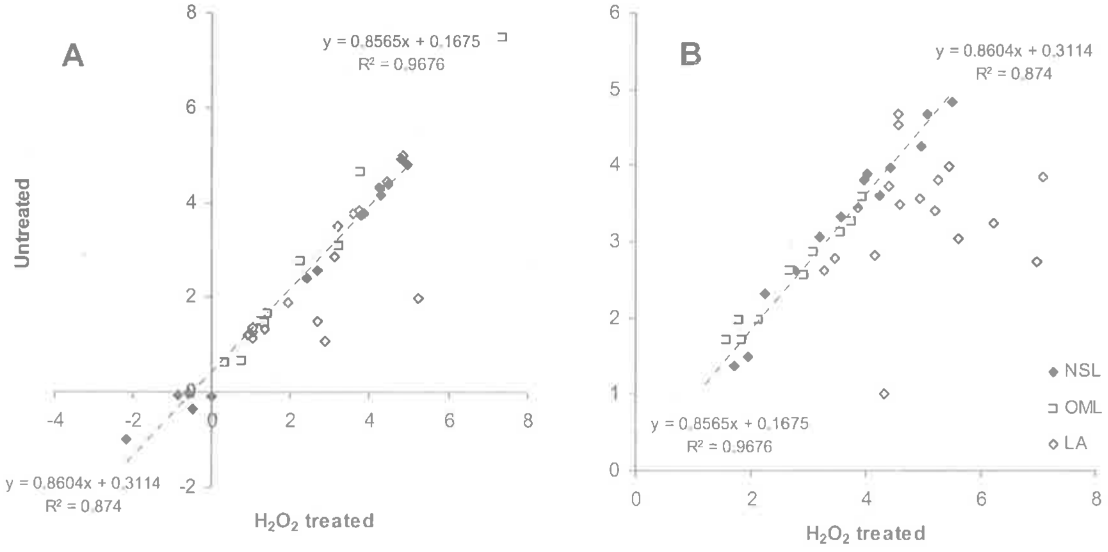

Figure 6.6: Comparative plots of A) $\delta^{13}C_{carb}$ and B) $\delta^{18}O_{carb}$ data for H_2O_2 treated and untreated lacustrine sediment samples show that the treatment process unequally affected the isotopic results of the three studied lakes.

Table 6.2: Results of isotopic analysis of sedimentary carbonate (carbon and oxygen) for H_2O_2 treated and untreated samples from North Stromatolite Lake, Old Man Lake and Lake Amy.

Lake	Sample	Analysis	Depth cm	H_2O_2 treated		Non-H_2O_2 treated	
				$\delta^{13}C_{vpdb}$ ‰	$\delta^{18}O_{vpdb}$ ‰	$\delta^{13}C_{vpdb}$ ‰	$\delta^{18}O_{vpdb}$ ‰
NSL	1	AM-N01	12.5	2.69	4.96	2.58	4.24
	2	AM-N02	30.5	3.80	5.51	3.72	4.82
	3	AM-N03	44	4.98	5.08	4.79	4.68
	4	AM-N04	79	4.80	4.02	4.94	3.88
	5	AM-N05	98	3.87	3.57	3.75	3.32
	6	AM-N06	109.5	4.26	3.98	4.31	3.81
	7	AM-N07	127	4.30	4.24	4.15	3.60
	8	AM-N08	147.5	4.50	4.42	4.37	3.97
	9	AM-N09	168	2.42	3.87	2.39	3.43
	10	AM-N10	184.5	-0.84	2.24	-0.04	2.32
	11	AM-N11	198.5	-2.18	1.71	-0.98	1.38
	12	AM-N12	207.5	-0.44	3.21	-0.34	3.06
	13	AM-N13	226.5	0.00	2.76	-0.09	2.63
	14	AM-N14	244.5	-	-	1.18	1.93
	15	AM-N15	263.5	-	-	0.05	1.45
	16	AM-N16	284	-0.57	1.96	-0.03	1.49
OML	1	AM-OM01	11	3.80	3.10	4.64	2.87
	2	AM-OM02	23.5	7.39	2.69	7.49	2.61
	3	AM-OM03	44	0.78	3.77	0.66	3.25
	4	AM-OM04	56	2.29	2.92	2.76	2.55
	5	AM-OM05	86.5	0.38	3.94	0.62	3.58
	6	AM-OM06	96.5	3.26	3.58	3.09	3.11
	7	AM-OM07	106.5	1.30	2.15	1.51	1.98
	8	AM-OM08	124	1.34	1.80	1.49	1.97
	9	AM-OM09	145.5	1.39	1.86	1.48	1.71
	10	AM-OM10	166	1.46	1.58	1.65	1.71
LA	1	AM-A01	31.5	1.96	4.55	1.89	4.66
	3	AM-A03	69.5	3.14	4.56	2.84	4.54
	4	AM-A04	82.5	1.05	3.47	1.26	2.78
	5	AM-A05	95.5	0.97	4.16	1.22	2.82
	6	AM-A06	110.5	1.40	3.26	1.34	2.62
	7	AM-A07	122.5	5.25	6.97	1.97	2.73
	8	AM-A08R	137.5	2.69	4.33	1.49	1.00
	9	AM-A09R	151	3.58	4.39	3.76	3.73
	10	AM-A10	164.5	4.46	7.10	4.44	3.85
	11	AM-A11	179	3.74	5.27	3.82	3.80
	12	AM-A12	191.5	4.83	5.46	5.01	3.98
	13	AM-A13	204	3.21	4.95	3.50	3.57
	14	AM-A14	215	2.90	6.23	1.09	3.24
	15	AM-A15	226.5	1.08	5.61	1.13	3.04
	16	AM-A16	237.5	1.08	5.21	1.35	3.40
	17	AM-A17	247	1.01	4.60	1.23	3.48

Both NSL and OML show a high degree of correlation between the treated and untreated samples for $\delta^{13}C_{carb}$ ($R^2 = 0.87$) and $\delta^{18}O$ ($R^2 = 0.97$). Therefore, the treatment process did not significantly alter the isotopic results for these two lakes. While most of the LA samples have returned similar $\delta^{13}C_{carb}$ values from the treated and untreated aliquots, the overall correlation is significantly reduced ($R^2 = 0.58$) by three samples that fall away from this trend. As these three samples (A07, A08, A14) are neither significantly different in mineralogy to the rest of the LA samples, nor all similar to each other in terms of stratigraphic position, TOC content or $\delta^{13}C_{org}$ value it is difficult to suggest why only they were affected by the treatment process. Moreover, all $\delta^{18}O$ values from LA show no correlation ($R^2 = 0.04$) between the treated and untreated sample suites. It may be that ostracods, which are present through most of the LA profile and not the other two lakes, have been dissolved by the H_2O_2 treatment resulting in different treated and untreated isotopic values. Most importantly, as the treatment process unequally affected the $\delta^{13}C$ and $\delta^{18}O$ results from across the three lakes, the treated samples are omitted from further discussion in favour of the untreated samples, which are plotted against the core stratigraphy in Figures 6.7 and 6.8.

In NSL, $\delta^{13}C_{carb}$ is close to zero in both the basal unit (-0.03‰) and Sapropel A (average: –0.04 ± 0.7‰). $\delta^{13}C_{carb}$ increases through Sapropel B (2.4‰) and into the laminated unit (mean $\delta^{13}C_{carb} = 4.4 \pm 0.4$‰). Thereafter, the massive unit exhibits a slightly negative trend (mean $\delta^{13}C_{carb} = 3.2 \pm 0.8$‰). A progressive ^{18}O-enrichment of the NSL carbonates is evident up-section from a $\delta^{18}O$ of 1.5‰ in the basal unit as follows: Sapropel A, 2.1 ± 0.7‰; Sapropel B, 3.7‰; laminated unit, 3.9 ± 0.5‰; massive unit 4.5 ± 0.4‰.

In OML there is a clear isotopic distinction between the lagoonal and lacustrine carbonate sediments. The lagoonal unit is remarkably uniform with average $\delta^{13}C_{carb}$ and $\delta^{18}O$ values of 1.5 ± 0.1 and 1.8 ± 0.2‰, respectively. In the lacustrine sediments, $\delta^{13}C_{carb}$ fluctuates within the range 0.7 to 7.5‰ with no discernible stratigraphic trend. $\delta^{18}O$ is much less variable, averaging 3.0 ± 0.4‰. Thus, OML lacustrine carbonates show broadly similar ^{18}O enrichment to that observed up section in NSL.

The $\delta^{18}O$ profile of LA is notably different. Over the lower half of the LA core $\delta^{18}O$ values are uniform and have an average of 3.6 ± 0.3‰. Approximately 15 cm below the transition into the upper sapropel there is a sharp ^{18}O-depletion to 1.0‰. Although this negative excursion is most evident in a single data point it is presumed to reflect an actual change to the lacustrine system, rather than a measurement error, because $\delta^{18}O$ values in the overlying upper sapropel interval (2.7 ± 0.1‰) are consistently lower than those in the underlying sediments. Up section ^{18}O enrichment, similar to that in NSL and OML, is evident in the surficial organically lean sediments (average = 4.6 ± 0.1‰). $\delta^{13}C$ values are 1.2 ± 0.1‰ within the lower sapropel unit, and increase in the overlying laminated unit (average = 4.1 ± 0.6‰) until a sharp depletion to 1.5‰ that occurs coincident with the aforementioned ^{18}O-depletion. Above this point, $\delta^{13}C$ values are relatively steady. However, sample A03, from a weakly cemented hardpan at the top of the upper sapropel (70cm depth), is isotopically distinct (2.8‰). On the grounds of its stratigraphic distinction from the remainder of the mudstone it has been omitted in calculation of the average $\delta^{13}C$ value for the upper half of the LA core (1.5 ± 0.3‰).

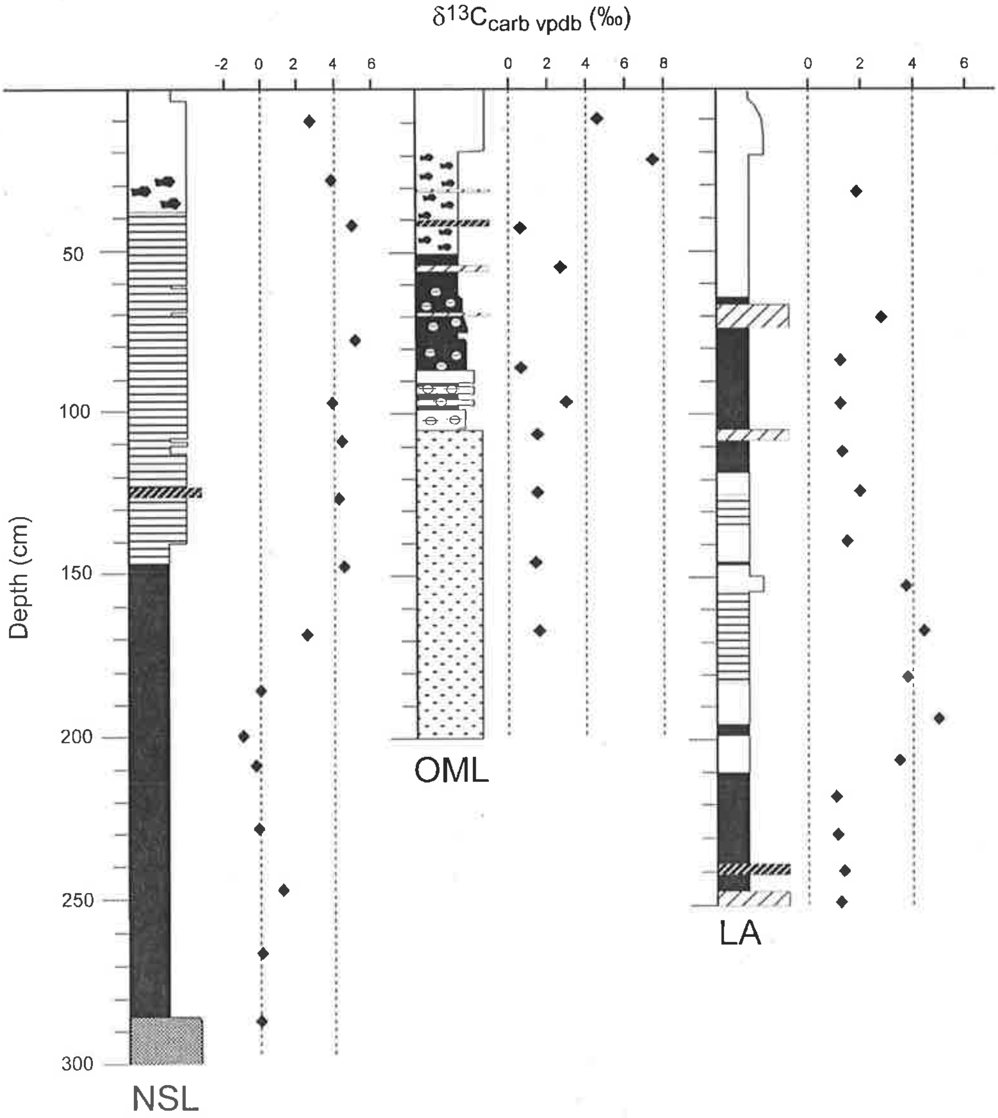

Figure 6.7: Depth profiles of carbonate carbon isotopes ($\delta^{13}C_{carb}$, ‰) in the untreated sediments from NSL, OML and LA.

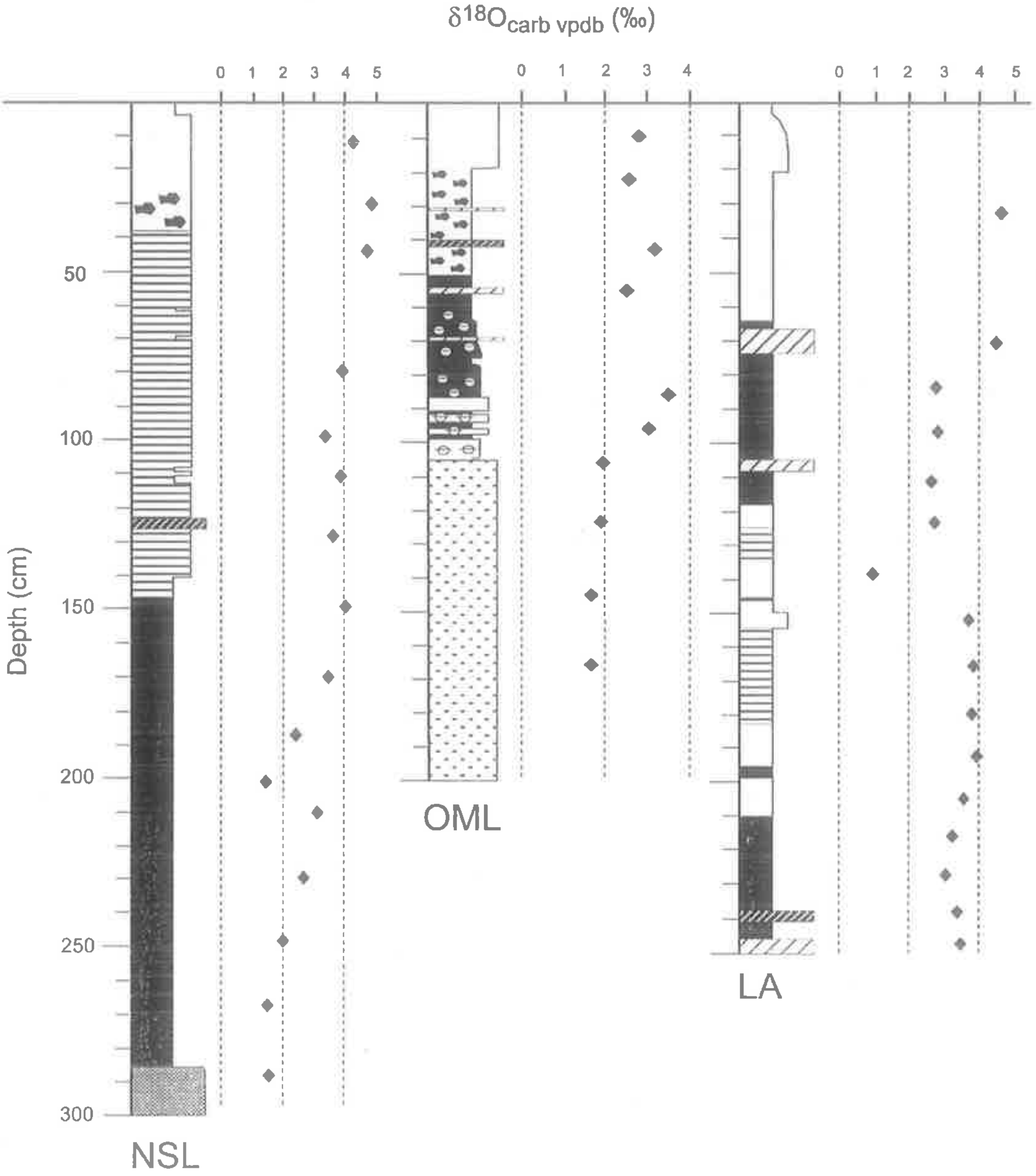

Figure 6.8: Depth profiles of carbonate oxygen isotopes ($\delta^{18}O$, ‰) in the untreated sediments from NSL, OML and LA.

6.5 ^{13}C-Nuclear Magnetic Resonance Spectroscopy

Major resonances of the ^{13}C-NMR spectra from all three lakes are centred around 31, 53, 72, 102, 130 and 173 ppm. All spectra are dominated by alkyl (0-45 ppm) and O-alkyl (45-110 ppm) carbon with only minor signals in the remaining chemical-shift ranges. The relative proportions of each carbon type were determined by integration of the signal intensity observed for each chemical-shift range in comparison with the total signal intensity (Appendix II). These proportions are listed in Table 6.3, displayed in Figure 6.9 and summarised below. Original ^{13}C-NMR spectra for each individual sample are located in Appendix IV.

Table 6.3: Carbon type percentages as determined from the relative proportion of total signal intensity represented within the six major chemical-shift ranges of their ^{13}C-NMR spectra. Geochemical data (C/N, $\delta^{13}C_{org}$) and the percent of total carbon observed using the CP/MAS technique (C_{obs}, see text) are also listed.

Sample	**Depth** cm		**aldeh/ket**	**carbonyl**	**o-aryl**	**aryl**	%C (aromatic)	**o-alkyl**	**alkyl**	(alkyl + unsat)	**C/N**	**Cobs** %	**$\delta C^{13}org$** ‰
		ppm	220-190	190-165	160-145	145-110	(160-110)	110-46	46-0	(46-0 + 160-110)			
NSL 1	65-72		1.1	9.2	2.0	8.1	10.1	30.7	48.9	58.9	14.3	68	-19.4
NSL 2	145-152		0.5	11.2	1.6	7.1	8.7	37.7	41.8	50.5	10.5	52	-19.2
NSL 3	178-181		0.8	8.1	1.7	7.3	8.9	38.8	43.3	52.2	13.7	77	-17.5
NSL 4	220-224		0.4	8.1	1.6	7.6	9.3	39.8	42.4	51.7	13.5	74	-18.6
NSL 5	233-237		0.5	7.3	2.2	8.4	10.6	39.8	41.7	52.3	13.4	81	-18.6
OML 1	15-19		1.1	9.7	1.9	8.3	10.2	40.1	39.0	49.2	11.6	70	-17.5
OML 2	35-39		0.8	9.0	3.0	8.7	11.7	36.6	41.8	53.6	11.3	79	-18.8
OML 3	60-63		0.3	8.1	2.8	8.1	10.9	35.8	45.0	55.9	11.7	71	-21.1
OML 4	80-83		1.1	8.2	2.5	8.0	10.4	38.5	41.8	52.2	13.8	75	-20.0
OML 5	98-101		0.5	8.7	3.3	10.9	14.2	35.8	40.7	54.9	11.8	79	-22.2
OML 6	133-139		7.3	4.8	4.2	13.7	17.9	32.5	37.5	55.5	11.0	60	-19.7
LA 1	20-24		0.5	9.8	1.9	4.6	6.6	33.9	49.2	55.7	12.8	73	-18.3
LA 2	60-64		0.6	10.3	1.7	8.6	10.3	36.5	42.3	52.6	9.8	70	-17.1
LA 3	86-90		0.6	9.0	1.7	7.6	9.3	31.7	49.4	58.7	10.7	60	-15.9
LA 4	121-125		0.8	8.7	2.8	8.4	11.2	32.9	46.3	57.6	10.4	77	-16.2
LA 5	174-178		0.3	9.4	1.6	9.4	11.1	35.6	43.7	54.7	11.0	71	-17.2
LA 6	211-214		1.1	8.8	1.9	9.9	11.9	34.8	43.4	55.2	10.6	76	-19.1

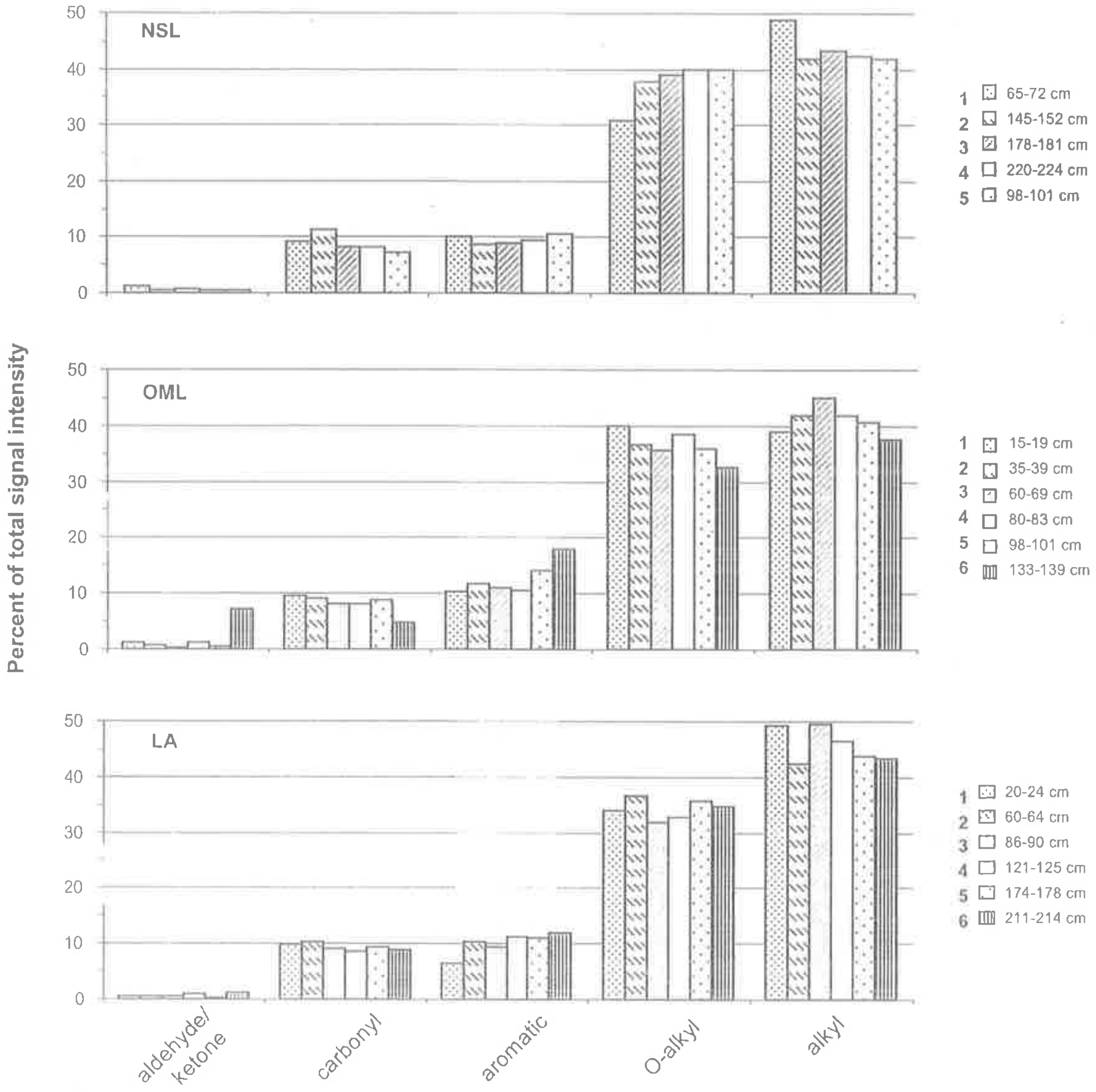

Figure 6.9: Percent of the total signal intensity represented by each carbon type, showing aromatic carbon, rather than the individual resonances of aryl and O-aryl carbon, for the chemical-shift range 160-110 ppm. Sample ID and depth are displayed for each lake.

In the laminated unit of NSL (represented by sample NSL1), the relative proportions of alkyl and O-alkyl C are 49 and 31%, respectively. Samples from the underlying sapropel units display a relative decrease in alkyl and increase in O-alkyl signal intensity to an average of 42 ± 0.7 and 39 ± 1.0% carbon, respectively. Resonance in the aromatic region (110-165 ppm) accounts for approximately 10% of the total signal intensity throughout the entire sedimentary succession.

The spectra from the laminated lacustrine mudstone of OML have 39-45% and 36-40% of their total signal intensity in the alkyl and O-alkyl regions, respectively. In comparison, the lagoonal unit (represented by sample OML6) displays slightly lower signal intensities in these regions (alkyl 38%, O-alkyl 33%) and a higher signal intensity in the aromatic region (lagoonal 18%, lacustrine 11%). Along with this change in aromatic resonance strength between the lagoonal and lacustrine units of OML there is a notable difference in the shape of the aromatic peak centred at 130ppm (Figure 6.10). Whilst sample OML6 displays a reasonably symmetrical aromatic peak, all the remaining samples from this core exhibit an asymmetrical peak with a 'shoulder' on the higher chemical shift side. Sample OML5 is from the base of the lacustrine mudstone and its intermediate aromatic resonance (14%) reflects the transition between the two units.

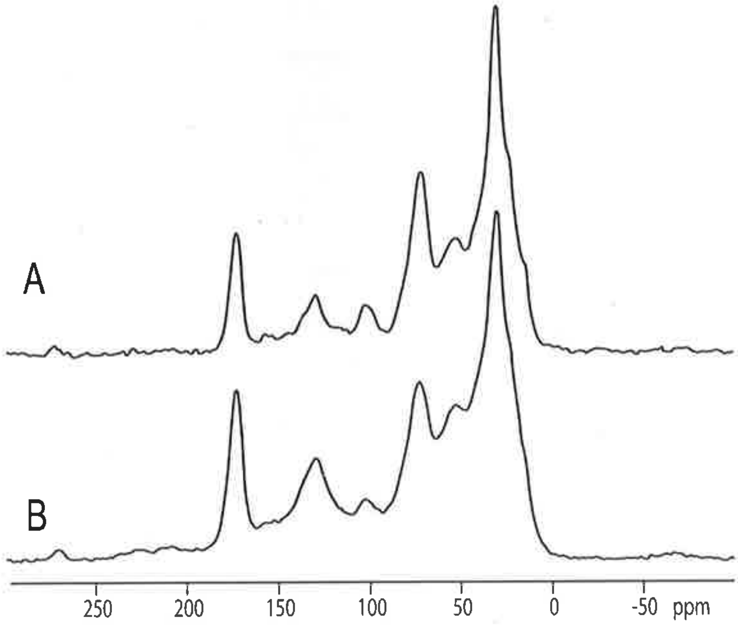

Figure 6.10: ^{13}C-NMR spectra of lacustrine organic matter of A) OML3, which is representative of the truly lacustrine samples and B) OML6, from the lagoonal unit of OML, which differs most particularly in the aromatic region (~130 ppm).

The sedimentary succession in LA displays the least variation in its ^{13}C-NMR spectra throughout the sedimentary succession. There is no significant shift in the position or the shape of any of the peaks. Alkyl and O-alkyl carbon account for 43-49% and 32-37% of the resonance signal, respectively. The massive unit (AMY1) has a lower proportion of aromatic carbon (6.6% of the total signal intensity) than the sediments of the laminated unit (mean 10.7%).

CHAPTER 7: DEPOSITIONAL CHRONOLOGY

A thorough understanding of lacustrine stratigraphy (preferentially both litho- and biostratigraphy), and the application of a detailed chronological framework to it, are essential requirements in establishing the depositional history of any lake. Detailed stratigraphic descriptions of the three lakes investigated in this study have been given in Chapter 5. The present chapter reports the results of radiocarbon dating of their sedimentary organic matter with the intention of addressing the following questions:

- When did sapropel deposition begin and cease in the three lakes?
- Was sapropel deposition continuous or punctuated (variable) in each lake?

Some of the information contained in this chapter has been reported elsewhere (Mee et al., 2004; 2007). However, the discussion presented herein is more detailed and therefore the final interpretation slightly different.

7.1 Radiocarbon Chronology

Conventional radiocarbon ages for 25 samples taken from the D-section cores are shown in Table 7.1. The oldest ages (yr BP) on bulk organic matter are 6210 ± 60 for NSL, 4550 ± 150 for OML and 4140 ± 50 for LA. The age for a single charcoal sample from the lagoonal unit of OML (OZH208) is 6890 ± 50 yr BP. Two further samples from OML plus a sample from the basal unit of NSL were submitted for radiocarbon analysis of their charcoal fraction for comparison with bulk organic matter from the same depth. Unfortunately, there was insufficient charcoal in the sedimentary samples so the three paired dates are all from bulk organic matter only. Whilst the absence of more charcoal or macrofossil dates is regrettable, it is encouraging to see that all paired samples returned comparable radiocarbon dates.

The three lakes of the present study are fed by groundwater that flows through the unconfined Gambier Limestone aquifer and the permeable and calcareous Pleistocene beach ridge arenites (Bridgewater Formation) that dominate the surficial geology of the Coorong and Robe-Naracoorte coastal plains (Schwebel 1983; Cann et al. 1999). Therefore, it is likely that some portion of the DIC in the continental groundwaters that charge these lakes will be inert carbon entrained from the host limestone aquifers. Photosynthetic incorporation of this inert carbon by aquatic biomass causes the apparent radiocarbon ages of lacustrine organic matter to be somewhat older than the actual time of deposition. Thus, the radiocarbon ages from their sedimentary organic matter are likely to have been influenced to some extent by the hard-water reservoir effect. This effect is always difficult to quantify. Although parallel dating of bulk sediment and terrestrial macrofossils can be used to ascertain the magnitude of any hard-water reservoir effect (Törnqvist et al., 1992; Geyh et al., 1998), such fossils are absent from the present lacustrine sedimentary sequences and this comparative dating technique cannot be used.

In the following discussion, two approaches are taken. The first approach (calibration) presumes that, as all lakes in the present study have been shallow (<4 m) from their inception, rapid equilibration of their dissolved inorganic carbon with atmospheric radiocarbon has minimised the reservoir effect (to 100s not 1000s of years). Using the assumption that the lacustrine organic matter was produced via photosynthesis of DIC that was in radioactive equilibrium with atmospheric CO_2, the radiocarbon ages of the bulk organic matter are calibrated against the atmospheric radiocarbon curve. However, in the present lacustrine settings, radioactive disequilibrium is more probable than not, and the radiocarbon ages of the bulk organic matter are no doubt influenced to some extent by the hard-water reservoir effect. Therefore, the calibrated radiocarbon ages discussed below should be considered as maximum ages.

Indeed, modern water samples from OML and LA confirm radioactive disequilibrium and the existence of a reservoir effect in these lakes. Carbonate dissolved in the lake waters comprises less than 100 percent modern carbon (90.35 and 94.26 pmC, respectively), giving rise to radiocarbon ages of 815 and 475 yr BP (Table 7.1). The older of these two ages reflects the larger catchment area for the groundwater entering OML and NSL from the coastal hinterland and hence its longer interaction with the Bridgewater Formation. The much smaller local catchment of the perched water table at LA means that its water has had less contact with the calcarenite of the surrounding Robe Range. Accordingly, a higher proportion of its DIC is modern carbon.

In the absence of macroscopic terrestrial plant remains or the availability of palynological analyses from the lacustrine sediment cores, the apparent ages of contemporary water in OML and LA provide the best available constraints on the magnitude of the hard-water effect on the radiocarbon dates obtained in this study. Thus, in the second approach (reservoir correction), the activity of these water samples (A_{lake}, pmC) have been used to recalculate the radiocarbon age (t, yr BP) of each bulk organic matter sample, using the equation:

$$t = -8033 \ln\left({A_{measured}}/{A_{lake}} \right)$$

where $A_{measured}$ is the activity each radiocarbon sample has (pmC) as per method 1 described by Leaney et al. (1995, p.128).

As this approach acts to remove the influence of radiocarbon input via groundwater, it can be assumed that the reservoir corrected radiocarbon ages reflect equilibrium with atmospheric radiocarbon (R. Gillespie, pers. comm.). Subsequently, calibration of these corrected ages against the atmospheric radiocarbon curve can be used to convert the radiocarbon years into calendar years for comparison with other reported data sets.

7.1.1 Calibration

Conventional radiocarbon dates were calibrated against the Southern Hemisphere atmospheric ^{14}C curve (McCormac et al., 2004) using the internationally ratified online calibration program OxCal v3.10 (Bronk Ramsey, 1995, 2001). The raw output from calibration of a single radiocarbon date using OxCal is regularly in the form of multiple age ranges, each with an associated statistical probability (Appendix V). The calibration program rounds dates for the upper and lower limits of each age range to the nearest decade. For the radiocarbon samples that yield multiple age ranges, when the lower limit of the older age range and the upper limit of the younger age range differed by only 10 years, the two age ranges were combined. For example, calibration of sample OZH207 from OML produced two raw age ranges, 5320-4950 cal yr BP (relative probability 0.88) and 4940-4870 cal yr BP (relative probability 0.12), which are combined into the one age range, 5320-4870 cal yr BP for the purpose of discussion. Where multiple age ranges remain, discussion refers to the age range with the highest statistical probability. For example, where radiocarbon sample OZH370 from NSL yields two age ranges, 7160-6850 cal yr BP (relative probability 0.98) and 6820-6800 cal yr BP (relative probability 0.02), discussion in the text will refer to the former age (7000 ± 150 cal yr BP). For the (few) input dates that give a single calibrated age range, no additional data processing was required and discussion is straightforward. Calibrated ages are shown in Table 7.1. Sedimentation rates calculated using these (maximum) ages must be considered as minimum (Table 7.2).

Table 7.1: Conventional and calibrated radiocarbon ages for the two depositional scenarios described in the text: no lacustrine reservoir effect (maximum ages), and a reservoir effect calculated using modern lake water samples (reservoir corrected ages). * denotes modern lake water samples, ** denotes charcoal sample.

Lake	ANSTO code	Depth	$\delta^{13}C$	Conventional ^{14}C Age			Calibrated ^{14}C Age (Maximum)			Reservoir Corrected Age			Calibrated ^{14}C Age (Reservoir Corrected)		
		cm	‰	yr BP		1σ error	cal yr BP		1σ error	yr BP		1σ error	cal yrs BP		1σ error
NSL	OZH369	118	-19.0	5470	+/-	180	6200	+/-	200	4650	+/-	220	5280	+/-	330
	OZH213	152	-17.1	5120	+/-	50	5820	+/-	80	4300	+/-	90	4730	+/-	150
	OZH214	183	-18.6	4980	+/-	50	5650	+/-	60	4160	+/-	90	4620	+/-	110
	OZH215	237	-18.6	5980	+/-	50	6740	+/-	65	5170	+/-	80	5840	+/-	100
	OZH216	282	-21.1	6310	+/-	50	7210	+/-	60	5500	+/-	80	6250	+/-	75
	OZH370	297	-19.5	6150	+/-	90	7000	+/-	150	5340	+/-	130	6070	+/-	150
	OZH371	297	-17.6	6210	+/-	60	7070	+/-	95	5400	+/-	100	6110	+/-	110
OML	OZI264*	-	0.1	815	+/-	40									
	OZH204	52	-20.8	3120	+/-	50	3290	+/-	70	2310	+/-	90	2250	+/-	110
	OZH365	69	-21.9	3830	+/-	50	4160	+/-	80	3020	+/-	90	3130	+/-	140
	OZH205	85	-19.6	4420	+/-	50	5030	+/-	20	3610	+/-	90	3840	+/-	140
	OZH366	104	-22.2	4330	+/-	50	4850	+/-	40	3520	+/-	90	3730	+/-	120
	OZH206	105	-22.7	4170	+/-	50	4620	+/-	100	3360	+/-	90	3530	+/-	115
	OZH367	131	-19.2	4250	+/-	80	4730	+/-	120	3440	+/-	120	3620	+/-	150
	OZH368	131	-17.7	4290	+/-	55	4700	+/-	65	3480	+/-	100	3700	+/-	140
	OZH207	182	-25.0	4550	+/-	160	5100	+/-	225	3730	+/-	200	4000	+/-	300
	OZH208**	182	-24.0	6900	+/-	50	7670	+/-	60	-			-		
LA	OZI263*	-	1.1	475		30									
	OZH360	66	-17.7	2430	+/-	40	2400	+/-	65	1950	+/-	70	1830	+/-	100
	OZH361	76	-16.9	2640	+/-	40	2730	+/-	35	2160	+/-	70	2290	+/-	20
	OZH362	101	-18.5	3060	+/-	50	3200	+/-	65	2580	+/-	80	2620	+/-	130
	OZH209	109	-18.0	3120	+/-	50	3290	+/-	75	2640	+/-	80	2640	+/-	140
	OZH363	146	-19.3	3340	+/-	50	3510	+/-	70	2860	+/-	80	2900	+/-	110
	OZH364	197	-17.6	3620	+/-	40	3890	+/-	70	3150	+/-	70	3300	+/-	90
	OZH210	211	-19.2	4070	+/-	50	4490	+/-	80	3590	+/-	80	3800	+/-	120
	OZH211	223	-20.9	4170	+/-	50	4620	+/-	95	3700	+/-	80	3980	+/-	120
	OZH212	245	-23.0	4160	+/-	40	4590	+/-	65	3680	+/-	70	3920	+/-	90

Table 7.2: Sedimentation rates calculated from calibrated radiocarbon dates. The given ranges result from omitting and including a reservoir correction, with the maximum rates being given by the reservoir corrected dates. No sedimentation rate can be calculated for the NSL basal unit as there is no data available from deeper within the sedimentary succession.

Lake	Depositional Unit	Thickness cm	Sedimentation Rate cm/100 yrs
NSL	Massive	38	2.5 - 3.2
	Pelletal Laminated	112	
	Sapropel B	34	~ 10 - 11
	Sapropel A	102	
	Basal	14	-
OML	Massive	19	1.5 - 2.2
	Laminated Lacustrine		
	* Mottled	32	
	* Sapropel	35	~ 4
	* Sapropelic	20	
	Lagoonal	94	~ 12 - 17
LA	Massive	42	2.8 - 3.6
	Laminated Lacustrine		
	* Mottled	22	
	* Upper Sapropel	53	5.8 - 6.7
	* Finely Laminated	77	11.2 - 11.6
	* Lower Sapropel	56	8.1 - 9.0

North Stromatolite Lake

There is an inversion in the radiocarbon ages (both conventional and calibrated) with depth in the NSL core (Figure 7.1). Organic matter from the pelletal laminated unit (sample OZH369)[6] appears to be appreciably older than that within the underlying sapropel unit, Sapropel B (OZH213 and OZH214). Either the two radiocarbon ages from the sapropel are somewhat too young, or the single radiocarbon age from the laminated unit is too old for chronostratigraphic consistency. This is likely to be a result of a secular change in the magnitude of the hard-water reservoir effect. However, as calibration assumes the absence of any such reservoir effect, discussion of this possibility is reserved for the following section.

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[6] The relatively large error (± 200 yr) in the age of this sample may be attributed to the low TOC content of the laminated unit (<1%) and the small sample size (U. Zoppi, pers. comm.).

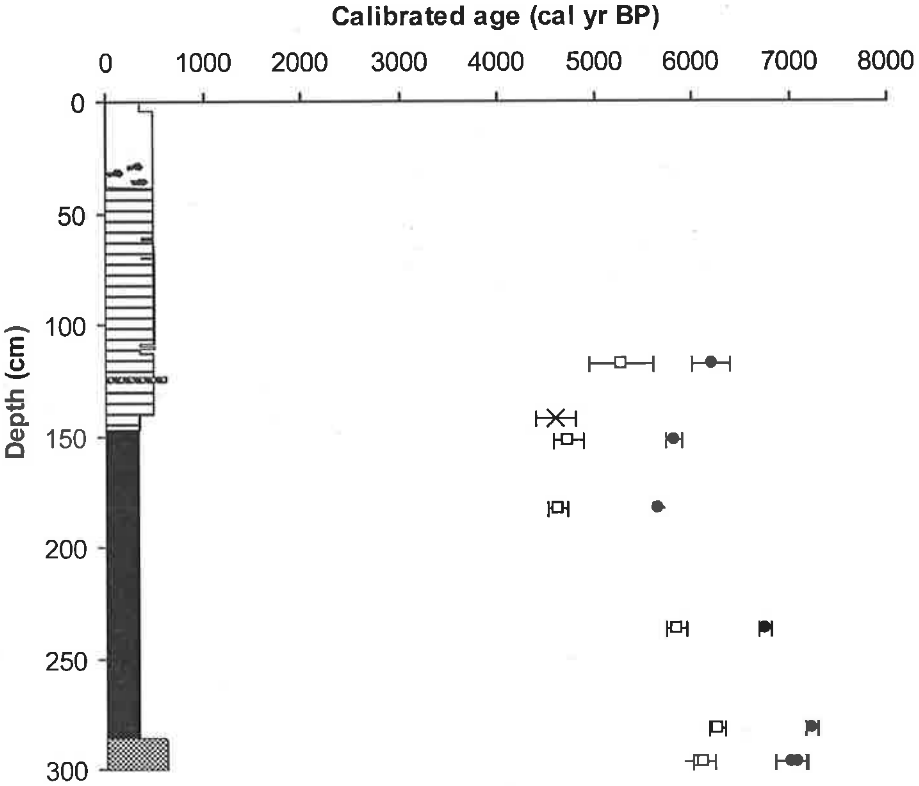

Figure 7.1: Calibrated radiocarbon ages of NSL sediments. In-filled circles (●) indicate maximum possible ages and open squares (□) show the ages after reservoir correction (see text). A cross (×) indicates the single OSL sample age. For all samples error bars represent one standard deviation.

Both the basal unit and the sapropel immediately overlying it are dated at c. 7100 cal yr BP. This similarity in ages could be attributed to the downward infiltration of organic matter from the sapropel into the basal unit. However, the age similarity could equally exemplify the recognised uncertainty associated with radiocarbon dating, while also reflecting a rapid onset of sapropel deposition at this time.

For the purpose of discussing NSL sedimentation rates sample OZH216 (sapropel), rather than OZH370 or OZH371 (basal), is chosen as the true onset of sapropel deposition (c. 7070 cal yr BP). Its cessation is marked by sample OZH213 at c. 5800 cal yr BP where the base of the laminated unit indicates a transition to shallower and less productive lacustrine conditions. The two contiguous organic-rich sapropel units (total thickness 140 cm) were deposited in ~1300 years at approximately four times the rate (~11 cm/100 years) of the organic-poor laminated and massive units (150 cm in ~5800 years; ~2.5 cm/100 years). This decrease in sedimentation rate may in part reflect a reduced contribution of autochthonous organic matter to these organically lean sediments but is also a result of the 'fill and spill' sedimentation process operating in the lake (Warren, 1990). This may be summarised as follows. Once the surface connection with the Coorong lagoon was severed, vertical accretion of lacustrine sediments gradually filled deeper parts of the interdunal depression. At this stage, the lake was perennial and carbonate mud was precipitated in response to summer evaporation. As the lake basin filled with sediment the same volume of annual inflow was forced to spill out over the original lake margins so that the same amount of precipitated carbonate was spread over a wider area, thereby decreasing the vertical sedimentation rate. The transition from perennial to ephemeral conditions in NSL is not yet accurately dated.

Old Man Lake

The OML core in this study did not reach the basal Pleistocene aeolianite nor intersect the transgressive humic unit that in places overlies it. Radiocarbon dates from the lagoonal unit indicate its rapid deposition around 4700 - 5100 cal yr BP (Figure 7.2). However, the relatively large error (± 225 yr) associated with the lower sample (OZH207) means that the sedimentation rate is difficult to calculate accurately (Table 7.2). The charcoal sample (OZH208) from this unit has a radiocarbon age ~1500 years older than the bulk sedimentary organic matter from the same depth. This indicates that the charcoal ($\leq$1 cm^3) was burnt earlier and later carried into the lagoonal system of the Robe-Woakwine corridor by runoff, high onshore coastal winds or, possibly, by human activity (Cann et al., 1991) and deposited at c. 5100 cal yr BP.

A minor radiocarbon age inversion is apparent in the transition from the lagoonal unit to the overlying lacustrine unit and, as for NSL, is discussed in the following section with regard to a possible change in the magnitude of the reservoir effect at this time. On the assumption of there being no reservoir effect in OML, the transition from lagoonal to lacustrine conditions in OML, marked by samples OZH366 and OZH206, occurred at c. 4700 cal yr BP. Thereafter, the sapropel and sapropelic intervals of the laminated lacustrine mudstone record 55 cm of sediment accumulation in ~1400 years (Table 7.2). The uppermost 51 cm of the core (mottle interval plus massive unit) was deposited in ~3300 years, which is approximately half the rate of sapropel accumulation. Thus, the rate of sapropel deposition here is one third of that in NSL. The halt in deposition of these organic-rich sediments in OML occurs some 2500 years later than the equivalent palaeolimnological event in NSL.

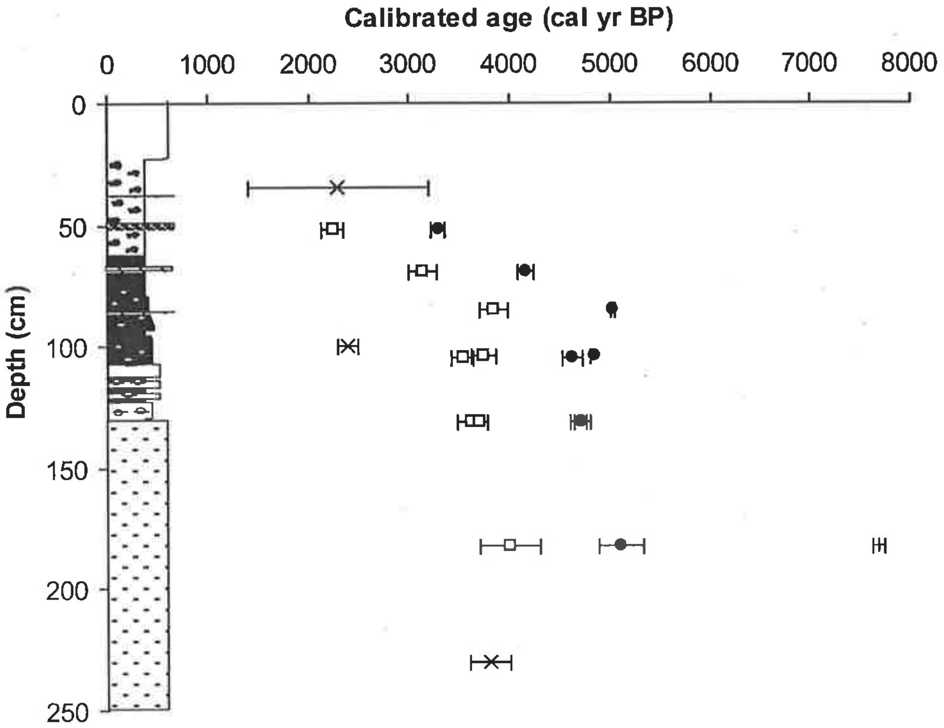

Figure 7.2: Calibrated radiocarbon ages of OML sediments. In-filled circles (●) indicate maximum possible ages, open squares (□) show the ages after reservoir correction (see text), and crosses (×) indicate OSL ages. No reservoir correction is required for the single charcoal sample (+). All error bars represent one standard deviation.

Lake Amy

This core represents ~4600 years of lacustrine sedimentation (Figure 7.3). The nine radiocarbon dates over the lower 185 cm of the core indicate a variable rate of accumulation of organic-rich mudstone for some 2200 years (Table 7.2). Within this succession two sapropel intervals (14-22% TOC: dated at c. 4600-3900 and 3300-2400 cal yr BP) are separated by an interval of more rapidly accumulating, variably laminated and pelletal mudstone (119-196 cm depth in core) that is also relatively organic-rich (10-12% TOC) but lacks the characteristic gelatinous texture of a typical Coorong lacustrine sapropel.

The transition into the organically leaner (2.5%<TOC<6.9%) massive unit at 66 cm marks a two-thirds reduction in sedimentation rate (Table 7.2) and is dated at c. 2400 cal yr BP (sample OZH360). This is some 800 years later than a similar reduction in sedimentary OM content in nearby OML.

The two lowermost samples (OZH211 and OZH212) yield similar ages of c. 4600 cal yr BP despite being separated by a 2 cm-thick massive hardpan. This implies that the formation of hardpan intervals, either massive or fragmented, within this lacustrine setting can be a rapid process.

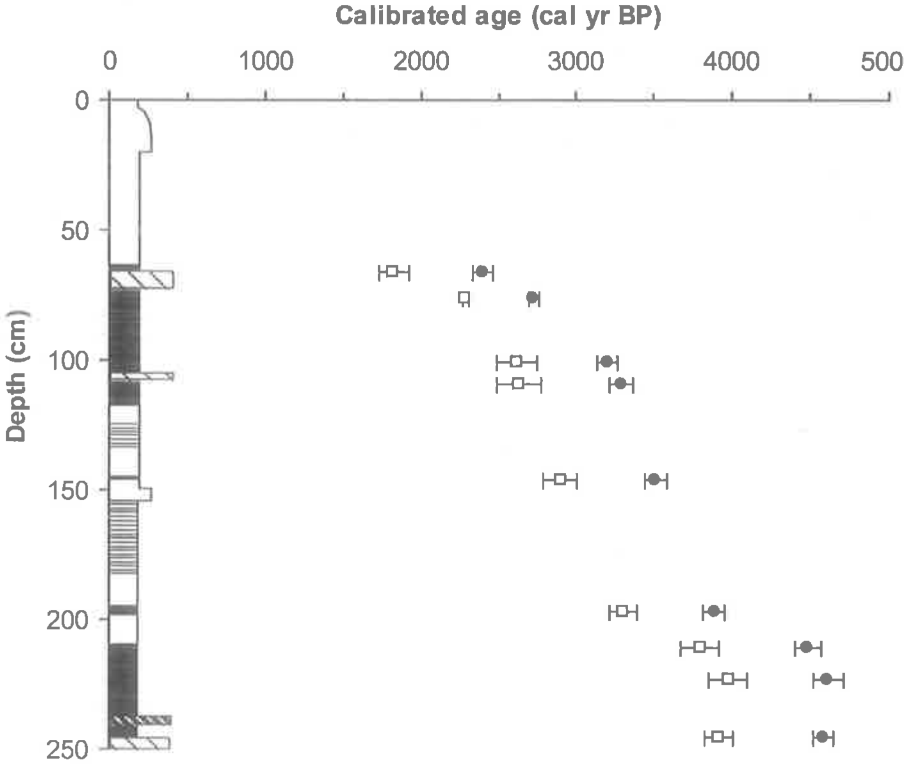

Figure 7.3: Calibrated radiocarbon ages of LA sediments. In-filled circles (●) indicate maximum possible ages and open squares (□) indicate reservoir corrected ages (see text). Error bars represent one standard deviation.

7.1.2 Reservoir Correction

In applying the reservoir correction, the following assumptions were made:

1) There has been no significant secular change in the volume/surface ratio of each lake, and hence in the relative proportion of the two principal sources of ^{14}C entering its water column (viz. atmospheric CO_2 and DIC in groundwater and runoff) during growth of the aquatic biomass that was eventually preserved in the sediments; and

2) That as NSL and OML are charged by the same westward-flowing saline continental groundwater, the activity of the modern OML water sample can be used for NSL.

It is unlikely that the reservoir effect in each of the three lakes has been constant over the entire period of deposition represented by these sedimentary sequences. This is particularly true for NSL and OML, which have each evolved from an estuarine setting into isolated lacustrine systems. As the initial estuarine waters are likely to have had a different radiocarbon activity than the groundwater that subsequently fed the lakes, the first assumption (above) is less likely to be accurate in NSL and OML than in LA, which has been charged primarily from a local perched water table over the entire course of its sedimentary deposition. However, the assumption of a constant reservoir effect based on the activity of the present-day water samples is the best available approach to quantifying the possible magnitude of the reservoir effect in all three of these shallow hard-water lakes.

Reservoir-corrected radiocarbon ages are shown in Table 7.1 and plotted in Figures 7.1-7.3 for each of the three lakes. The range of ages has been determined through the combined use of upper and lower (1σ error) activities of the modern water samples and sedimentary organic matter. The oldest reservoir corrected radiocarbon ages result from the combination of the 'oldest' organic matter (lowest activity) in combination with the lowest reservoir effect (highest water sample activity). Conversely, the youngest reservoir-corrected radiocarbon ages result from the combination of the 'youngest' organic matter (highest activity) in combination with the highest reservoir effect (lowest water sample activity).

North Stromatolite Lake

Applying a constant reservoir correction does not remove the radiocarbon age inversion that was noted in section 7.1.1. The organic matter of the pelletal laminated unit (OZH369) has a reservoir corrected radiocarbon age of 5280 ± 330 cal yr BP, whilst that of two samples from the underlying sapropel unit (OZH213 and OZH214) has ages of 4730 ± 150 and 4620 ± 110 cal yr BP, respectively. This radiocarbon age inversion must be due to a change in the reservoir correction with depth, as radiocarbon cannot be lost from organic matter other than by radioactive decay (Geyh et al., 1998). Either the reservoir-corrected ages from the sapropel are somewhat too young, or from the laminated unit too old, to be chronologically consistent. This suggests that the magnitude of the reservoir effect may have been either lesser during deposition of the sapropel B unit and/or greater during deposition of the laminated unit than the value implied through using a present-day water sample to approximate the past activity of the lake.

Generally, in a lacustrine setting subject to some reservoir effect, the activity of the lake water will approach 100 pmC as either the lake shallows or the mean water residence time increases (Leaney et al., 1995). In these situations, as the relative fraction of atmospheric CO_2 exchange to groundwater derived carbon increases, the $\delta^{13}C_{carb}$ becomes more positive and the reservoir effect decreases (Leaney et al., 1995; Geyh et al., 1998). Moving up section, $\delta^{13}C_{carb}$ values increase from ~0 in Sapropel A to ~4‰ in Sapropel B and the laminated unit (Table 6.2). This indicates that a higher proportion of lacustrine radiocarbon was indeed in equilibrium with atmospheric CO_2 during the deposition of Sapropel B and the laminated unit than during deposition of Sapropel A, which suggests that there should be a reduction in the magnitude of the reservoir effect associated with the latter sediments. However, this does not aid in evaluating the difference in reservoir correction that must apply across the Sapropel B - laminated unit boundary.

Further interpretation of the radiocarbon age inversion across this boundary is made possible through comparison of the reservoir-corrected ages with the results from OSL dating of sedimentary quartz grains. Only a single sample from NSL contained sufficient quartz for OSL measurement. Stratigraphic correlation between the D-section core and the sliphammer core from NSL (incorporating the calculated extent of sliphammer core compaction) shows that this OSL sample would approximate a depth of ~142 cm in the D-section core, nearing the base of the pelletal laminated unit. With only one exception the repeated quartz aliquots produced consistent deposition dates that averaged at 4.6 ± 0.2 ka, which renders this sample more closely associated with the reservoir-corrected radiocarbon age of Sapropel B than of the laminated unit (Figure 7.1). This suggests that the radiocarbon age inversion is more likely a reflection of an enhanced reservoir effect during deposition of the laminated unit than a temporarily reduced reservoir effect during deposition of Sapropel B.

The apparent increase in the reservoir effect during deposition of the laminated unit in NSL is somewhat contrary to expectation, as the effect generally tends to decrease, through increased exchange with atmospheric CO_2, as a lake shallows. This exemplifies the complexities associated with the application of reservoir corrections to radiocarbon ages on lacustrine sediments. One explanation may be that during deposition of the laminated unit under ephemeral water conditions, periodic evaporation of the water body acted to concentrate the reservoir of relatively old carbon in the lacustrine basin. This effect is seen in the sediments of brackish Laguna Lejía, Chile, where the radiocarbon dates on lacustrine organic matter required an increased reservoir correction with decreasing water depth (Geyh et al., 1998).

Alternatively, it may be that the over the entire course of deposition of the upward-shoaling sedimentary sequence in NSL the reservoir effect was generally decreasing, as is typically expected in a shallowing water body, but showed a brief and much more marked reduction during deposition of the Sapropel B unit. Indeed, it may have been that this particular reduction was not due so much to an increase in exchange of atmospheric CO_2 across the lake surface, but rather to a higher input from rainfall and/or surface runoff in radioactive equilibrium with the atmosphere than during any time either before or after this time period. While it seems that the reservoir correction was diminished during deposition of the Sapropel B unit, it nonetheless existed to some extent at all other times of lacustrine deposition, probably requiring a correction of <1000 years.

Old Man Lake

Although of a much smaller scale than that seen in NSL, it appears that there is also an inversion in the reservoir-corrected radiocarbon ages between the lagoonal unit of OML and the overlying lacustrine unit (Figure 7.2). The organic matter of the sapropel interval within the laminated lacustrine mudstone (OZH205) has a reservoir-corrected radiocarbon age of 3840 ± 140 cal yr BP, whilst that of two samples at the transition between the lacustrine and the lagoonal units (OZH366 and OZH206) has ages of 3730 ± 120 and 3530 ± 115 cal yr BP. Another two samples from ~25 cm beneath this transition (OZH367 and OZH368) have ages of 3620 ± 150 and 3700 ± 140 cal yr BP, respectively. These ages may indicate that a smaller reservoir effect was associated with the estuarine waters that initially flooded this basin than with the groundwater that subsequently charged the lacustrine system. The radiocarbon age of the modern OML water sample is 815 yr BP, whereas seawater along the coast of southeastern South Australia currently has a reservoir effect of only ~250 years (Figure 7.4). The application of this lesser reservoir correction to the lagoonal unit of OML would effectively remove the slight radiocarbon age inversion that is otherwise evident across the stratigraphic transition from lagoonal to lacustrine settings by shifting the radiocarbon ages toward those indicated as the maximum ages in Figure 7.2.

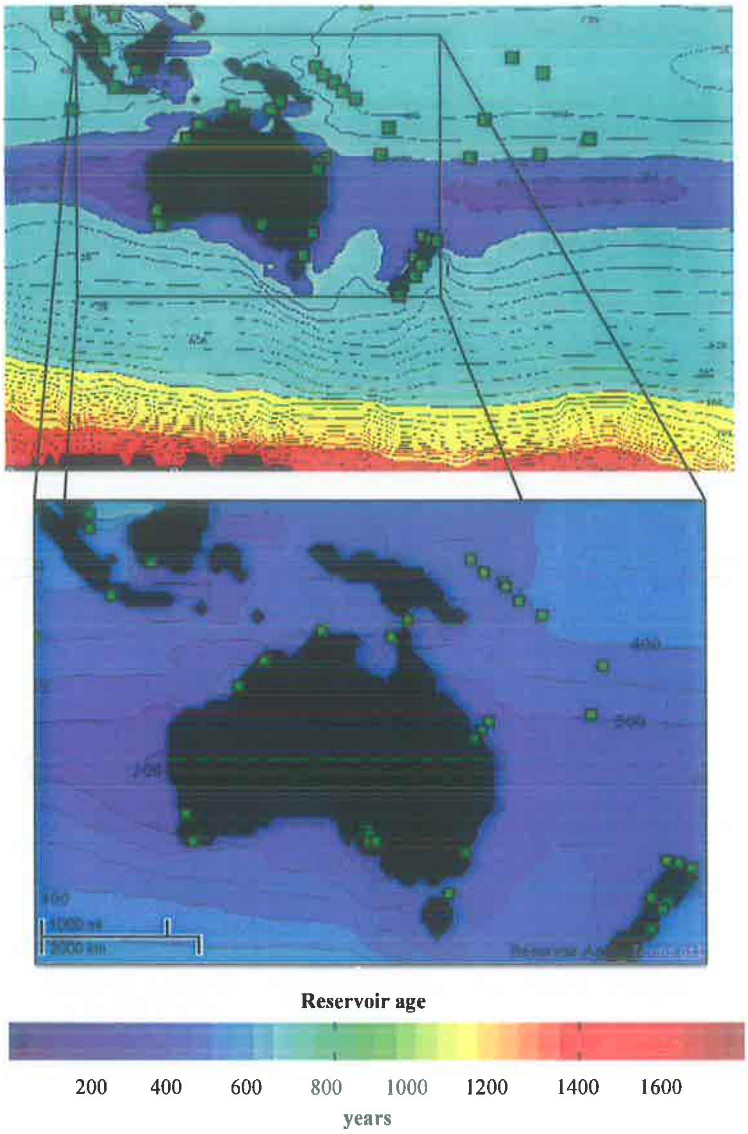

Figure 7.4: Model estimates of radiocarbon reservoir ages for the marine waters surrounding Australia (Butzin et al., 2005). Green squares indicate locations where these reservoir ages have actually been measured.

Although this consideration amends a somewhat minor inconsistency in the radiocarbon ages, it should by no means suggest that the remainder of the reservoir-corrected radiocarbon ages are entirely accurate. Indeed, a sample taken for OSL measurement near the transition from lagoonal to lacustrine conditions returned ages of 2.7 ± 0.4 and 2.4 ± 0.1 ka for the quartz and fine grained fractions, respectively. These OSL ages are some 1000 years younger than the reservoir-corrected radiocarbon ages from approximately the same depth, thus suggesting that the contribution of old radiocarbon from groundwater may have been much more significant at this time than it is at present. Sediment infilling and shallowing of the lake could have gradually reduced the reservoir correction from ~1800 years at the initiation of lacustrine deposition (as implied by the OSL dating) to ~800 years (as implied by the radiocarbon activity of the present-day water samples). An OSL sample from within the mottled interval of the laminated lacustrine mudstone returned a broad range of ages (Figure 7.2) and therefore does not help constrain the magnitude of the secular change to the reservoir effect in OML.

Lake Amy

No OSL dating has been completed on the LA core at this stage, and thus the present-day water sample provides the only available means of estimating reservoir-corrected radiocarbon ages for these lacustrine sediments. Any variation in the magnitude of the reservoir effect would typically have been a gradual decrease as the lake filled and shallowed. If this is the case, the reservoir-corrected radiocarbon ages shown in Figure 7.3 would in actual fact be even younger toward the base of the LA core than the present estimate. Therefore, the sedimentary sequences may have accumulated at an even more rapid rate than that implied herein. This cannot be quantified from the presently available data. However, LA is charged by a perched water table with only a small local catchment. Thus, its water has had only minimal contact with the surrounding Robe Range and is unlikely to have entrained considerable quantities of old radiocarbon from the Pleistocene calcarenite. Therefore, the reservoir-corrected radiocarbon ages calculated using the activity of the modern lake water are considered the best estimate of LA's depositional chronology and indicate ~3900 years of lacustrine sedimentation. The application of a constant reservoir correction to the LA core brings the ages of its two sapropelic intervals to c. 3900-3300 and 2600-1800 cal yr BP and places the transition into the organically leaner massive unit at c. 1800 cal yr BP.

7.2 Synthesis

Small shallow lakes could be presumed to equilibrate rapidly with the atmosphere, particularly where located in the windy coastal zone. However, modern water samples from OML and LA show that these two lakes are not at radioactive equilibrium with the atmosphere and that they are therefore subject to a reservoir effect resulting from the inflow of old radiocarbon in the groundwater of this limestone-dominated landscape. Calibrated radiocarbon dates based on the assumption of an absence of this reservoir effect provide maximum age estimates for samples from throughout their sedimentary sequences. Taking into account the modern water activities and assuming that the reservoir effect within these lakes has remained constant over time provides a younger and relatively more realistic estimate of their radiocarbon ages. As radiocarbon cannot be lost from organic matter other than through radioactive decay, the presence of age inversions with depth in the sedimentary sequences of NSL, and to a lesser extent OML, indicates that there have been secular changes in the magnitude of the reservoir effect in these lakes. While acknowledging this, the radiocarbon chronologies outlined below (Figure 7.5) are considered to provide the best possible estimates for the timing and duration of sapropel deposition within the three lakes of the present investigation.

North Stromatolite Lake

Isolation of NSL from the Coorong Lagoon and the onset of sapropel deposition in NSL is dated at a maximum of c. 7000 cal yr BP (Figure 7.5). Correcting for the reservoir effect reveals that this event more likely occurred at c. 6000 cal yr BP. According to the radiocarbon dating, and ignoring any reservoir effect, this period of sapropel deposition ceased at c. 5700 cal yr BP. However, the OSL age at the base of the pelletal laminated unit suggests that sapropel deposition halted at c. 4.6 ka. A similar timing for this event is given by two radiocarbon samples in Sapropel B after applying a constant reservoir correction to the entire organic-rich mudstone in NSL. The radiocarbon sample from the overlying organic-poor laminated unit is spuriously old, and requires a larger reservoir correction than that which has currently been applied to make it chronostratigraphically consistent. This anomaly is interpreted as resulting from periodic evaporation of ephemeral NSL, thereby concentrating the reservoir of old carbon in the lacustrine basin. As such, the ages of the Sapropel B radiocarbon samples are taken as a more accurate reflection of the timing of the transition from organic-rich to organic-poor sediments in NSL. Therefore, sapropel deposition in NSL lasted for ~1300 years and ceased at c. 4700 cal yr BP (c.f. c. 4.6 ka as per OSL dating).

Old Man Lake

A single radiocarbon date on a piece of charcoal from the lagoonal unit of OML provides a maximum age for this (c. 7700 cal yr BP). However, charcoal is known to be easily transported by water movement, high coastal winds and even human activity. This makes it likely that the charcoal in question was burnt and later carried into the lagoonal system of the Robe-Woakwine corridor. Thus, the other sedimentary organic matter in the lagoonal unit of OML is interpreted to give a more realistic maximum age of c. 5100 cal yr BP.

Deposition of the lagoonal unit occurred rapidly between ~4700 and 5100 cal yr BP. Use of the lacustrine reservoir effect suggested by present-day water sample activity reduces this age span to ~3500-4000 cal yr BP. However, the existence of a slight age inversion at the transition into the overlying lacustrine unit suggests that it is possible that this reservoir correction is too large and the resulting age range too young. Application of a local marine reservoir correction to the radiocarbon ages from these lagoonal sediments would provide slightly older dates (tentatively suggested as ~4500-4000 cal yr BP), which would be somewhat more chronostratigraphically consistent. An OSL sample from near the base of the lagoonal unit has an age that is somewhat younger (3.8 ± 0.2 ka) than the radiocarbon age estimated through the use of a marine reservoir correction. However, OSL can define ages as arbitrarily young if quartz grains from higher in the sedimentary sequence are translocated down section. Such movement could have easily occurred in a high-energy lagoonal environment. Therefore, the application of a marine reservoir correction is suggested as the most accurate measure of the lagoonal unit age.

The transition from lagoonal to lacustrine conditions in OML has a maximum radiocarbon age of c. 4700 cal yr BP. However, the timing of this event is suggested as c. 3600 cal yr BP or c. 4000 cal yr BP by correcting for the reservoir effect implied by the modern lake water and marine water, respectively.

The episodic sapropel deposition recorded in the stratigraphic succession of OML ceased at a maximum of c. 3200 cal yr BP, although is more likely to have actually been as recently as c. 2200 cal yr BP.

Lake Amy

The LA core represents a maximum of ~4600 years of lacustrine sedimentation. By correcting for the reservoir effect implied by the modern lake water, this is reduced to ~3900 years. Applying this constant reservoir correction to the maximum radiocarbon ages of c. 4600-3900 and 3200-2400 cal yr BP obtained for the two gelatinous sapropelic intervals within the organic-rich mudstone results in more realistic estimates of c. 3900-3300 and 2600-1800 cal yr BP, respectively.

The halt in deposition of organic-rich sediments is dated at a maximum of c. 2400 cal yr BP, but correcting for the reservoir effect brings the timing of this event to c. 1800 cal yr BP.

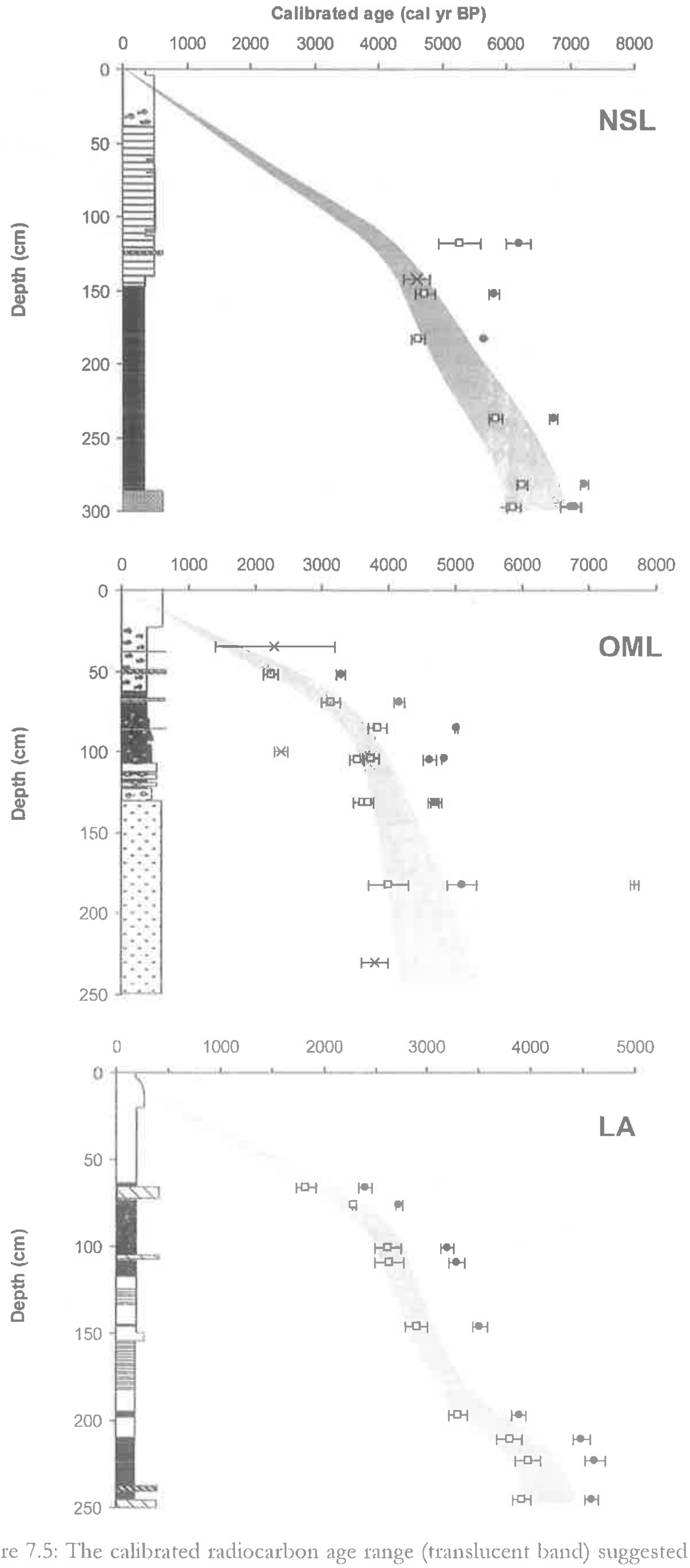

Figure 7.5: The calibrated radiocarbon age range (translucent band) suggested most probable by the present study. In-filled circles (●) indicate maximum possible ages and open squares (□) indicate reservoir corrected ages.

CHAPTER 8: ORIGIN OF LACUSTRINE ORGANIC MATTER

Lacustrine organic matter can be a mixture of material derived from multiple sources, including terrestrial plants, aquatic macrophytes, algae (both benthic and planktonic) and bacteria. Each of these biota is influenced by different environmental factors, such as water availability, seasonality, temperature, and light intensity. Geochemical analysis of lacustrine organic matter has the potential to reveal information on the nature of these environmental factors and how they change during the sediment accumulation history of the lake. The geochemical parameters so obtained may yield information that is specific to organic matter type. For example, the carbon isotope composition of terrestrial organic matter is primarily a reflection of the photosynthetic pathway (C3 or C4) employed by the precursor biota. As these two pathways are adapted to different environmental conditions the predominance of one plant type over the other can be used to infer conditions of water availability and the concentration of atmospheric CO_2 (Farquhar et al., 1989; Tieszen, 1991; Boutton, 1996). When it can be shown that lacustrine organic matter is primarily allochthonous, a shift in $\delta^{13}C_{org}$ of >2‰ generally reflects a change in the proportion of C3:C4 vegetation in the surrounding watershed (e.g. Nordt et al., 2002; Krull et al., 2003). A positive shift indicates an increase in C4 vegetation, which is commonly interpreted as reflecting a transition to drier conditions (e.g. Ehleringer et al., 1997, Lamb et al., 2004). On the other hand, a negative shift reflects an increasing proportion of C3 organic matter in the sediments, which could reflect a transition to more humid conditions in the watershed. However, as C3 vegetation is isotopically indistinct from freshwater C3 algae, $\delta^{13}C_{org}$ values must be interpreted differently when the organic matter contains any significant contribution from autochthonous sources. Accordingly, it is fundamental to establish the origin(s) of the lacustrine organic matter prior to attempting any palaeoenvironmental reconstruction from its geochemical analysis.

The present study of these shallow lakes on the Coorong coastal plain employed a suite of analytical techniques to characterise the organic matter preserved in their Holocene carbonate sediments. This chapter reports on the origin of the lacustrine organic matter as interpreted from the resulting data, which were presented against core stratigraphy in Chapter 6.

8.1 Atomic C/N ratios

The measurement and comparison of sedimentary organic C/N ratios with those values typical for aquatic and terrestrial biomass has often been used to help determine the origin (autochthonous versus allochthonous) of marine and lacustrine organic matter (e.g. Talbot and Lærdal, 2000; Tolun et al., 2002). Sampei and Matsumoto (2001) demonstrate that the relationship between C/N ratios and the relative proportions of terrestrial and planktonic organic matter is nonlinear. C/N ratios are much less sensitive to changes in planktonic input when it is proportionately high. For example, increasing the proportion of planktonic (versus terrestrial) organic matter from 10 to 20% leads to a decrease in C/N of 8, but increasing the proportion from 80 to 90% only causes a C/N decrease of 1.2 (Lamb et al., 2006). Therefore, comparison with typical C/N values should only be used to give a preliminary indication of the relative proportions of aquatic and terrestrial contributions to the lacustrine organic matter pool.

Atomic C/N ratios from all three lakes fall predominantly between the values typical for terrestrial vascular land plants and aquatic algal and bacterial organic matter (Figure 8.1). Therefore, as a C/N based first approximation, the organic matter pools of these three lakes comprise a mixture of allochthonous and autochthonous sources. Some samples from OML have markedly lower C/N values (<10) and thus seem to have been derived purely from aquatic (autochthonous) sources (discussed below).

In NSL, C/N values are relatively constant and average 16.4 throughout the 1.3 m-thick sapropel interval (Figure 8.2 A). Therefore, this sapropelic organic matter appears to be a mixture of vascular land plants and aquatic algae and bacteria. However, soil organic matter commonly has C/N ratios of between 8 and 15 (Nadelhoffer and Fry, 1988), and is thus indistinguishable from lacustrine organic matter derived from a combination of aquatic and terrestrial sources, and could be responsible for the C/N values of the NSL sapropel. Alternatively, these C/N values could indicate a planktonic source grown under conditions of either abundant nutrient supply or nitrogen deficiency. Such conditions could increase planktonic C/N values to as high as 18-20 (Meyers, 1997; Talbot and Lærdal, 1999).

A marked increase in C/N values within the organically lean pelletal laminated unit of NSL is masked by the scale of the axes in Figure 8.1 but is clearly evident in Figure 8.2 A. This shift to higher C/N values could result from the preferential digestion of nitrogen-rich proteinaceous planktonic material by grazers, such as brine shrimps, worms and gastropods (e.g. *C. striata*). Indeed, the pelletal texture of this unit is indicative of the ingestion of muddy sediments and excretion of faecal pellets that is common to low energy, saline waters (Scoffin, 1987).

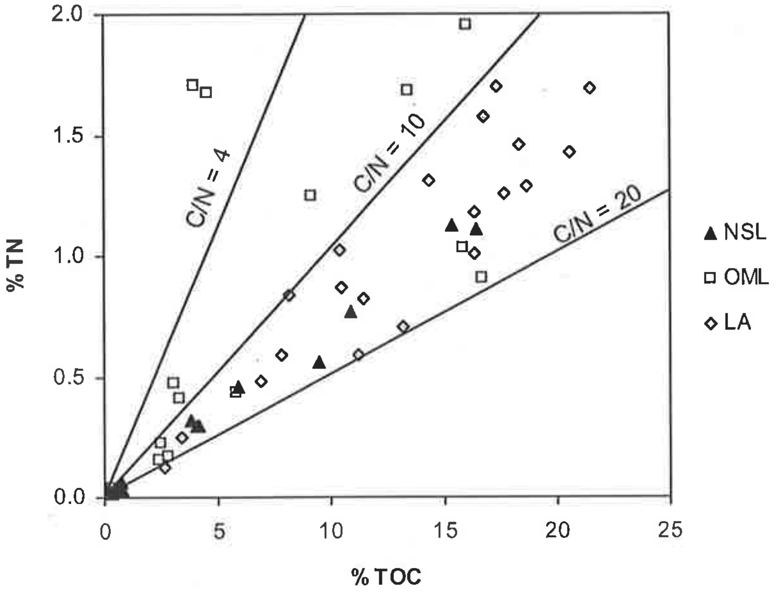

Figure 8.1: Percent TOC versus percent TN for the cores from NSL, OML and LA. Boundary lines at C/N = 4, 10 and 20 define the typical ranges for organic matter derived from terrestrial plant (C/N>20) and aquatic algal and bacterial (4<C/N<10) sources.

As in NSL, the C/N profiles of OML and LA could simply imply a mixed source for their organic matter. However, C/N values higher than those typical of aquatic organic matter could equally result from a predominantly aquatic source linked with conditions of high productivity, nitrogen deficiency or significant degradation of proteinaceous components. Contrary to the NSL profile, neither OML nor LA display a relationship between C/N and stratigraphy (Figure 8.2 B,C). In OML, C/N values range from 2.7 to 18 within the 35 cm-thick sapropel interval alone. Here, the association of high C/N values with high TOC contents could be a reflection of selective recycling of nitrogenous organic components under suboxic conditions (van Mooy et al., 2002). Although groundwater does supply significant amounts of nitrate to the lakes of limestone-rich regions (Wetzel, 1983), nitrogen levels can deplete to the extent that such nitrogen recycling is promoted under conditions of high lacustrine primary productivity.

Although C/N values <10 imply an aquatic origin for sedimentary organic matter, such values are not consistently associated with any one sedimentary unit, texture or TOC content in the OML core. Thus, the dramatic C/N fluctuations throughout the OML profile preclude a simple C/N-based classification of its lacustrine organic matter.

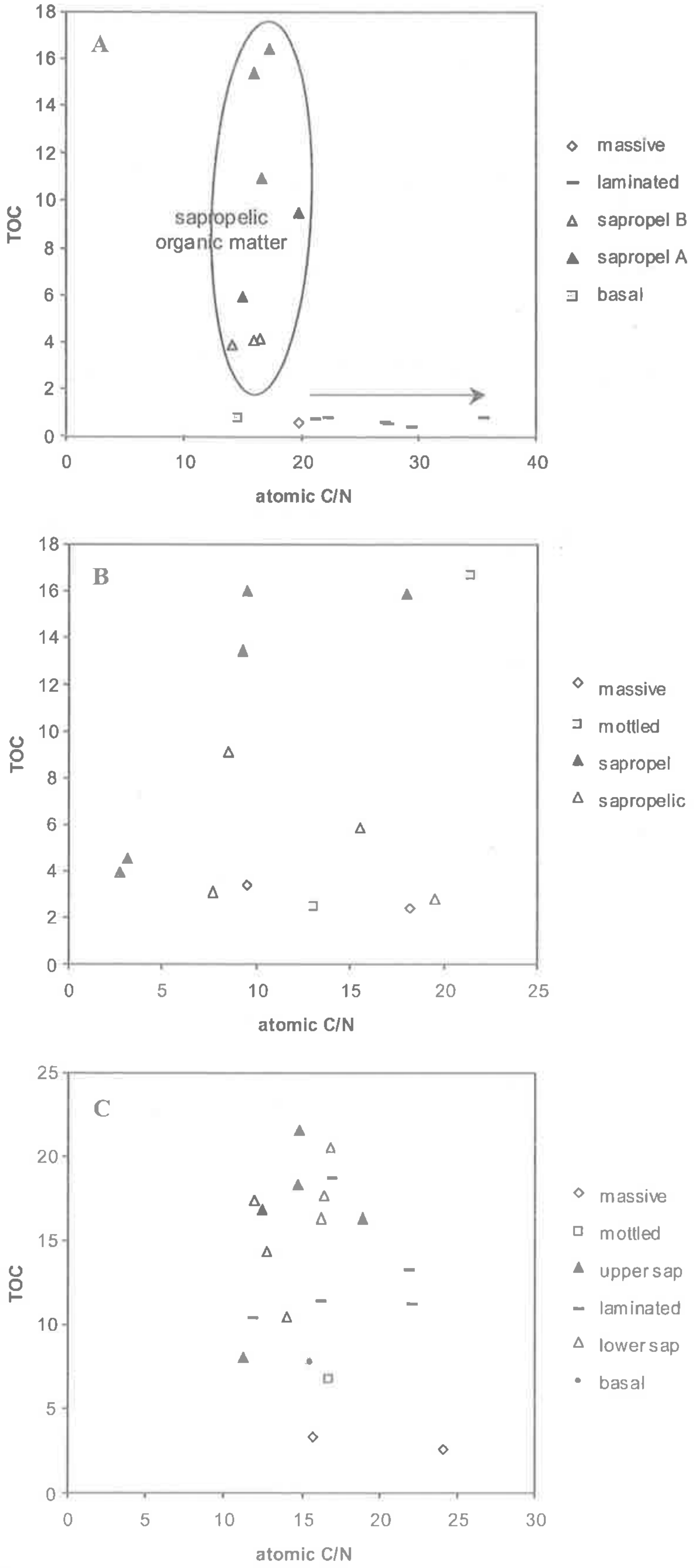

Figure 8.2: Percent TOC versus atomic C/N values for A) NSL, B) OML and C) LA. Contrary to sedimentary intervals in OML and LA, data from the sapropel and pelletal laminated units of NSL may be distinguished on the basis of C/N values.

In the sediments of LA, C/N also varies but less widely. Here, slightly lower C/N values in the sapropel intervals (upper, 14.4 ± 2.9; lower, 14.7 ± 2.1) could imply that this organic matter is either somewhat more aquatic in origin, or is less degraded, than that in the remainder of the sedimentary succession.

Clearly any attempt to identify the source(s) of sedimentary organic matter in these lakes using the atomic C/N ratio alone is bound to be inconclusive. This exemplifies the importance of using multiple proxies in palaeoenvironmental investigations, such as the present study. Indeed, all palaeoproxies suffer some degree of uncertainty as a result of imperfect signal preservation and the complexities of the natural processes being investigated (Bard, 2002). The use of multiple palaeoproxies minimises the influence of any one particular uncertainty on the overall outcome of the investigation. To this aid a cross-plot of C/N values against organic carbon isotopes ($\delta^{13}C_{org}$) can prove useful when evaluating the relative contribution of different organic matter types to subaqueous sediments (Figure 8.3). The data points for all three lakes tend to fall between the

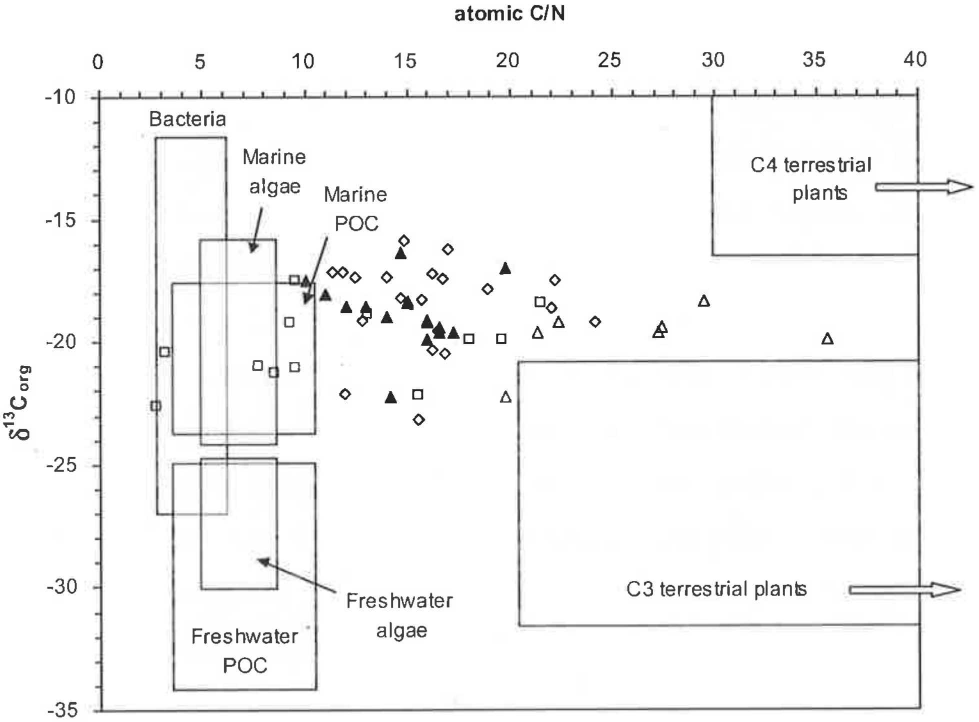

Figure 8.3: Representative $\delta^{13}C$ and C/N ranges for major organic inputs to subaqueous sediments (modified from Lamb et al., 2006). Particulate organic carbon (POC) encompasses suspended organic matter such as phytoplankton, and to a lesser extent, zooplankton. Data plotted for NSL sapropel (▲), NSL organic-poor sediments (△), OML (□) and LA (◇) tend to fall between these generalised ranges, indicating either a mixed organic matter origin or the influence of a range of environmental conditions on the formative aquatic organic matter (see text).

generalised ranges that are indicated for terrestrial plants and aquatic algae, bacteria and particulate organic carbon. Therefore, this comparison with $\delta^{13}C_{org}$ data does not enhance the organic matter source information provided by the C/N values alone. There appears to be a greater association of the OML sediments with aquatic bacterial organic matter and marine particulate organic carbon as well as a greater association of the NSL organically-lean sediments with terrestrial plant material (a mixture of C3 and C4 species). Overall, the data suggests that the sedimentary organic matter of these three lakes has either a mixed aquatic/terrestrial origin or is dominated by soil organic matter, which can be a significant contributor to the organic matter pool within tributary-fed aquatic settings or where there is a large aeolian flux to the lake system. However, as discussed above, the possibility of a predominantly aquatic organic matter source produced under atypical environmental conditions (e.g. abundant nutrient supply, nitrogen deficiency) cannot be discounted. Clearly, additional data are required before the origin of this lacustrine organic matter can be identified.

8.2 ^{13}C-NMR spectra

There are many proxies available that can aid organic matter source identification. Here, the NMR spectra of these sediments provide valuable information on the chemical structure of their organic matter. Each of the major resonances in these spectra (Figure 8.4) are herein assigned to a molecular structure of carbon and the distribution of structures then assigned to a particular organic matter type.

The largest peak in all 17 spectra is at ~31 ppm and is attributed to aliphatic carbon. These are commonly derived from long-chained lipids and aliphatic biopolymers (Kögel-Knaber, 1997). Such paraffinic structures are found in the resistant biopolymers of algae, and typically resonate at ~32 ppm (Zelibor et al., 1988; Knicker et al., 1996). In contrast, extensively branched alkyl structures resonate at ~15 ppm (Hedges et al., 2002). A shoulder at this resonance on the lower field side of the alkyl peak indicates a minor contribution of branched methyl structures to some of these samples, and is particularly noticeable for those from LA. It may be that this resonance reflects highly branched isoprenoid hydrocarbons previously identified at NSL and OML and derived from a significant contribution of diatoms to these sediments (McKirdy et al., 1995).

The peak at ~53 ppm is only a third to half the height of the alkyl peak, and is at least partially obscured by the larger peaks in both the upper (72 ppm) and lower (31 ppm) chemical shift fields. Nonetheless, the presence of this peak indicates some contribution from NH_2-substituted carbon (45-60 ppm), most probably in the form of amino acids and proteins (Knicker et al., 1996; Hedges et al., 2002). The broad, rather than sharp, nature of this peak suggests that it is not attributable to lignin (Figure 2.6A).

The peaks at ~72 and 102 ppm correspond to carbohydrate structures, which are major components of both aquatic and terrestrial biomass (Wilson, 1987). These peaks fall within the resonance fields of aliphatic carbon single-bonded to one (60-95 ppm) and two (95-110 ppm) hydroxyl groups, respectively. The former range is typical of pentoses and hexoses (Hedges et al., 2001) and the (stronger) peak at ~72 ppm represents glucosidic carbon structures (Dereppe et al., 1980).

The peak at ~130 ppm, along with the peak at ~102 ppm, are the weakest of the six major resonances in these samples. The field of 110-160 ppm corresponds to unsaturated carbon atoms, which may be either aromatic or olefinic in structure (Wilson, 1987). Broad resonances in this region are often attributed to charcoal (Figure 2.6B). However, the asymmetry of the peak at ~130 ppm in these lacustrine samples suggests that it represents unsaturated compounds or aromatic amino acids, such as phenylalanine, tyrosine and histidine (Knicker et al., 1996), rather than charcoal.

The absence of much resonance in the higher aldehyde/ketone field (190-220 ppm) shows that most carbonyl groups occur in acid, ester, amide and quinone structures (Dereppe et al., 1980). As the major resonance in this field peaks at ~173 ppm it corresponds primarily to carbon double-bonded to oxygen in amide or ester groups (Wilson, 1987; Hedges et al., 2001), and is therefore attributable to proteins and glucosides (Dereppe et al., 1980).

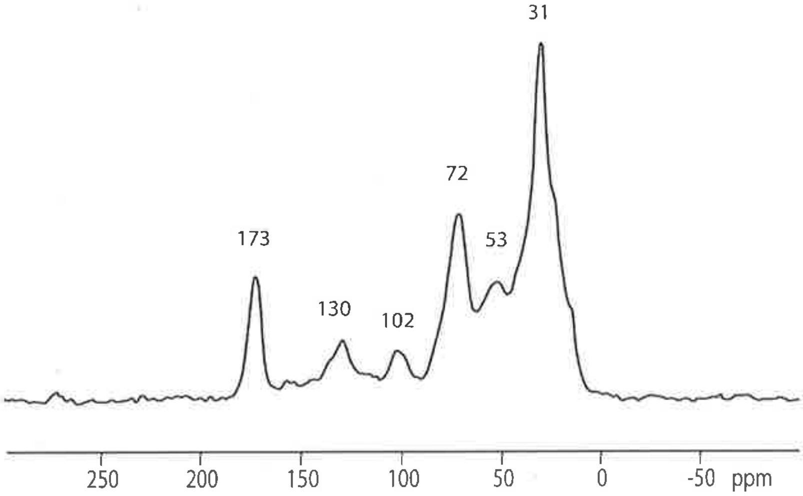

Figure 8.4: ^{13}C-NMR spectrum of lacustrine organic matter (OML3) representative of most Coorong samples. Major resonances are indicated (see text).

In summary, the ^{13}C-NMR spectra for all samples from the three lakes are dominated by alkyl carbon (carbohydrates and proteins), with only minor signals in the unsaturated region. Sedimentary organic matter of planktonic and bacterial origin is rich in nitrogen-containing proteinaceous material, and contains large amounts of alkyl carbon and relatively little aromatic or olefinic carbon (Dickens et al., 2006). On the contrary, terrigenous plant material contains a higher proportion of aromatic and O-alkyl carbon, attributed to the higher cellulose content in vascular plant residues. (Hedges et al., 1997, 2002). In particular, there is a notable absence of peaks at ~56, 115 and 148 ppm, which are usually indicative of lignin and/or tannin from vascular plants as well as at 145 ppm, which is attributed to the carbohydrate in cellulose (Golding et al., 2004). Therefore, the ^{13}C-NMR spectra of the Coorong lacustrine sediments are likened to those typical of planktonic and bacterial organic material.

This conclusion supports the findings of previous studies on Coorong lacustrine sapropels (e.g. McKirdy et al., 2002; Edwards et al., 2006) in indicating an organic matter pool composed largely of lacustrine photoautotrophs (algae and bacteria) and augmented by minor contributions from allochthonous terrestrial biomass. In fact, the Coorong lacustrine organic matter has a spectral distribution similar to that of sinking planktonic particles from a moderately productive, moderately oxygenated (100-200 μmol/l) equatorial site in the Pacific Ocean (Hedges et al., 2001, 2002), sediments from the continental slope off the coast of Washington, (Dickens et al., 2006), and the lower estuarine sediments from Durras Lake, southern NSW (Golding et al., 2004) (Figure 8.5).

The major resonance positions are almost identical for all 17 of the Coorong spectra. However, at OML the relative proportions of carbon structures in the lagoonal unit (OML6), and to a lesser extent near the transition out of lagoonal conditions (OML5), differ slightly from those of its truly lacustrine sediments (Figure 8.6). Most significantly, there is a greater proportion of carbon represented in the unsaturated (110-160 ppm) and aldehyde/ketone (190-220 ppm) chemical shift ranges, and a lesser proportion of alkyl (0-45 ppm) and carbonyl/amide (165-190 ppm) carbon, in the lagoonal samples (Table 6.3). These differences are similar to those between marine and terrestrial end-member sediments off the coast of Washington, U.S.A. Here, the terrestrial end-member displays a relatively higher resonance in the unsaturated, and lower resonance in the alkyl, chemical shift ranges (Dickens et al., 2006). Therefore, the lagoonal unit of OML is interpreted as having received more terrigenous input to its organic matter pool than did the remainder of the Coorong lacustrine sediments examined in this study.

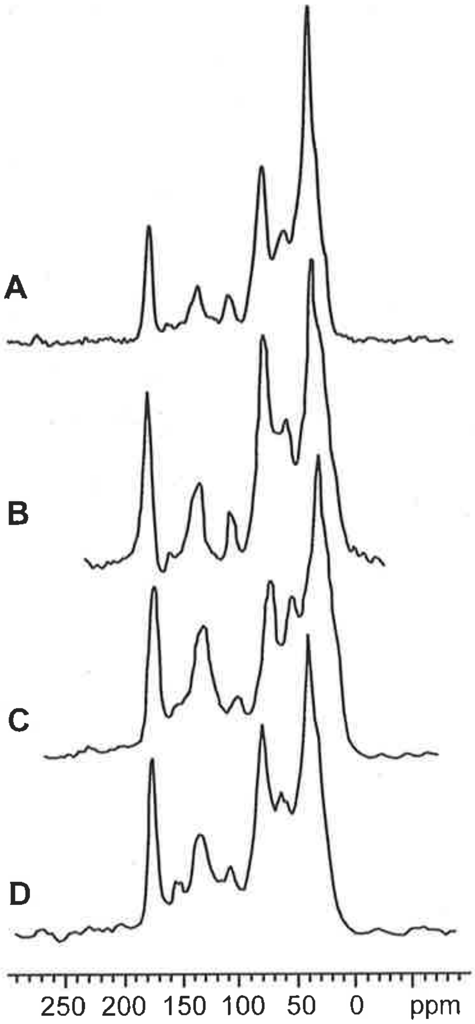

Figure 8.5: Comparative ^{13}C-NMR spectra for A) OML3, B) sinking particles in the upper water column (~500-1000 m) of the equatorial Pacific Ocean (Hedges et al., 2001), C) the 2.0-2.5 g/cm^3 density fraction of Washington coastal slope sediments (Dickens et al., 2006), and D) lower estuarine sediments at Durras Lake, southern NSW (Golding et al., 2004)

The presence of a broad symmetrical peak at ~130 ppm in sample OML6 may suggest that this terrestrial input is in the form of charcoal that was washed into the lagoonal system, or alternatively, carried in by high coastal winds. For all other samples, the asymmetrical peak at ~130 ppm with a 'shoulder' on the higher chemical shift side, is interpreted as a reflection of unsaturation associated with alkyl carbon or with aromatic structures, such as certain amino acids, rather than indicating the presence of charcoal. The interpretation of a higher charcoal contribution to sample OML6 than to all other samples is reinforced by the lower percentage of carbon that is 'observed' (C_{obs}) by NMR of the lagoonal unit sample (Table 6.3). Charcoal is typically under-represented by cross-polarisation (CP) spectra reported herein (Skjemstad et al., 1996, 1999; Golding et al., 2004). Therefore, it can be assumed that the lower C_{obs} for OML6 reflects a higher proportion of 'unseen' charcoal carbon in this sample. This assumption could be tested by comparison with spectra obtained using the Bloch decay (BD) polarisation technique, which provides a more quantitative estimate of total carbon proportions (Skjemstad et al., 1996). However, longer acquisition times are required for BD spectra and the subsequent high cost of sample analysis prohibited use of this technique in the present study. Nonetheless, the CP spectra provide valuable information on the relative distribution of carbon structures within these samples, and indicate that the majority of the sedimented lacustrine organic matter at all three sites is primarily autochthonous in origin.

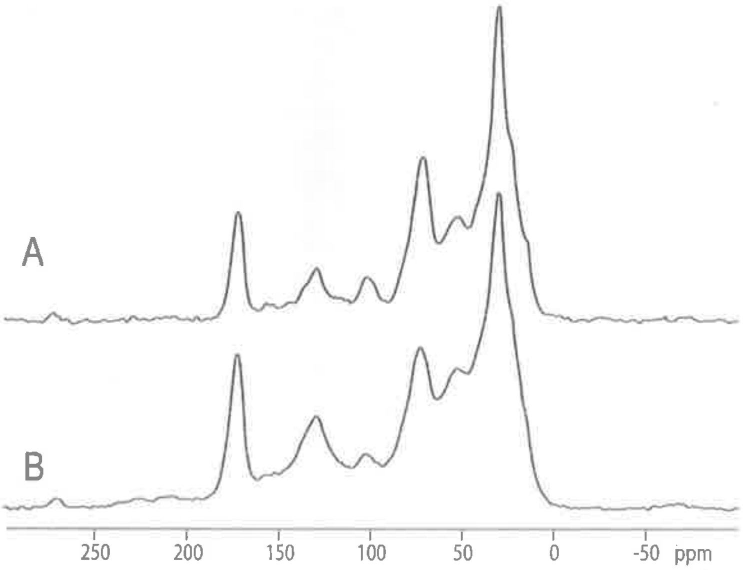

Figure 8.6: Comparison of ^{13}C-NMR spectra for organic matter representative of most lacustrine samples (A) and from the lagoonal unit of OML (B). The distinct shoulder on the weaker peak in the aromatic region (~130 ppm) of the lacustrine samples suggests that this resonance results from unsaturation associated with the alkyl carbon, whereas the stronger symmetrical peak in this region of the second spectrum is attributed to charcoal in the lagoonal system.

8.3 Carbon isotopes

In a eutrophic lake, where the organic matter is shown to be primarily autochthonous, $\delta^{13}C_{org}$ values will depend on the composition and availability of DIC, and on both the level and type of primary productivity and subsequent organic matter preservation (Meyers, 1994; Hassan et al., 1997; Tolun et al., 2002). The ^{13}C-NMR spectra (described above) reinforce the findings of earlier workers (e.g. McKirdy et al., 2002; Edwards et al., 2006) in indicating that the organic matter pool of all three lakes is largely autochthonous in origin. Therefore, the $\delta^{13}C_{org}$ values primarily reflect in-lake conditions and processes rather than climate-induced changes in the vegetation communities of the surrounding watershed.

The principal control on the $\delta^{13}C_{org}$ signatures of aquatic biomass is the DIC source utilised during photosynthesis (Benedict et al., 1980; Hassan et al., 1997). The DIC of the water column is controlled by an array of factors including rates of atmospheric CO_2 exchange, carbonate weathering, watershed vegetation type and lacustrine rates of photosynthesis and respiration (Brenner et al., 1999; Leng and Marshall, 2004). Phytoplankton preferentially take up CO_2 until it is exhausted. Rapid rates of primary production can easily deplete dissolved CO_2 levels in shallow, high pH lakes to the extent that aquatic biota increasingly utilise bicarbonate as a carbon source (Wetzel, 1983).

The $\delta^{13}C_{org}$ values from the Coorong lakes (viz. NSL –22.3 to –16.4‰; OML –22.6 to –17.5‰; LA –23.2 to –15.9‰)[7] fall closest to those typical of photosynthetic bicarbonate uptake by aquatic plants (average –21‰: Figure 8.7). Weathering of their calcareous hinterland supplies ample carbonate and bicarbonate to these groundwater-fed lakes. Moreover, similarly alkaline conditions to the present day (pH ~8: Henderson, 1997) are likely to have existed throughout the history of each lake. At pH levels of ~9 the DIC pool comprises almost entirely bicarbonate (Anderson and Leng, 2004). Organic matter produced via photosynthetic incorporation of bicarbonate is relatively ^{13}C-enriched because the carbon in bicarbonate is ~8‰ heavier than the carbon in aqueous CO_2 (Keeley and Sandquist, 1992; Fogel and Cifuentes, 1993). Therefore, the $\delta^{13}C_{org}$ signatures of these three lakes are interpreted as predominantly reflective of lacustrine algae that used bicarbonate as their source of DIC. Further consideration of the stratigraphic variation of these signatures is reserved for the discussion on productivity changes that occurred during the evolution of each lake (Chapter 9).

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[7] These results are from the extensive isotopic analysis completed at CSIRO Land and Water, not the analysis completed in conjunction with radiocarbon dating at ANSTO.

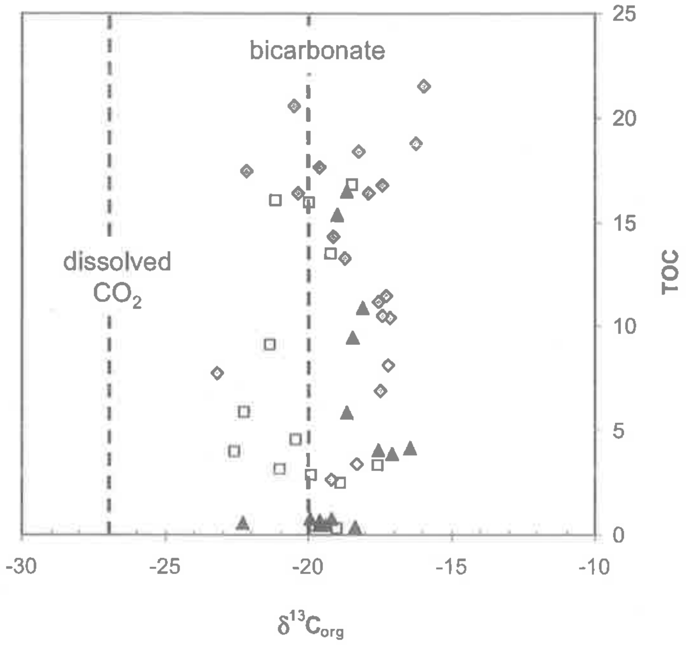

Figure 8.7: Percent TOC versus $\delta^{13}C_{org}$ for samples from NSL (▲), OML (□) and LA (◇). The $\delta^{13}C_{org}$ values from all three lakes fall between the values typical of lacustrine algal and bacterial organic matter produced using CO_2 (average –27‰) and bicarbonate (average –20‰) as its DIC source.

A contribution from aquatic macrophytes, such as *Ruppia* sp. ($\delta^{13}C_{org}$: –16‰; Appendix VI), may account for some of the mixed source affinity suggested by the $\delta^{13}C_{org}$ values of these lakes. Indeed, the yoghurt-like consistency of surface sediments in the Salt Creek lake chain is associated with the degraded remains of *Ruppia* sp. plants and cyanobacterial binding (Wright, 1999). Freshwater macrophytes display a wide range of $\delta^{13}C$ values (~ –30 to –12‰; Boutton, 1991). The different carbon sources used by emergent and submergent species are reflected by lower $\delta^{13}C$ values for the emergent macrophytes utilising atmospheric CO_2 and higher $\delta^{13}C$ values for submergent macrophytes that rely on lacustrine DIC (Hoyer et al., 1997).

An additional component of allochthonous terrestrial biomass may contribute to the lacustrine organic matter pool but remains unquantified. However, a single piece of charcoal from the lagoonal unit of OML has a $\delta^{13}C_{org}$ of –24.0‰[8], reflecting its likely derivation from C3 land plants. Indeed, the $\delta^{13}C_{org}$ values of modern day lakeside vegetation (Appendix VI) reflect a predominantly C3 isotopic signature. Even *Halosarcia sp.* (saltbush: C4) displays a $\delta^{13}C_{org}$ value typical of C3 (–27.3‰), rather than C4 vegetation.

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[8] ANSTO analysis.

8.4 Nitrogen isotopes

$\delta^{15}N$ data can help identify the source(s) of subaqueous sedimentary organic matter because of the differences in the isotopic composition of the inorganic nitrogen reservoirs available to plants on land and in water. However, the interpretation of this data is rarely simple. $\delta^{15}N$ values can reveal shifts in both phytoplankton and heterotroph assemblages by indicating periods when biota capable of nitrogen fixation became significant contributors to an autochthonous organic matter pool (e.g. Calvert et al., 1992; Brenner et al., 1999; Struck et al., 2001; Lehmann et al., 2002; Meyers and Bernasconi, 2005). Alternately, $\delta^{15}N$ values can purely reflect secular changes in the dissolved inorganic nitrogen (DIN) reservoir, such as increased nitrogen availability or photosynthetic nitrogen-drawdown, rather than changes in the biotic assemblage.

$\delta^{15}N$ values range from ~0 to 6‰ in both OML and LA, but in NSL reach as high as 16.2‰ (Table 6.1). Also, the sapropel interval in NSL is marginally richer in ^{15}N ($\delta^{15}N$ 1.5 to 6.9‰) than those in both OML and LA ($\delta^{15}N$ 1.3 to 5.0‰). This suggests that the overall contribution from nitrogen-fixers to the autochthonous organic matter pool was less in NSL than either of the southern lakes. On the other hand, as $\delta^{15}N$ values generally increase from oligotrophic to eutrophic lakes (Gu et al., 1996; Brenner et al., 1999), these values may indicate that the sapropel in NSL accumulated under relatively more eutrophic conditions than did those in OML and LA.

Low $\delta^{15}N$ values (1-3‰) can be a reflection of phytoplankton that grew in a lake with an abundant supply of DIN (Talbot, 2001). Therefore, the excursion (toward 1.5‰) in the lower half of Sapropel A could be interpreted as a reflection of phytoplankton produced under conditions of enhanced nitrate availability in NSL at this time. Inputs of nitrogen (as nitrate) by groundwater can be a major part of the annual nitrogen loading in many lakes, especially in regions rich in limestone (Wetzel, 1983). Therefore, the waters of NSL were most likely rich in nitrate prior to its drawdown by excessive photosynthetic production and the subsequent burial of organic matter that led to sapropel formation.

Alternatively, these relatively ^{15}N-depleted values may indicate a period where there was a significant contribution by nitrogen-fixing biota (e.g. cyanobacteria) to the organic matter pool in NSL. This could be a reflection of the influence that microenvironmental conditions within an algal bloom can have on lacustrine element cycling. For example, nitrogen fixation has been positively correlated with the concentration of organic nitrogen compounds, such as those secreted by algae, in the water column (Wetzel, 1983). This is exemplified by a study on the common nitrogen-fixing cyanobacteria, *Anabaena*, which showed that bacterial colonisation of algal blooms created oxygen-depleted microzones (Figure 8.8) that apparently enhanced the overall nitrogen-fixing capability of the biota (Paerl, 1978).

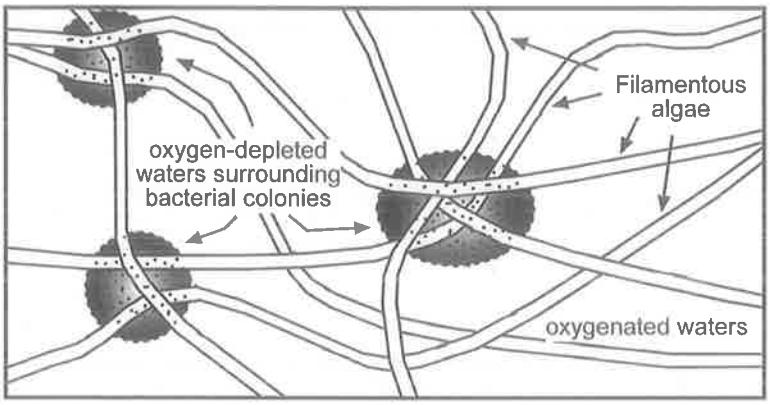

Figure 8.8: Schematic illustration of oxygen-depleted microzones that can be created by bacterial colonisation within an algal bloom.

The most notable feature of the $\delta^{15}N$ data from NSL is the trend toward significantly ^{15}N-enriched values in the laminated unit (Figure 8.9). These values are interpreted as reflecting abundant ammonia production in the shallow alkaline waters of NSL, as is also inferred for Pleistocene Lake Bosumtwi (Talbot, 2001). Subsequent volatilisation of this ammonia would cause considerable ^{15}N-enrichment in the DIN pool (Table 2.2), and thus lead to the production of organic matter with such markedly ^{15}N-enriched values. Furthermore, the loss of nitrogen across the lake water surface would be reflected by an increase in the C/N ratios of organic matter produced under these conditions. Indeed, the distinctly elevated C/N ratios throughout the laminated interval of NSL (Figure 8.10) provide further evidence that ammonia production and volatilisation is responsible for the ^{15}N-enriched values of these sediments.

A shift toward less elevated $\delta^{15}N$ values in the massive unit of NSL may represent an increase in the impact of cyanobacteria on the isotopic signature of these recent sediments. Indeed, the presence of cyanobacteria (stromatolites and free-floating autotrophs) has been recorded in all lakes of the Salt Creek Lake Chain (Wright, 1999), and stromatolite occurrence near the margins of NSL is undoubtable evidence of nitrogen-fixation in this modern lake. As the observed decrease in $\delta^{15}N$ values coincides with a significant shift of –2.65‰ in $\delta^{13}C_{org}$ across the transition from laminated to massive units it is likely that an alteration to the organic matter assemblage is responsible for the change in $\delta^{15}N$.

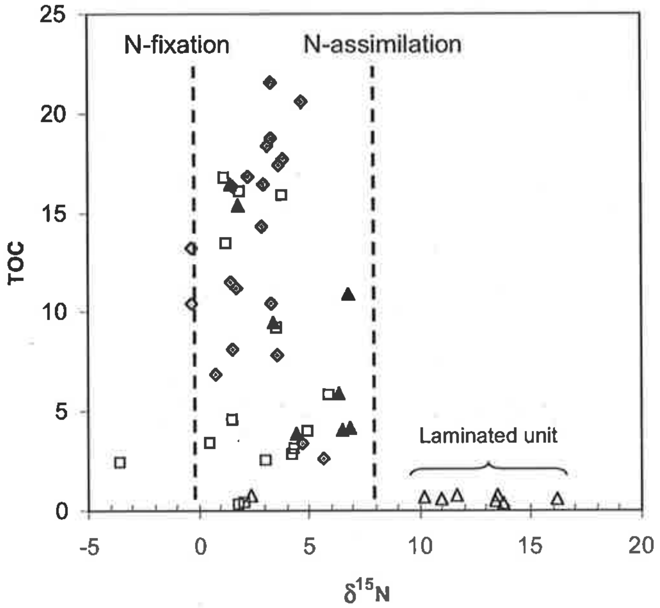

Figure 8.9: Percent TOC versus $\delta^{15}N$ for samples from NSL sapropel (▲), NSL organic-poor sediments (Δ), OML (□) and LA (◆) sediments. $\delta^{15}N$ values tend to fall between those typical for nitrogen-fixing and nitrogen-assimilating biota, thus indicating the likelihood of a mixed contribution to the predominantly autochthonous organic matter pool of these three lakes.

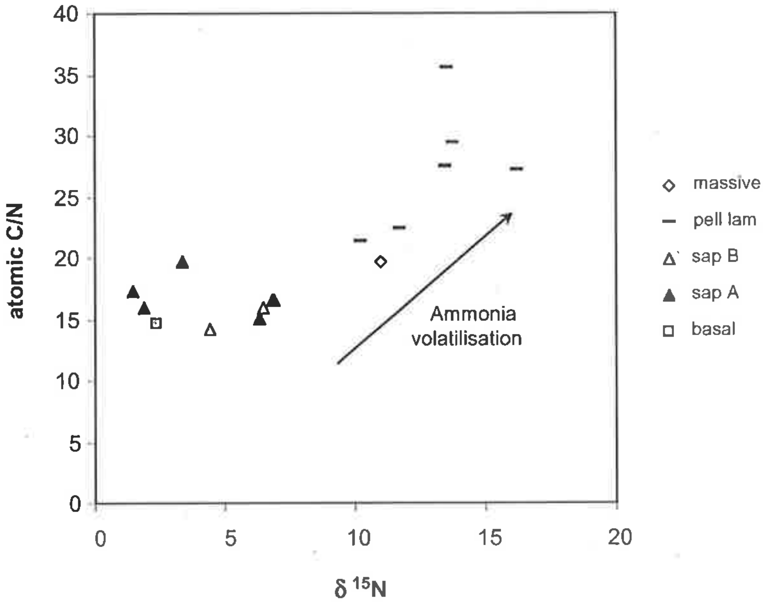

Figure 8.10: Atomic C/N versus $\delta^{15}N$ for each of the sedimentary units in NSL. The pelletal laminated unit is marked by distinctly elevated C/N and $\delta^{15}N$ values, thus implying that the process of ammonia volatilisation became important during this period of sediment deposition.

Periods of enhanced contribution from photosynthetic nitrogen-fixing bacteria, including cyanobacteria, to the organic matter pool of OML are suggested by lower $\delta^{15}N$ values within the lagoonal unit (~2.0‰), the sapropel interval (~1.6‰) and the organic-poor massive unit (–3.5 to 0.5‰: Figure 8.11). The sapropelic interval and the transition from the sapropel into the overlying mottled interval are comparatively ^{15}N-enriched ($\delta^{15}N$ ~4.4 and 4.0‰, respectively), although still depleted with respect to phytoplankton ($\delta^{15}N$ ~8: Peterson and Howarth, 1987). The apparent shift toward conditions that favour nitrogen-fixing species during the period of sapropel deposition suggests a progressive reduction in the DIN pool. However, the prevalence of nitrogen-fixers implied by the sapropel $\delta^{15}N$ values may not mean that the entire water column was depleted in molecular nitrogen at this time. Instead, ^{15}N-depleted values may be a reflection of oxygen-depleted microzones within the algal bloom that is eventually preserved as sapropel. Regardless, $\delta^{15}N$ values reveal episodes of enhanced and reduced nitrogen fixation in OML. Here, it seems that nitrogen assimilators were somewhat more abundant during the periods of transition into and out of sapropel deposition than during the period of sapropel deposition itself.

In contrast, the organic matter of LA is relatively ^{15}N-enriched in the lower and upper sapropel intervals ($\delta^{15}N$ = 3.6 and 2.6‰, respectively: Figure 8.11). This suggests that nitrogen assimilators remained the more dominant autochthonous contributors to the organic-rich intervals in LA than was the case in OML. Also, in contrast to OML, the sediments of the massive unit in LA are relatively ^{15}N-enriched ($\delta^{15}N$ ~5‰), and thus represent nitrogen assimilating, rather than fixing, species. A gradual upsection decrease in $\delta^{15}N$ between the two sapropel intervals suggests that nitrogen fixation became increasingly more significant during the deposition of these moderately organic-rich laminated sediments. This is likely a reflection of the progressive removal of DIN from the water column by the algal bloom (represented by sapropel) and continued throughout deposition of the laminated unit. A negative excursion in $\delta^{15}N$ is also evident from through the upper sapropel into the overlying mottled unit, thus reinforcing the interpretation of progressive photosynthetic DIN uptake promoting nitrogen fixation in LA. This being the case there must have been some input/recycling of ^{15}N-enriched nutrients toward the halt in deposition of the laminated sediments to account for the similar $\delta^{15}N$ values in both the upper and lower sapropels.

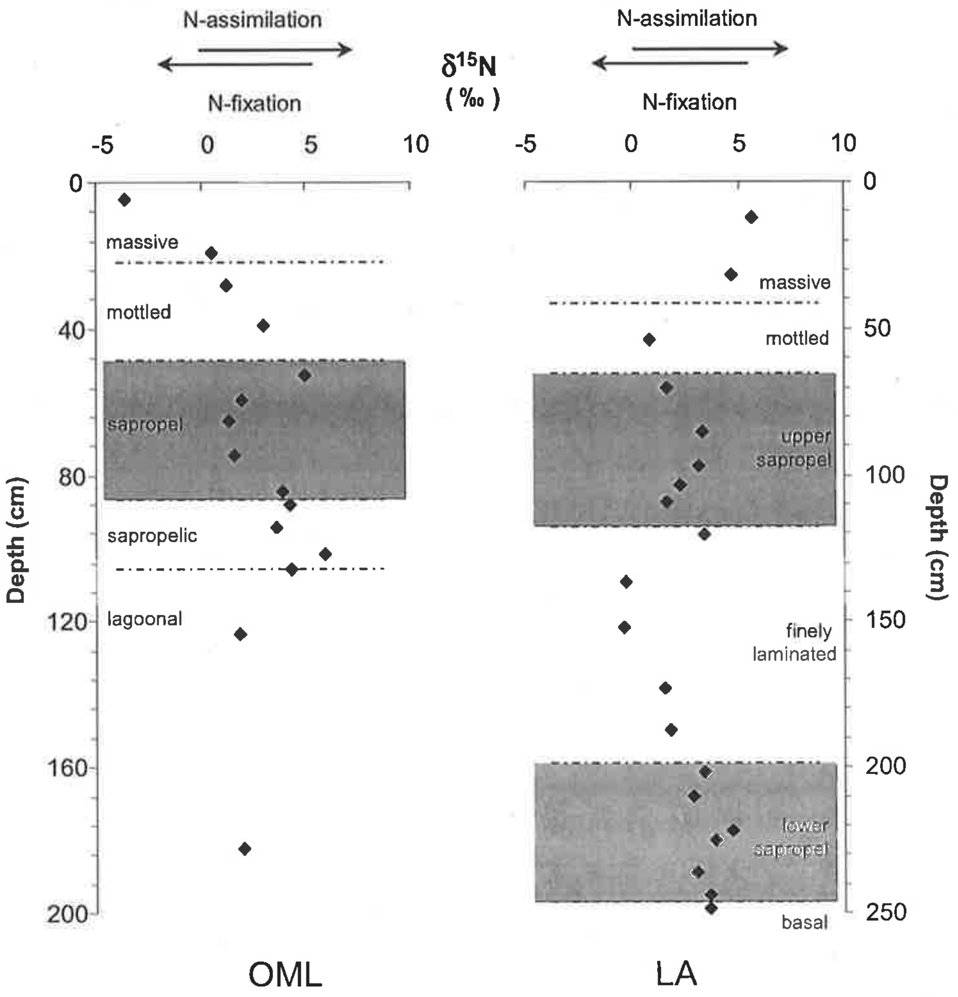

Figure 8.11: Comparison of $\delta^{15}N$ in the sediments of OML and LA. Shifts toward positive $\delta^{15}N$ values reflect an increase in the proportion of nitrogen-assimilating biota to the organic matter pool whilst shifts toward negative values reflect an increase in nitrogen-fixing species.

It cannot be established from the present data set whether low $\delta^{15}N$ values in any of the three lakes reflect an abundance of nitrate available to phytoplankton or a dominance of photosynthetic nitrogen-fixing bacteria. However, this information could be obtained through biomarker analysis. For example, the occurrence of isorenieratene in sapropel intervals of the Mediterranean Sea is indicative of green sulphur bacteria, which are obligate anaerobes (Sinninghe Damste et al., 2001). These sapropels are ^{15}N-depleted (e.g. Calvert et al., 1992; Struck et al., 2001), so it seems that nitrogen-fixing microbes are either themselves a significant component of the primary production that is eventually preserved as sapropel, or play an important role in providing bioavailable nitrogen to the phytoplankton (Meyers and Bernasconi, 2005).

8.5 Synthesis

To summarise, C/N ratios do not point unambiguously toward a predominantly aquatic origin for the lacustrine organic matter, but instead suggest a mixed aquatic and terrestrial source. However, ^{13}C-NMR analysis indicates that the organic matter pool of all three lakes is very similar to published NMR spectra from plankton, thus implying that the Coorong lacustrine organic matter is largely autochthonous in origin. This reinforces the previous findings that indicated an organic matter pool composed primarily of lacustrine photoautotrophs. In areas with a high algal contribution to the organic matter pool, it can be difficult to distinguish organic matter sources based on $\delta^{13}C_{org}$ values, even with the aid of C/N (Chivas et al., 2001). This study would have benefited from the use of additional parameters such as compound specific isotope or biomarker analyses (e.g. Wilkes et al., 1999; Hollander and Smith, 2001).

The elemental and isotopic signatures of organic matter in the present study are considered to primarily reflect changes in internal lacustrine conditions and processes, rather than alterations to the terrestrial ecosystem of their hinterland. Higher C/N ratios than those typical of algae and bacteria are interpreted as reflecting conditions of either nitrogen-deficiency or a nutrient abundance, the latter promoting primary productivity in the epilimnion and leading to oxygen depletion in the hypolimnion and preferential degradation of nitrogen-rich proteinaceous organic matter. $\delta^{13}C_{org}$ values of around –20‰ reflect the photosynthetic use of bicarbonate by these aquatic biota and indicate variations in the extent of lacustrine productivity and respiration. $\delta^{15}N$ values provide information on shifts in the phytoplankton and heterotroph assemblages that may be related to changes in the trophic state of the lake waters.

CHAPTER 9: ISOTOPE CHEMOSTRATIGRAPHY OF CARBONATE AND ORGANIC CARBON AS A KEY TO LAKE EVOLUTION

In general, organic-rich sediments, such as the sapropels of the present study, are linked to periods of relatively high productivity in low-energy, commonly oxygen-depleted environments. Sufficiently high productivity is essential for organic matter to reach the sediment in any quantity and subsequently stand a chance of preservation. Conditions of oxygen depletion that aid organic matter preservation may be either a by-product of high productivity levels (e.g. Martinez-Ruiz et al., 2000; Meyers and Bernasconi, 2005), or be unrelated to productivity (e.g. result from stratification: Rossignol-Strick, 1985; Aksu et al., 1995). According to Pedersen and Calvert (1990) and Calvert et al. (1992) restricted circulation and bottom water anoxia enhance sapropel preservation but are not necessarily prerequisites for sapropel formation.

The extent of primary productivity in the epilimnion is by and large considered the most significant biogeochemical control on the $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ values in highly productive lacustrine systems (e.g. McKenzie, 1985; Schelske and Hodell, 1991; Meyers, 1997; Tolun et al., 2002). Therefore, secular variations in sedimentary $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ values will, to some degree, reflect changing productivity levels in these shallow coastal lakes. However, to assume that primary productivity is the principal control on lacustrine carbon cycling is an oversimplification. A range of environmental factors, such as water temperature, salinity and turbidity, can influence the isotopic evolution of a lake and its sediments. Also, as organic matter is a mixture of variably resistant biochemical fractions that have different isotopic signatures, selective degradation of the more labile components has the potential to modify bulk $\delta^{13}C_{org}$ values (Herczeg, 1988). Finally, under anoxic conditions, such as those created by the degradation of large amounts of organic matter in highly productive lacustrine systems, microbially mediated carbon cycling processes are enhanced (Hollander and Smith, 2001). Because anaerobic processes such as sulphate reduction and methanogenesis can significantly impact on the carbon isotopic signature of sedimentary organic matter and carbonate (see section 2.2.2), the conditions of both productivity and preservation must be considered when interpreting sedimentary $\delta^{13}C$ values.

In the present study, isotopic analysis was used to investigate secular changes in lacustrine environment that may have been linked to sapropel deposition. This chapter discusses the isotopic data from sedimentary carbonate ($\delta^{13}C_{carb}$, $\delta^{18}O$) and coexisting organic matter ($\delta^{13}C_{org}$) and their implications for the evolutionary history of each lake.

9.1 Evolution of the Studied Lakes

North Stromatolite Lake

$\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values fall into two distinct groups. Those of the basal and Sapropel A units are depleted in ^{13}C relative to the remainder of the sedimentary succession (Figure 9.1). The upsection enrichment in ^{13}C and ^{18}O may be attributed to the progressive evaporative removal of the lighter isotopes from the lake waters and the subsequent deposition of isotopically heavier carbonates over time. Rosen et al. (1988) and Edwards et al. (2006) also interpret a similar increase in $\delta^{13}C_{carb}$ and $\delta^{18}O$ as evidence of evaporation in shallowing lakes of the Salt Creek lake chain.

Variable levels of lacustrine productivity can be responsible for changes in $\delta^{13}C_{carb}$. At first glance, Figure 9.1 could be interpreted as evidence for the association of high productivity with saline conditions brought about by evaporation, and low productivity with fresher conditions at NSL. Indeed, conditions of increased evaporation can act to promote lacustrine productivity by both concentrating the available nutrients and raising lake water temperatures (Mayer and Schwark, 1999). However, this interpretation cannot explain the apparent association of low TOC contents in the laminated and massive units with periods of supposed enhanced productivity in NSL. Li and Ku (1997) provide an alternative explanation: "As fresh (rain) water is usually more depleted in ^{13}C than lake water, under conditions of evaporation exceeding precipitation, photosynthetic removal of organic carbon will lead to an increase of lake $\delta^{13}C$ even if the lake productivity remains unchanged." Hence, notwithstanding their isotopic signatures, it seems that the organic-poor carbonate sediments of NSL were not actually deposited during periods of increased productivity. Rather, they formed within a water column from which the lighter carbon isotope had been preferentially removed via photosynthetic uptake during the preceding sapropel event, as well as during continual evaporation of the shallowing water body.

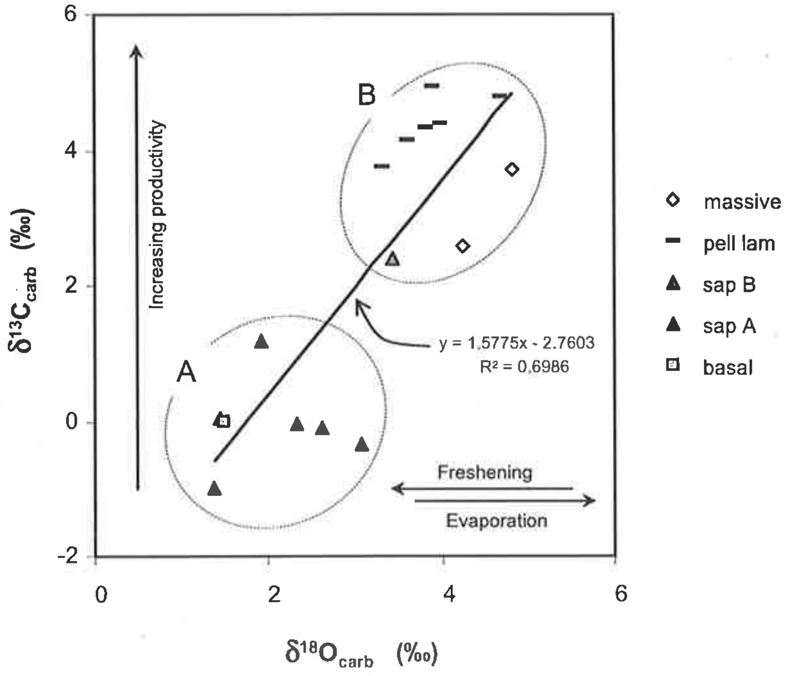

Figure 9.1: Cross-plot of $\delta^{13}C_{carb}$ versus $\delta^{18}O_{carb}$ (vpdb) for A) the organic-rich and B) the organically-lean sedimentary units of NSL. The apparent association of high levels of productivity with saline conditions brought about by evaporation, and low levels of productivity with fresher conditions, becomes weaker when TOC content is taken into account (see text).

The positive shift in $\delta^{13}C_{carb}$ through the Sapropel B unit of NSL coincides with a positive shift in $\delta^{13}C_{org}$ (Figure 9.2). The ^{13}C-enrichment of the DIC reservoir that results from increased lacustrine productivity leads to a progressive $\delta^{13}C$ increase in both newly produced organic matter and carbonate within a sedimentary succession (Hollander and Smith, 2001; Meyers, 2003). Therefore, the synchronous increase of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ through the sapropel B unit of NSL is here attributed to photosynthetic ^{12}C uptake during sapropel formation.

This positive carbon isotopic trend appears to have been initiated by a freshening episode, which is evident in a 1.6‰ decrease in $\delta^{18}O$ values at around 200 cm depth. A 20 cm-thick gastropod-rich layer immediately precedes the depth of this hypothesised freshening episode. As high salinity levels contribute to the demise of *Coxiella* (De Deckker, 1988), the halt in accumulation of significant numbers of these gastropods at around 200 cm depth supports this theory of a mid-sapropel freshening.

Edwards et al. (2006) observe a similar mid-sapropel decrease in $\delta^{18}O$ and $\delta^{13}C_{carb}$ at approximately this point in the NSL sedimentary sequence and attribute it to enhanced meteoric input triggering a short-lived decline in productivity. Why such a freshening would decrease productivity in this system is not considered in that study. An alternative

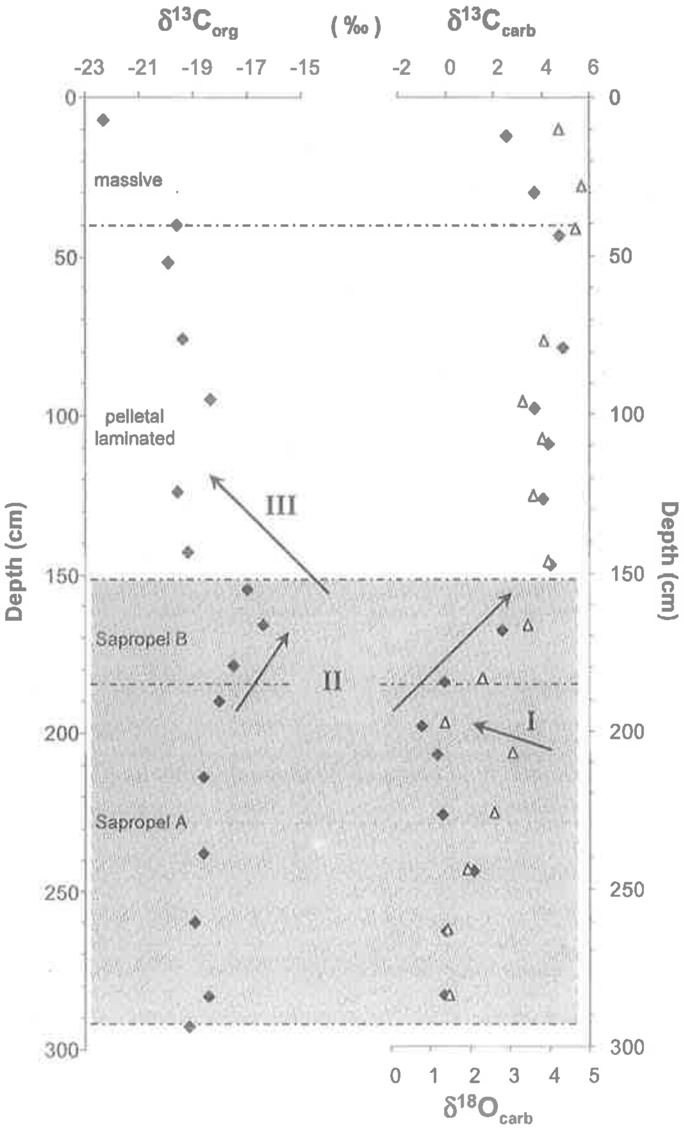

Figure 9.2: Comparison of $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$ (◆) and $\delta^{18}O_{carb}$ (△) in the NSL1 core. I) A marked negative excursion in $\delta^{18}O$ is interpreted as evidence of a freshening episode toward the end of Sapropel A deposition. II) The increase of all three isotopic parameters is attributed to the photosynthetic and evaporitic removal of ^{12}C and ^{16}O from the aqueous reservoir during deposition of Sapropel B. III) A decrease in $\delta^{13}C_{org}$ suggests an enhanced contribution of bacterial biomass to the sediments during deposition of the pelletal laminated unit. See text for further discussion.

interpretation would be that the $\delta^{13}C_{carb}$ decrease results not so much from a drop in productivity, but rather from an increase in respiration or oxidation of previously deposited ^{13}C-depleted organic carbon. However, enhanced meteoric input typically induces stratification in a water body, which can promote hypolimnic organic matter preservation. The $\delta^{13}C_{carb}$ and $\delta^{18}O$ data of Edwards et al. (2006) were obtained from benthic ostracods, and therefore reflect changes in the hypolimnion. The simultaneous decrease of $\delta^{13}C_{carb}$ and $\delta^{18}O$ recorded in authigenic carbonates of the present study reflects conditions in the epilimnion. Therefore, in combination the two studies indicate that the entire water column freshened at this time. It is here suggested that enhanced meteoric input was accompanied by wind-induced mixing that returned $^{12}CO_2$ released via organic matter degradation in the hypolimnion back into the epilimnion and thus caused the slight mid-sapropel decrease in $\delta^{13}C_{carb}$ (<0.7‰) (Figure 9.2). Indeed, the degree of ostracod varve ornamentation observed by Edwards et al. (2006) implies that the bottom waters of NSL were well oxygenated during sapropel deposition, which suggests that any stratification in the system was weak and could be easily broken down by a mechanism such as wind shear.

The subsequent increase in $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$ and $\delta^{18}O$ implies that there was some perturbation to the hitherto apparently steady-state lacustrine system, and closely corresponds to the transition from Sapropel A into the organically leaner Sapropel B. At this transition point in the lake's history some geochemical threshold was surpassed. The lower TOC values of Sapropel B initially suggest that the isotopic evolution of the lake waters did not result from increasing productivity. However, TOC content can be diluted by an increase in mineral matter (Figure 9.3). Therefore, the lower TOC values in Sapropel B may simply be a reflection of increased carbonate precipitation resulting from productivity-induced CO_2 drawdown. They need not preclude enhanced productivity as the cause of the isotopic enrichment evident in Sapropel B. More accurate information on the secular variability of organic carbon delivery to the sediments would likely be given by mass accumulation rates, which are expressed as mass of TOC per unit of lake-bottom area per unit of time, typically mg cm^{-2} y^{-1} (Meyers and Teranes, 2001). However, these are difficult to calculate accurately because of our poor understanding of how the topography and area of the lake floor has changed as this shallow basin gradually filled with sediment (Warren, 1990).

Within the overlying laminated unit of NSL, $\delta^{13}C_{carb}$ and $\delta^{18}O$ remain approximately steady at 4.4 ± 0.4 and 3.9 ± 0.5‰, respectively. However, $\delta^{13}C_{org}$ values initially decrease by ~2.5‰ across the transition from Sapropel B into the laminated unit before averaging out at –19.4 ± 0.5‰ (Figure 9.2). This negative isotopic shift toward the end of sapropel deposition may be evidence for anaerobic respiration of organic carbon producing ^{13}C-depleted methane and CO_2. Subsequent incorporation of this ^{13}C-depleted carbon by methanotrophic and chemoautotrophic microbial biomass is recorded by a trend of $\delta^{13}C_{org}$ depletion in the sediments, whilst the bicarbonate pool and carbonate precipitates exhibit the opposing trend of ^{13}C-enrichment (Talbot and Kelts, 1990; Hollander and Smith, 2001). The apparent decoupling of $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ in NSL suggests the existence of a stratified water column in which the contribution of microbial biomass to the hypolimnion and sediments was significant enough to impart a negative isotopic shift to the $\delta^{13}C_{org}$ profile whilst the near-vertical $\delta^{13}C_{carb}$ profile reflects steady state conditions in the epilimnion.

Regardless of the lack of opposing trends in the $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ profiles (Figure 9.2), bacterial processes are implicated by the carbon isotopic signature of the laminated unit. As outlined in section 2.2.2, bacterial methanogenesis is associated with strong kinetic isotope fractionation and results in markedly positive $\delta^{13}C_{carb}$ values (Figure 2.4). On the contrary, bicarbonate formed from the carbon liberated via sulphate reduction inherits the original isotopic composition of the organic matter (Talbot and Kelts, 1990). Repeated bands of black sulphide-rich sediment throughout the laminated unit of NSL, as well as the distinct smell of H_2S gas during core extraction, indicate that bacterial sulphate reduction has taken place in these sediments. However, an elevated mean $\delta^{13}C_{carb}$ value of 4.4 ± 0.4‰ for the laminated unit suggests that bacterial methanogenesis has been the dominant process of organic matter degradation in this interval. Therefore, sulphate reduction must have acted, at least periodically, to deplete sulphate levels to the point where bacterial methanogenesis was triggered.

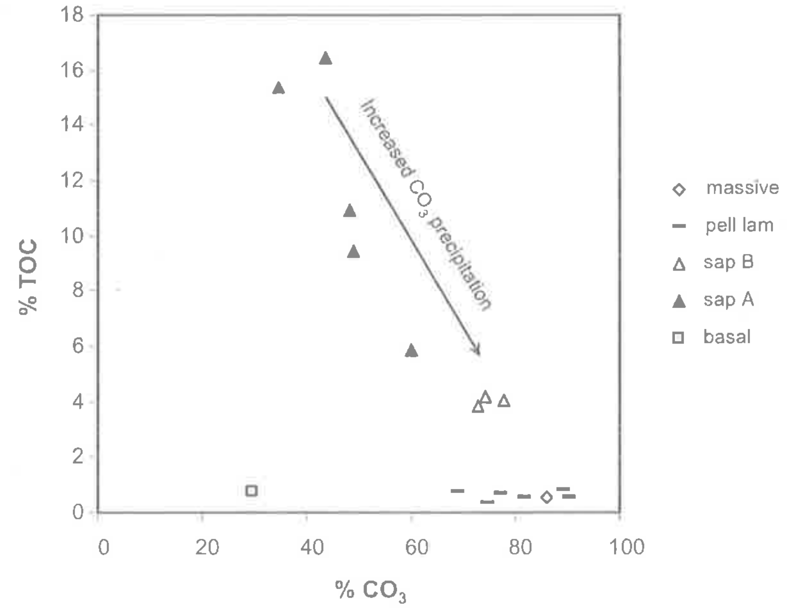

Figure 9.3: Cross-plot of percent TOC versus percent carbonate for NSL. In sediments with TOC >2%, the two components co-vary suggesting that organic matter was diluted as the rate of carbonate precipitation increased.

The negative isotopic shift recorded by both the organic and inorganic carbon pools in the massive unit of NSL indicates ^{13}C-depletion in the DIC. Such a depletion could result from increased oxidation of biogenic methane at the oxic/anoxic interface, which by now was located well within the photic zone (Hollander and Smith, 2001).

Old Man Lake

$\delta^{18}O_{carb}$ and $\delta^{13}C_{carb}$ show a more significant correlation for OML's lacustrine sediments ($R^2=0.5458$) than for the entire sedimentary sequence ($R^2=0.0043$: Figure 9.4). The former correlation is negative, which indicates that, unlike NSL, periods of higher evaporation do not coincide with increased levels of productivity in OML. Also, the slope of the line of best fit is shallow in comparison to that for NSL. Large variations in $\delta^{13}C_{carb}$ are accompanied by only small shifts in $\delta^{18}O$. Clearly, the secular isotopic variability within the OML sedimentary succession records the impact of driving forces different from those in NSL. In OML, the observed variations of $\delta^{18}O$ and $\delta^{13}C_{carb}$ do not reflect the continued evaporative concentration of a hydrologically isolated, shallowing water body because neither isotopic parameter increases steadily up-section. Rather, both display marked fluctuation. Obviously other environmental factors (e.g. water temperature, primary productivity, bacterial activity) have acted to influence the isotopic evolution of this small, perennial coastal lake. However, the small number of lacustrine samples ($n = 6$) taken for $\delta^{18}O$ and $\delta^{13}C_{carb}$ analysis precludes detailed interpretation of these effects within this system.

The much slower rate of lacustrine sediment accumulation in OML means that a greater time span is represented by each standard sample thickness[9]. This artefact of sampling hinders the detail and/or validity of any subsequent environmental interpretation. Of even more significance in the present study is the mismatch between depths at which samples were taken for organic and inorganic isotopic analysis. Even a slight mismatch could represent 10s to 100s of years. Therefore, comparison of the sparse carbonate and organic carbon isotopic data sets permits only provisional interpretation.

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[9] Here a 1 cm-thick sample size represents ~25 years of sapropel deposition and ~50 years of massive unit accumulation (refer to Table 7.2).

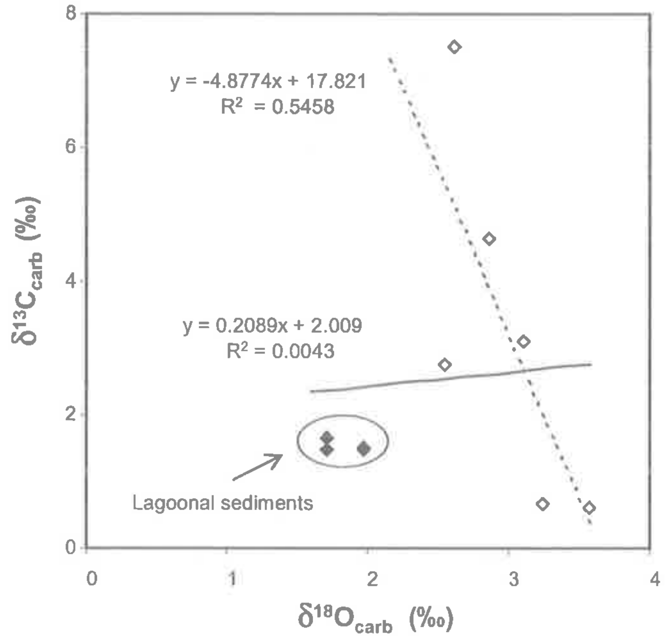

Figure 9.4: Cross-plot of $\delta^{13}C_{carb}$ versus $\delta^{18}O_{carb}$ (vpdb) in OML. The values display no correlation if considering the entire sedimentary sequence (solid line). The correlation strengthens if considering only sediments deposited since isolation of the depocentre from the local back-barrier lagoon and the onset of truly lacustrine conditions (◇, dashed line). Large $\delta^{13}C$ variations are associated with small changes in $\delta^{18}O$, implying that productivity is a more significant influence on the isotopic evolution of this lake than is evaporation. Also, in contrast to NSL, the correlation is negative indicating that in OML high levels of productivity are associated with fresher conditions, and low levels of productivity with increased evaporation.

The lagoonal unit of OML displays a distinct uniformity in its $\delta^{18}O$ and $\delta^{13}C_{carb}$ signatures (Figure 9.5). An increase in $\delta^{18}O$ from 1.8‰ in the lagoonal unit to 3.0‰ in the overlying lacustrine sediments is considered primarily a reflection of the isolation of the depocentre from the marine system (~0‰) and the shift to a groundwater-controlled hydrology. Stratigraphic changes in isotopic composition can reflect changes in the relative abundance of carbonate components (Leng and Marshall, 2004). Therefore, the shift from aragonite to calcite mineralogy across the lagoonal-lacustrine boundary may be partially responsible for the $\delta^{18}O$ increase. However, subsequent isotopic variations throughout the entire lacustrine succession and within each individual sedimentary unit do not correspond to mineralogical changes.

A progressive ^{13}C-enrichment of epilimnic DIC is indicated by an increase of $\delta^{13}C_{org}$ values through the sapropelic interval. A concurrent rise in $\delta^{13}C_{carb}$, which would identify increased productivity as the cause of the observed increase of 2.3‰ in $\delta^{13}C_{org}$, is only displayed over the lower part of the sapropelic interval. Thus, increased productivity during the build-up to sapropel formation is implied, but not conclusively demonstrated by the available data. A subsequent decrease of $\delta^{13}C_{carb}$ at the transition into the sapropel interval could denote the impact of organic matter decay and ^{12}C-recycling in this increasingly productive system.

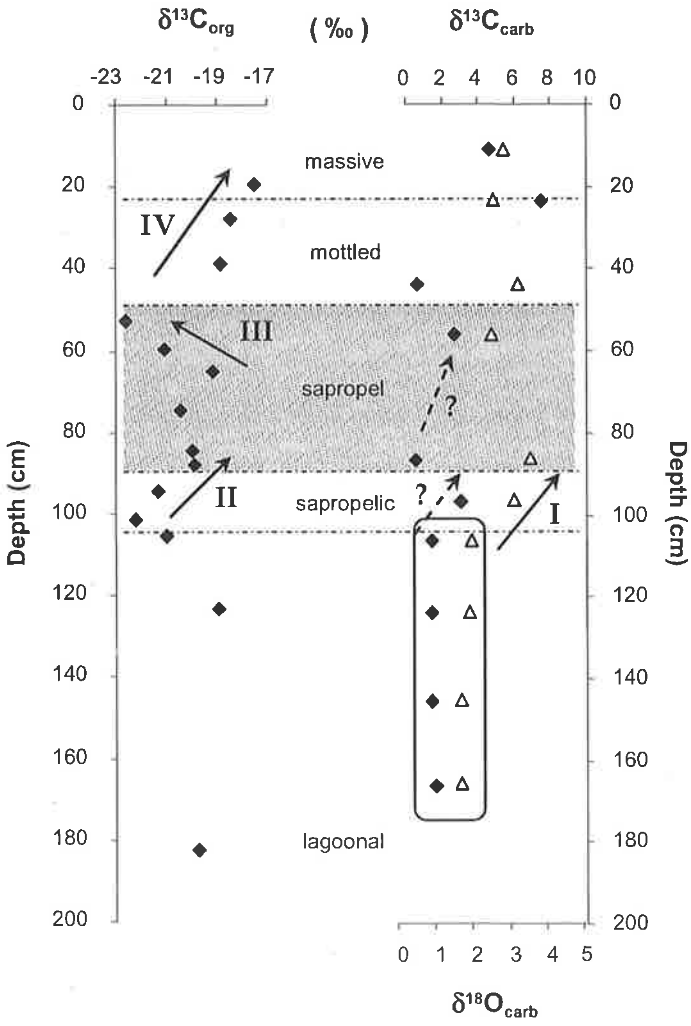

Figure 9.5: Comparison of $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$ (◆) and $\delta^{18}O_{carb}$ (△) in the OML1 core. I) An increase in $\delta^{18}O$ likely reflects the isolation of the lake from the marine system. II) A positive shift in $^{13}C_{org}$ (and questionably in $\delta^{13}C_{carb}$) through the sapropelic interval may imply an increase in aquatic productivity during deposition of this unit. III) A decrease in $\delta^{13}C_{org}$ (and questionable $\delta^{13}C_{carb}$ increase) suggests an amplified contribution of anaerobic bacterial biomass to the hypolimnion during the latter stage of sapropel deposition. IV) This positive shift in $\delta^{13}C_{org}$ reflects a return to a largely photoautotrophic biomass as sapropel deposition ceased. See text for further discussion.

A 3.4‰ decrease in $\delta^{13}C_{org}$ through the upper half of the sapropel interval is interpreted as an amplified contribution of anaerobic bacterial biomass to the sediments during the latter period of sapropel deposition, as was noted and discussed previously for NSL. This inference cannot be substantiated by a concurrent increase in $\delta^{13}C_{carb}$ due to the scarcity of such data for the OML sapropel. However, as $\delta^{13}C_{carb}$ is ~2‰ greater at the end of sapropel accumulation than at its start, an enhanced contribution of such bacterial biomass to these highly organic sediments is not ruled out. A study of sedimentary biomarkers would need to be undertaken to test this hypothesis (Killops and Killops, 2005).

The final notable carbon isotopic trend within the sedimentary succession of OML is an increase of ~5‰ in $\delta^{13}C_{org}$ upsection beyond the halt in sapropel accumulation. This increase accompanies the shift to slow accumulation of organically-lean sediments and is, therefore, not attributed to enhanced levels of productivity. Instead, the bulk of the observed increase in $\delta^{13}C_{org}$ is thought to represent a diminished eutrophic state in OML and the return to a predominantly oxygenic photoautotrophic biomass as sapropel deposition ceased. Indeed, factors such as changes in the predominant algal species, growth rate and water temperature have the potential to significantly affect the carbon isotopic signature of a primarily aquatic biomass (Mayer and Schwark, 1999). Therefore, a shift in aquatic versus terrigenous input need not necessarily be responsible for an increase in $\delta^{13}C_{org}$ of this magnitude. A positive shift in $\delta^{13}C_{org}$ within the mottled and massive intervals of the sedimentary succession is likely the result of preferential photosynthetic uptake of $^{12}CO_2$ from the semi-closed DIC reservoir within the epilimnion. As the $\delta^{13}C_{carb}$ data on these sediments are sparse and fluctuate somewhat erratically, this interpretation cannot be proven. However, as the massive unit is comprised almost entirely of *C. striata* remains, there is a high probability of biogenic calcite contamination of the bulk $\delta^{13}C_{carb}$ data, and hence the results from this sedimentary unit are best omitted from further interpretation.

Lake Amy

LA is effectively the surface expression of a perched water table and, as it was never directly connected to the marine system, secular variations in the isotopic composition of its carbonates must reflect internal lake processes. The lowermost two-thirds of the lower sapropel interval display steady $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values that average 1.2 and 3.3‰, respectively. $\delta^{13}C_{carb}$ increases markedly across the transition into the overlying laminated interval, representing a distinction between the sedimentary units rather than a steady increase up-section. As there is no parallel change in $\delta^{18}O$, this increase of $\delta^{13}C_{carb}$ cannot be due to evaporation alone. Moreover, it coincides with a slight drop in TOC, which could be interpreted as a result of decreased aquatic productivity. However, the steady increase in $\delta^{13}C_{org}$ through the lower sapropel interval precludes the likelihood of bacterial input to the sediments being responsible for the observed enrichment of ^{13}C in the coeval carbonate (Figure 9.6). Instead, the $\delta^{13}C_{org}$ increase accords with the process of photosynthetic removal of ^{12}C from the DIC reservoir that accompanies conditions of elevated aquatic productivity, thus leaving a ^{13}C-enriched DIC pool for subsequent assimilation by primary producers (Hayes, 1993; Meyers, 1997). Also, isotopic discrimination toward ^{12}C decreases with diminishing CO_2 availability (Laws et al., 1995; Lücke et al., 2003). Therefore, some of this $\delta^{13}C_{org}$ increase may be a reflection of reduced isotopic fractionation associated with intense photosynthetic DIC uptake during sapropel formation.

Such increased levels of productivity cause disequilibrium in the bicarbonate system and can therefore promote calcite precipitation within the epilimnion (McKenzie, 1985). As mentioned above, the observed drop in TOC need not actually indicate decreased aquatic productivity during deposition of the laminated interval. Indeed, the significant inverse correlation between percent TOC and carbonate ($R^2=0.727$) in LA implies that dilution of one sedimentary component by the other is real (Figure 9.7). This inverse relationship between organic and inorganic sedimentary carbon results from conditions within both the water column and the sediments. Decomposition of buried organic matter lowers the pH of interstitial waters, thus promoting carbonate dissolution within organic-rich sediments (Dean, 1999). Therefore, the more rapid rate of accumulation of the laminated interval relative to the lower sapropel could result from either increased carbonate deposition within the laminated interval and/or increased carbonate dissolution within the sapropel.

The different relative amounts of organic matter and carbonate preserved within the sapropel and the laminated interval suggest some change in lacustrine conditions between deposition of the two sedimentary units. It could be that organic matter was produced year-round during sapropel formation, but only seasonally or episodically during accumulation of the laminated interval. Under the conditions of year-round organic matter production and its subsequent degradation, the build up of organic acids may have reached levels capable of promoting carbonate dissolution within the sediments that become sapropel. In contrast, the overlying organic-rich, finely laminated sediments may

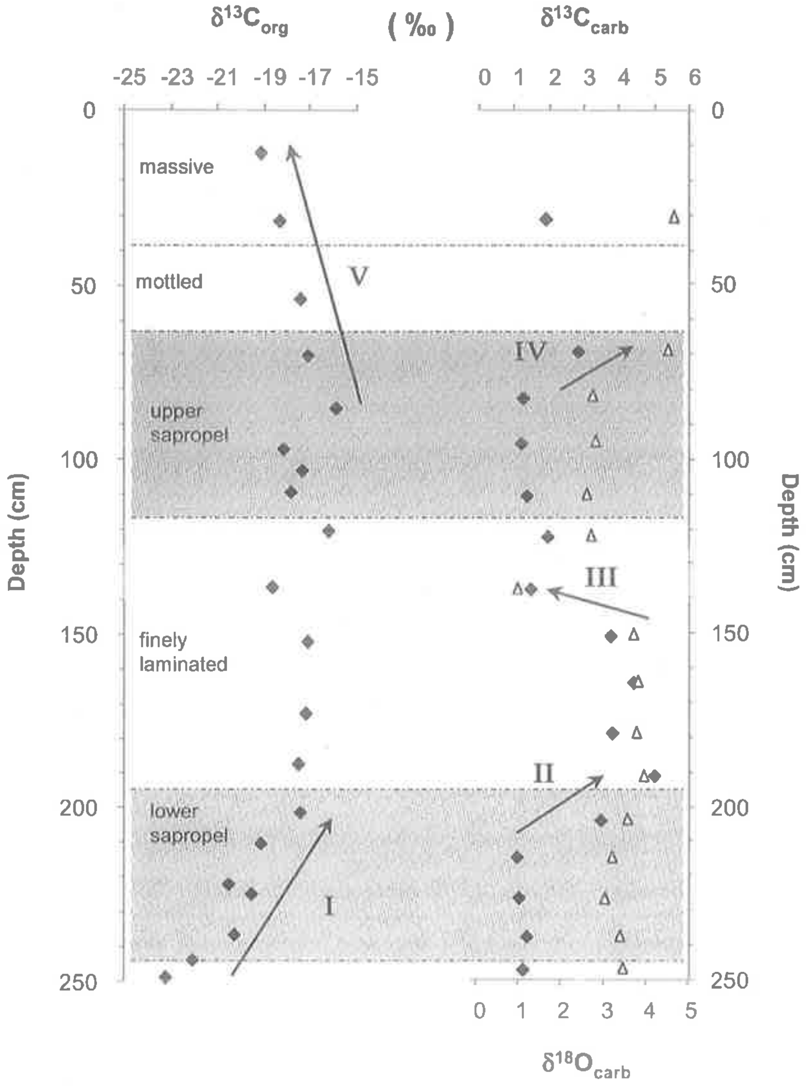

Figure 9.6: Comparison of $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$ (◆) and $\delta^{18}O_{carb}$ (Δ) in the LA1 core. I) The $\delta^{13}C_{org}$ increase through the lower sapropel is here suggested to result from continued photosynthetic ^{12}C uptake during sapropel deposition. II) An increase in $\delta^{13}C_{carb}$ through the upper sediments of the lower sapropel reinforces the interpretation of the preceding trend in $\delta^{13}C_{org}$. III) A freshening episode is implied by a marked decrease in $\delta^{18}O$, coincident with decreases in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$. IV) This increase in $\delta^{13}C_{carb}$ through the upper sediments of the upper sapropel results from photosynthetic ^{12}C uptake. V) A gradual decrease in $\delta^{13}C_{org}$ may reflect the preferential degradation of ^{13}C-enriched organic matter components. See text for further discussion.

represent conditions of enhanced seasonality as well as anoxicity at and below the sediment-water interface. Indeed, the relatively ^{15}N-depleted values of these sediments are indicative of increased nitrogen fixation and enhanced anoxia during deposition of this laminated interval (Libes and Dueser, 1988). The anoxic conditions are likely a consequence of the preceding sapropel formation, during which large amounts of organic matter degraded beneath a stratified water column. Once anoxia was established, organic matter degradation would have decreased, thus contributing to reduced carbonate dissolution within the laminated sediments.

A ~2.5‰ drop in $\delta^{18}O$ toward the top of the laminated unit is interpreted as a significant freshening episode. The concurrent drop in both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ at this depth suggests that the ^{18}O-depletion represents an actual event in LA, rather than being an erroneous data point (Figure 9.6). This interpretation is reinforced by the fact that $\delta^{18}O$ above this point does not return to the values of the underlying sediments.

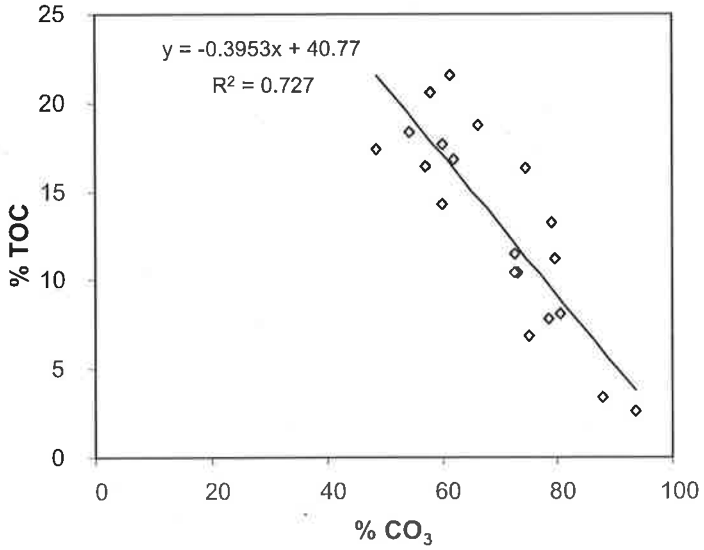

Figure 9.7: Cross-plot of percent TOC versus percent carbonate for LA showing the inverse relationship between the two sedimentary components. One is clearly diluted by the other as organic matter and carbonate accumulation rates vary.

The coincident decrease in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ at this level indicates some recharging of the lacustrine DIC reservoir with the lighter carbon isotope. This could be via either an increase in respired $^{12}CO_2$, or the influx of isotopically light soil-derived DIC. In NSL, a freshening and mixing of the water column and the return of respired organic carbon to the epilimnion was invoked to explain a mid-sapropel decrease in $\delta^{18}O$ and $\delta^{13}C_{carb}$. A similar mechanism could be responsible for the isotopic depletion observed in LA. Indeed, nitrogen recycling associated with such a mixing of the water column and the return of nutrients to the epilimnion could have been enough to trigger the subsequent sapropel deposition in LA.

Temporary oxygenation of the sediment-water interface is suggested by a 5 cm-thick band of pelletal sediments at 150 cm-depth in the LA core, implying the presence of grazers at the lake floor, coincident with the observed isotopic depletion. The preferential digestion of nitrogen-rich proteinaceous planktonic material by these grazers could contribute to the increase in C/N ratios evident at this depth in the sedimentary succession (Table 6.1). However, such a marked increase (from ~11 to ~20) is typically related to a change in organic matter source and may thus reinforce the argument for some influx of soil at this time. Deposition of the uppermost sapropel could have been initiated by such an influx. Alternatively, it could have been triggered by the recycling of nutrients within the lacustrine system. Regardless, the preceding drop in $\delta^{18}O$, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ is evidence of a perturbation to the lacustrine system at this time. Either the delivery of soil organic matter or wind-induced mixing of the water column, in association with enhanced meteoric input, could have supplied sufficient ^{13}C-depleted DIC to explain the observed negative isotopic excursion as well as the nutrients required to subsequently promote sapropel deposition. The correct mechanism cannot be identified from the present data set. In fact it could be combination of the two, yet another reminder that palaeolimnologic studies are best served by the application of as many proxies as possible.

Towards the top of the upper sapropel unit, as at that of the lower sapropel, $\delta^{13}C_{carb}$ increases markedly (Figure 9.6). In the lower sapropel interval, a concurrent increase in $\delta^{13}C_{org}$ clearly indicates $^{12}CO_2$ drawdown associated with enhanced productivity as the cause of the observed rise in $\delta^{13}C_{carb}$. However, no such shift in $\delta^{13}C_{org}$ is evident in the upper sapropel interval. Rather, the upper 80 cm of the LA core displays a steady decline in $\delta^{13}C_{org}$ (discussed below). As for the transition out of sapropel deposition in both NSL and OML, these opposing carbon isotopic trends suggest an enhanced contribution of bacterial biomass to the sediments during the latter part of sapropel formation. Regardless, the $\delta^{13}C_{carb}$ increase in the upper sapropel of LA is also attributed to photosynthetic ^{12}C-uptake during sapropel formation. The presence of a 6 cm-thick weakly cemented calcitic hardpan across the uppermost portion of the upper sapropel is indicative of biologically-induced calcite precipitation associated with enhanced aquatic productivity. An increase of 2‰ in $\delta^{18}O$ at the top of the upper sapropel is interpreted as a result of the amplified influence of evaporation on carbonate deposition within the increasingly saline waters of this shallowing lake.

A steady decline in $\delta^{13}C_{org}$ across the upper 80 cm of the LA sedimentary succession is interpreted as primarily due to the preferential degradation of relatively ^{13}C-enriched carbohydrates and proteins within a decreasingly productive lacustrine setting. A slight drop in $\delta^{13}C_{carb}$, from the upper sapropel into the overlying organically-lean sediments, could be a reflection of enhanced organic matter respiration; however this conclusion cannot be substantiated from the presently available data on these sediments.

9.2 Synthesis

The observed secular variations in sedimentary $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$, at least in part, reflect changing productivity levels in these three shallow coastal lakes. However, changes in nutrient status and productivity do not necessarily yield linear shifts in $\delta^{13}C_{org}$ throughout a lake's history (Brenner et al., 1999). Indeed, variable levels of anoxia, aerobic respiration and microbially-mediated carbon cycling all seem to have influenced the isotopic evolution of these lakes, as summarised below.

North Stromatolite Lake

The carbon isotopic homogeneity of Sapropel A reflects a steady state system in which organic matter production and accumulation continued reasonably uninterrupted. A mid-sapropel freshening episode triggered an increase in aerobic respiration of organic carbon and the return of ^{12}C from the hypolimnion to the epilimnion via the breakdown of hitherto weak lacustrine stratification. Subsequent ^{13}C-enrichment of the DIC reservoir reflects continued photosynthetic ^{12}C-uptake during sapropel formation. This $^{12}CO_2$ drawdown promoted an increase in carbonate deposition, thus leading to the lower TOC content of Sapropel B.

The laminated unit of NSL represents the shift to a new steady state, in which the waters were likely stratified, and productivity was low and dominated by anaerobic microbial activity, chiefly methanogenesis. Distinctly elevated $\delta^{18}O$ values reflect an increased evaporative influence on the sediments of this shallowing lacustrine system. A negative carbon isotopic shift in the massive unit reflects the oxidation of biogenic methane and the release of isotopically light CO_2 back into the photic zone during deposition of these recent sediments.

Old Man Lake

Unlike NSL and LA, OML is unique in that conditions of enhanced productivity are apparently associated with freshening, rather than with increased evaporation. This could be a reflection of the influence of different environmental factors (e.g. water temperature, salinity, turbidity) on the isotopic evolution of this lake. Alternatively, it could be a result of the slower sediment accumulation rate in OML.

The available isotopic data clearly record the isolation of the lake from the marine system and the shift to a groundwater dominated hydrology. Marked ^{13}C-enrichment of the DIC reservoir within the lacustrine system is attributed to photosynthetic ^{12}C-uptake during the build up to sapropel formation. As noted for NSL, a negative carbon isotopic shift toward the top of the sapropel interval reflects the increased contribution of ^{13}C-depleted anaerobic bacterial biomass to the sediments of this increasingly eutrophic system. A return to the predominance of oxygenic photoautotrophic biomass and continued photosynthetic ^{12}C-uptake is evident in a marked positive carbon isotopic shift in the sediments subsequent to sapropel deposition.

Lake Amy

As evident in both NSL and OML, an increase in $\delta^{13}C_{org}$ during sapropel formation reflects photosynthetic removal of ^{12}C from LA's DIC reservoir. Here, this $^{12}CO_2$ drawdown apparently produced sufficient disequilibrium in the bicarbonate system to promote carbonate precipitation. This diluted the organic matter and led to a rapid rate of accumulation of the finely laminated interval. Large amounts of organic matter degradation associated with the preceding sapropel formation promoted the development of bottom water anoxia, which subsequently decreased organic matter degradation and, in turn, carbonate dissolution. Generally, anoxia is associated with organic-rich sediments. Thus, it is significant that the interplay between organic matter and carbonate deposition and dissolution results in anoxia being associated with the laminated interval, rather than the most organic-rich (sapropel) sediments in LA.

A freshening episode is coincident with some ^{12}C recharge of the DIC reservoir. This could have been the breakdown of lacustrine stratification and the return of $^{12}CO_2$ from the hypolimnion to the epilimnion, or could have been an influx of isotopically light soil-derived DIC. Either possibility would have also recharged the system with available nutrients, thus promoting deposition of the upper sapropel.

Toward the cessation of this second phase of sapropel deposition, a decrease in $\delta^{13}C_{carb}$ and the presence of a thick fragmented hardpan indicate that preferential photosynthetic uptake of $^{12}CO_2$ again reached levels capable of promoting biologically-induced carbonate precipitation.

The decline of $\delta^{13}C_{org}$ through the organically-lean mottled and massive units reflects enhanced degradation of organic matter in this decreasingly productive, shallowing lacustrine system. Indeed, mottled intervals overlying sapropel indicate the activity of burrowing metazoa (Taylor et al., 1998). Such bioturbation implies a re-establishment of oxic conditions at the lake floor, and here reflect the shift to a less productive system and the breakdown of productivity-induced hypolimnic anoxia.

Since the Coorong lakes are wholly groundwater-fed, amplified surface water flow arising from increased rainfall in the local catchment cannot have carried in the nutrients that triggered deposition of their sapropel units. In tributary-fed environments a wetter climate increases the inflow of nutrient-rich freshwater, which enhances aquatic primary productivity and leads to the deposition of sapropel intervals (e.g. Calvert et al., 1987, 1992; Martinez-Ruiz et al., 2000). It can also result in a significant influx of terrigenous plant detritus (e.g. Bouloubassi et al., 1999; Tolun et al., 2002; Menzel et al., 2004). However, the three lakes of the present study receive no fluvial input and probably only minor surface runoff from the surrounding dunes. The evidence for a mainly aquatic origin of their organic matter accords with this type of environmental setting. Any terrestrial contribution to both the organic and mineral components of the sediments within these groundwater-fed lakes is likely to be minor and entirely aeolian.

As coastal locations are commonly subject to strong winds, and the presence of linear dune fields and playa-lunette systems are evidence for aeolian transport in the region (e.g. Stephens and Crocker, 1946; Rogers, 1995), these three lakes were almost certainly exposed to the periodic influence of dust and aerosols (cyclic salt). The prevailing wind direction in the region is currently south-southwesterly resulting from the passage of mid-latitude anticyclonic high-pressure systems (summer) and cold fronts associated with cyclonic low-pressure systems (winter). Low, crescent-shaped lunette ridges border the eastern shore of many modern playa lakes across southeastern South Australia (Twidale et al., 1983), which suggests that the current wind regime has been in place for some time.

Although there is much evidence for aeolian dust being able to travel long distances (e.g. Hesse, 1994; Simonson, 1995; Zhao et al., 2003) often it is related to extreme and isolated storm events (e.g. Lourensz and Abe, 1983). Nonetheless, such events could be responsible for episodic transport of mineral matter and nutrients that could trigger periodic increases in lacustrine productivity. Alternatively, nutrients could be supplied biotically. Indeed, large densities of migratory waterfowl can represent a major input of nitrogen and phosphorous to some lakes (Hutchinson, 1950 as cited in Wetzel, 1983) and the Coorong today is home to much birdlife. However, the possibility of excrement from bird and fish stocks being responsible for the high productivity events represented by sapropel intervals cannot be quantified by the present data set. Thus, this chapter instead discusses the relationship between secular lacustrine productivity changes identified in the present study and previously recognized dust transport and climate change events at regional and global scales.

10.1 The Holocene in Southeastern Australia

The peak of the Holocene marine transgression was reached at ~6 ka (von der Borch, 1979; Belperio, 1995) and corresponds with the onset of sapropel deposition in NSL. Here, at the north of the ephemeral Coorong lagoon, this 'sapropel event' (6000-4700 yr BP) coincides with a prolonged warm period and maximum in effective precipitation (EP) that prevailed across southeastern Australia between 7000 and 5000 yr BP (Wasson and Donnelly, 1991; Shulmeister, 1999). Indeed, high levels of peat formation at Boat Harbour Creek in the Mount Lofty Ranges (7000-5000 yr BP: Bickford and Gell, 2005), warm water temperatures at Blue Lake, Mount Gambier (7000-5000 yr BP: Leaney et al., 1995) and low water salinities at Lake Leake, southeast South Australia (6900-5000 yr BP: Dodson, 1974) and West Basin Lake, western Victoria (7000-6000 yr BP: Gell, 1998) testify to the existence of generally warm, wet conditions in the region (Figure 10.1). Along with that at NSL, sapropel deposition near Lake Albert, close to the mouth of the River Murray (6900-5800 yr BP) and in two unidentified lakes adjacent to the Coorong Lagoon (~8000 and ~6600 yr BP) coincides with this early to mid-Holocene palaeoclimatic optimum (von der Borch and Altmann, 1979). Thus, it seems that sapropel deposition along the Coorong coastal plain may have been associated with a period of humid conditions in the region.

Low $\delta^{15}N$ values (1-3‰) likely suggest that there was a significant contribution of nitrogen-fixing biota (e.g. cyanobacteria) to the organic matter pool during the first stage (~half) of sapropel deposition in NSL. As nitrogen-fixing cyanobacteria flourish in warm, nutrient-rich waters and during periods of maximum water column stability (Talbot, 2001) these ^{15}N-depleted values are thought to reflect relatively uniform climatic conditions with little seasonal contrast and low wind stress. As such, these nitrogen isotope data provide evidence supporting the early to mid-Holocene period of relatively stable humid conditions that is already documented for southeastern Australia.

Rising $\delta^{15}N$ values imply an increasing contribution from nitrogen-assimilating phytoplankton as sapropel deposition continued. This shift in the organic matter assemblage is likely related to some change in the lacustrine conditions. It could be a reflection of diminishing light availability within the water column as can be brought about during periods of eutrophication. Indeed, the increase in $\delta^{13}C_{org}$ through Sapropel B has been interpreted herein as a result of increased primary productivity, and could thus reinforce the concept of water column eutrophication during sapropel formation. Alternatively, the change in conditions may be cooling of the NSL water column in line with that reported for Blue Lake, Mount Gambier, between ~5000-4000 yr BP (Leaney et al., 1995). Further clarification of the specific environmental parameter(s) responsible for the change in organic matter assemblage implied by the increase in $\delta^{15}N$ throughout the NSL sapropel is beyond the scope of the present study.

A marked freshening episode, implied by a negative shift in $\delta^{18}O$ at ~200 cm depth, could be a manifestation of reduced climatic stability and the transition toward a more variable late Holocene climate. Large storm events, such as that which may have triggered this freshening episode, could certainly lead to significant cooling of the water column, as well as increased lake water turbidity. By itself, this $\delta^{18}O$ shift provides no additional information on the environmental conditions responsible for the mid-sapropel $\delta^{15}N$ shift. Indeed, rather than reflecting a large-scale storm event, the negative $\delta^{18}O$ shift could actually reflect the final isolation of NSL from the open Coorong lagoon. Although Warren (1990) interprets the onset of sapropel deposition as marking the transition from estuarine to perennial lacustrine conditions, recent diatom analysis of the NSL sapropel suggests that estuarine conditions may have persisted for longer than previously thought and even for much of the period of sapropel deposition (D. Haynes, pers. comm.). As at Lake Alexandrina (Barnett, 1994) the transition from marine-brackish to oligosaline-freshwater conditions at NSL occurred 100s of years after the peak of the Holocene marine transgression.

A significant shift toward aridity commencing at ~5000 yr BP has been well documented in various palaeolimnological studies across southeastern Australia (e.g. von der Borch & Altmann 1979; Bowler 1981; Ahmad 1996; Dodson & Ono 1997; Stanley & De Deckker 2002). It was this decline in EP, also reflected in the level of Lake Keilambete in western Victoria (Figure 10.1), which appears to have halted deposition of organic-rich sediments in NSL. Such a decline in EP would have reduced the amount of carbonic acid that entered the lake water as rainfall and was available to buffer the alkaline groundwaters that charge NSL. This, in combination with the intense photosynthetic CO_2 drawdown by algal blooms that were eventually preserved as sapropel, perhaps increased the pH of the lake waters to such an extent that the lake was transformed into a poorly productive system dominated by carbonate precipitation. Indeed, the waters of the Salt Creek lake chain are presently hypersaline and characterised by elevated carbonate concentrations and high pH levels (Wright, 1999). High salinity and pH levels are known to trigger carbonate deposition (Mooney, 1997).

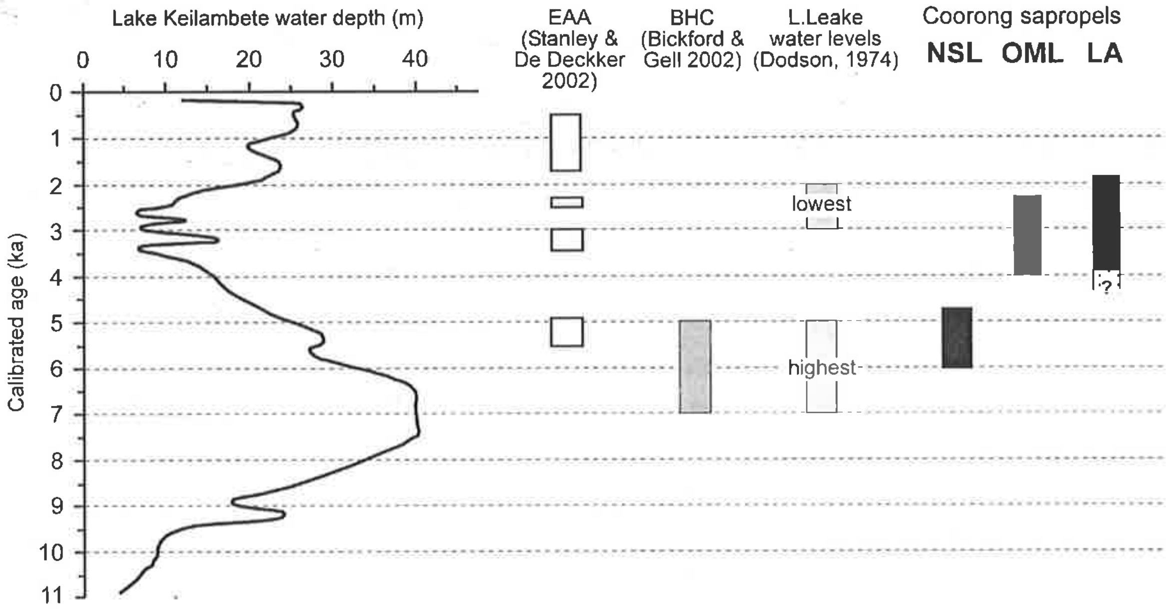

Figure 10.1: Comparison of periods of enhanced aeolian activity (EAA) at Blue Lake, Snowy Mountains, high levels of peat formation at Boat Harbour Creek (BHC), Mount Lofty Ranges, water levels at Lake Leake, southeastern South Australia and Lake Keilambete, western Victoria (modified from Bowler, 1981) with intervals of sapropel deposition at NSL, OML and LA.

The deposition of isotopically heavier carbonates in the NSL massive, laminated and Sapropel B units (relative to the underlying Sapropel A and basal units) suggests an increase in evaporative concentration of the water body over time. As increased evaporation is a result of higher water temperatures, increased windiness and low relative humidity, the reduction in NSL productivity levels since ~4700 yr BP is attributed to the shift to aridity that is already evident in numerous palaeoclimatic records from across southeastern Australia at about this time.

Regardless of this shift to aridity, subsequent 'sapropel events' are recorded in the sedimentary successions of OML (~4000-2200 cal yr BP) and LA (3900-1800 cal yr BP: Figure 10.1). This may suggest one of two things. Either the sapropels in these southern lakes were deposited during relatively arid times, thus differentiating them from sapropels associated with marine and deep-lake settings across the globe (e.g. Rossignol-Strick, 1985; Martinez-Ruiz, 2000; Tolun et al., 2002). Or, conditions were wet enough to maintain high levels of aquatic productivity in these (deeper, smaller) southern lakes at the same time as being too dry 100 km to the north at NSL. The latter possibility could result from poleward movement of the high-pressure system that dominates southern Australia's weather pattern. Indeed, a southern shift of the westerly maxima associated with this high pressure system is recorded in palynological data from a number of small islands south and east of New Zealand (McGlone, 2002) and likely culminated sometime between 8000 and 4000 yr BP (Wyrwoll et al., 2000). Vegetation at Lake Frome suggests that summer precipitation had significantly decreased in this part of South Australia by ~4500 yr BP (Luly, 1993). This timing coincides remarkably with the halt in sapropel deposition and probable EP decline at NSL. However, the lowest water stand at Lake Leake, which is situated closer to OML and LA, was not reached until ~3000 yr BP (Dodson, 1974). At Lashmars Lagoon, Kangaroo Island, an abrupt change in the diatom assemblage indicates a marked salinity increase at ~2500 yr BP (Gell et al., 2003). Thus, a latitudinal influence on the timing of an EP decline and the shift toward aridity across southeastern Australia is certainly conceivable. Sapropel deposition in the three shallow coastal lakes of the present study may be further evidence of this phenomenon.

At both NSL and LA, the halt in sapropel accumulation corresponds to a marked decrease in sediment accumulation rate. At OML, rapid deposition of the lagoonal unit prior to ~4000 yr BP greatly reduced the accommodation space available for lacustrine sediment over the remainder of the Holocene. The lacustrine sedimentary sequence of OML is relatively condensed (~55 cm) and does not display a marked reduction in sedimentation rate at the halt of sapropel deposition. The absence of a direct estuarine connection at LA resulted in a more gradual filling of that depocentre, and the preservation of an extended sedimentary sequence (~185 cm) in comparison to that of the equivalent 2000 years at OML. The resultant difference in information extractable from the two southern lakes is considerable. Hence, the remaining discussion is focussed on the similarities and differences between NSL and the southern lakes, rather than between OML and LA themselves.

The 'sapropel events' in all three lakes each partly overlap periods of enhanced aeolian input to Blue Lake in the Snowy Mountains of southeastern Australia (Figure 10.1). This correspondence of the Coorong lake 'sapropel events' with periods of aridification points toward aeolian dust as a possible trigger for sapropel formation (Mee et al., 2007). In the case of NSL, this likelihood is reinforced by the notable presence of albite, orthoclase, mica, kaolin and smectite (Appendix III), allochthonous siliciclastic components that suggest significant dust input to the lake during deposition of its sapropel. A likely source of such dust is the continental dunefield of the Mallee region, located due north of the Coorong coastal plain (Pell and Chivas, 1995).

Across Australia there is much evidence for a significant mid-Holocene change in climatic stability, in particular, for the onset of a more variable, ENSO-dominated climate at ~5000 yr BP (e.g. McGlone et al., 1992; Kershaw et al., 2002; Gagan et al., 2004). The rapidly fluctuating wet/dry periods of this late Holocene climatic regime tend to be recorded inconsistently by different proxies in a range of locations. It is likely that the absence of sapropel in NSL matching those deposited between ~4000 and ~2000 yr BP in the southern lakes is an example of this variability among Holocene palaeoclimatic records within southeastern Australia. In the case of the Coorong coastal plain it may be that lake geometry induces a different response to the mid-Holocene EP decline at NSL and the southern lakes. Indeed, the wide expanse of shallow water at NSL allows for greater exchange with the atmosphere that that at the smaller, deeper southern lakes. This, in combination with the possibility of the southern lakes receiving a greater proportion of freshwater input from southward migrating cold fronts, could have altered lacustrine conditions and surpassed some environmental threshold that prohibits sapropel deposition (e.g. salinity, alkalinity, pH) much more rapidly at NSL than in the southern lakes.

At OML and LA, sapropel deposition coincides with a period of generally low but rapidly fluctuating water levels at Lake Keilambete, as well as with the lowest water stand recorded in the sedimentary succession of Lake Leake (Figure 10.1). Thus, sapropel intervals in shallow, alkaline, hypersaline lacustrine settings are not necessarily indicative of a stable climate and relatively warm, wet environmental conditions. In fact, sapropel deposition in the coastal lakes of the present study may have been promoted by evaporation concentrating nutrients during low water stands, as well as by warming lake waters associated with the general shift to aridity in southeastern Australia. This being the case, the halt in sapropel deposition at OML and LA could indicate a return to either somewhat wetter or cooler conditions in the late Holocene. Although increasing water levels at Lake Keilambete support this possibility, there is no such increase at nearby Lake Leake. In fact, water levels at Lake Leake have remained relatively low after ~1360 yr BP (Dodson, 1974). The local proximity of Lake Leake to OML and LA suggests that the halt in sapropel deposition in the two Coorong lakes cannot be attributed to a sustained late Holocene rise in water level that acted to dilute nutrient concentrations. Instead, the cessation of sapropel deposition in these southern lakes may reflect reduced levels of aquatic productivity associated with a pH increase, as was previously suggested for NSL. Alternatively, the shallowing of these water bodies caused by gradual sediment infilling of these depocentres may have halted sapropel deposition by enhancing conditions of organic matter degradation. Shallower water bodies are less prone to stratification and thus allow for more oxidative exposure of sedimented organic matter, particularly in coastal settings where strong winds enhance turbulent re-suspension of bottom sediments. In fact, mottled intervals that overlie sapropel at both OML and LA testify to the burrowing action of bioturbating organisms and suggest that oxic conditions were re-established at the lake floor as sapropel deposition ceased (Taylor et al., 1998).

10.2 Global Context

The 'sapropel events' preserved in the sedimentary sequences of NSL, OML and LA each overlap periods of rapid climate change (RCC) recognised in an analysis of ~50 globally distributed Holocene palaeoclimatic records (Mayewski et al. 2004; Figure 10.2). The RCC intervals that correspond to the Coorong 'sapropel events' are characterised by low-latitude aridity and intensified levels of cooling and atmospheric circulation at high latitudes ('cool poles, dry tropics'). Thus, the sapropel intervals in the coastal lakes of the present study coincide with times of transition toward relatively arid conditions across the globe. Dust transport associated with these shifts to aridity may well have delivered essential nutrients such as silica, phosphate and iron to these coastal lakes, thereby enhancing aquatic productivity as a precursor to sapropel deposition. Indeed, the correspondence between the Coorong 'sapropel events' and periods of enhanced aeolian activity in southeastern Australia has already been noted (Mee et al., 2007).

The concurrence of Mayewski's arid RCC intervals and the Coorong 'sapropel events' highlights the variable palaeoenvironmental implications of sapropel deposition. Indeed, sapropel genesis in these shallow, groundwater-fed lakes differs remarkably from that of sapropels in marine and deep-lake settings across the globe. In the coastal lakes of the present study sapropel is associated with periods of global aridification, whereas in marine and deep-lake settings sapropel deposition tends to be associated with periods of climatic amelioration. These differences stem from the manner in which nutrients are predominantly delivered to the two types of environmental settings (aeolian versus tributary wash-in).

However, sapropel deposition is clearly driven by more than nutrient delivery. This is exemplified by the 'sapropel event' at NSL, which coincides with a well recognised period of generally warm, wet conditions in the region. This climatic amelioration likely contributed to warm lake water temperatures and pH levels. It seems to have been the combination of regionally influenced lacustrine conditions and increased aeolian input associated with global aridification that led to enhanced aquatic productivity in this shallow coastal lake, and eventually, sapropel deposition.

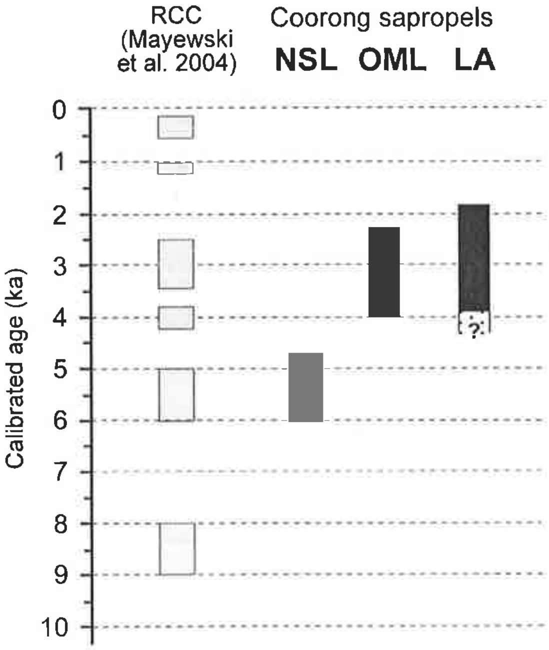

Figure 10.2: Correspondence between periods of rapid climate change (RCC) across the globe (Mayewski et al., 2004) and intervals of sapropel deposition in NSL, OML and LA.

CHAPTER 11: CONCLUSIONS

11.1 Timing of sapropel 'events' in the studied lakes

Modern water samples from OML and LA show that these two lakes are not in radioactive equilibrium with the atmosphere and that they are therefore subject to a reservoir effect resulting from the inflow of old radiocarbon in the groundwater of this limestone-dominated landscape. Reservoir-corrected radiocarbon ages were calculated for all three lakes through use of these modern water activities and by assuming reservoir effect constancy over time. However, apparent age inversions with depth in the sedimentary sequences of NSL and to a lesser extent OML indicate secular changes in the magnitude of the reservoir effect. The best possible estimates for the timing and duration of sapropel deposition within the three lakes of the present investigation are as follows:

In NSL, sapropel deposition commenced at ~6000 cal yr BP, lasted for ~1300 years and ceased at ~4700 cal yr BP. An OSL age at the base of the pelletal laminated unit provides a similar timing for the halt in deposition of organic-rich sediments. A single radiocarbon date from the pelletal laminated unit is spuriously old, and requires a larger reservoir correction than that which has currently been applied to make it chronostratigraphically consistent. This anomaly is interpreted as resulting from periodic evaporation of ephemeral NSL, thereby concentrating the reservoir of old carbon in the lacustrine basin.

A slight age inversion at the transition between lagoonal and lacustrine sediments in OML suggests that the lagoonal unit requires a smaller reservoir correction than that implied by present-day lake water sample activity. Application of a local marine reservoir correction to these lagoonal sediments provides the most chronostratigraphically consistent dates of ~4500-4000 cal yr BP. Episodic sapropel deposition recorded in the overlying lacustrine sediments of OML ceased at ~2200 cal yr BP.

The LA core represents ~3900 years of lacustrine sedimentation and displays no age inversions. The lower and upper gelatinous sapropelic intervals within the organic-rich mudstone were deposited at ~3900-3300 and 2600-1800 cal yr BP, respectively.

11.2 Origin of the sapropelic organic matter

C/N ratios suggest a mixed aquatic and terrestrial source for the organic matter in these lacustrine sapropels. However, their ^{13}C-NMR spectra are very similar to those published for phytoplankton, thus implying that the Coorong lacustrine organic matter is largely autochthonous. This reinforces the findings of previous organic geochemical studies that indicated an organic matter pool composed primarily of lacustrine photoautotrophs. Thus, the elemental and isotopic signatures of organic matter preserved in the Holocene sediments of these lakes are considered to primarily reflect changes in internal lacustrine conditions and processes, rather than alterations to the terrestrial ecosystem of their hinterland. Higher C/N ratios than those typical of algae and bacteria are interpreted as reflecting situations of either nitrogen-deficiency or a nutrient abundance, the latter promoting primary productivity in the epilimnion and leading to oxygen depletion in the hypolimnion and preferential degradation of nitrogen-rich proteinaceous organic matter. $\delta^{13}C_{org}$ values of around –20‰ reflect the photosynthetic uptake of bicarbonate by these aquatic biota and indicate variations in lacustrine productivity and respiration. $\delta^{15}N$ values provide information on changes in the phytoplankton and heterotroph populations that may in turn be related to changes in the trophic state of the lake waters (i.e. oligotrophic versus eutrophic).

11.3 The key to sapropel formation: productivity or preservation?

Secular variations in sedimentary $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ reflect at least in part, changing productivity levels in these three shallow coastal lakes. However, these shifts are not linear and it seems that variable levels of anoxia, aerobic respiration and microbially-mediated carbon cycling have influenced the isotopic evolution of these lakes. Although conditions of enhanced productivity are no doubt fundamental to the deposition of organic-rich sediments, no single key to sapropel formation can be ascertained from the present study. Instead, conditions that alter the extent of sapropel deposition and possibly contribute to reduced levels of lacustrine productivity are proposed.

At NSL, the carbon isotopic homogeneity of Sapropel A reflects a steady-state in which organic matter production and accumulation continued more or less uninterrupted. Progressive ^{13}C-enrichment of the DIC reservoir, triggered by a mid-sapropel freshening episode, reflects continued preferential uptake of $H^{12}CO_3^-$ by aquatic photoautotrophs during sapropel formation. This relentless bicarbonate drawdown by algal blooms promoted an increase in carbonate deposition, leading to the lower TOC content of Sapropel B. It also contributed to an increase in the pH of the lake waters and the eventual transformation of NSL into a poorly productive system dominated by carbonate precipitation. The organically lean laminated unit of NSL represents this shift to a new steady state, in which the waters were likely stratified, and productivity was low relative to anaerobic microbial activity, chiefly methanogenesis.

The slower rate of accumulation of the sapropelic sediments at OML results in a greater time span being represented by each standard sample thickness. As this artefact of sampling hinders the detail of any subsequent environmental interpretation, and there was also a mismatch between depths at which samples were taken for organic and inorganic isotopic analysis, only provisional interpretation of the sparse isotopic data was possible in the present study. The available data record the isolation of the lake from the marine system and the shift to a groundwater dominated hydrology. A negative (organic) carbon isotopic shift within the top of the sapropel interval reflects an increased contribution of ^{13}C-depleted methanotrophic and chemoautotrophic bacterial biomass to the sediments during this period of lacustrine organic enrichment. Sapropel deposition ceased as oxic conditions were re-established at the lake floor.

At LA, degradation of organic matter in the hypolimnion during deposition of the lower sapropel interval led to the development of bottom water anoxia. Under these conditions the rate of organic degradation and, in turn, carbonate dissolution decreased, promoting deposition of the finely laminated interval. Thus, contrary to numerous studies on sapropel genesis in other aquatic settings, this study links conditions of anoxia with the laminated interval, rather than with the most organic-rich (sapropel) sediments.

A freshening episode recharged LA with nutrients, or perhaps induced conditions that increased the availability of nutrients already within the system (via loss of stratification), and led to deposition of the upper sapropel interval. A mottled interval overlying this sapropel suggests that oxic conditions were re-established at the lake floor and is interpreted as reflecting the shift to a less productive system and the breakdown of productivity-induced hypolimnic anoxia

11.4 Palaeoenvironmental significance of the sapropels

Unlike sapropels deposited in tributary-fed marine and deep-lake environments, those preserved in shallow, groundwater-fed lakes on the Coorong coastal plain are not indicative of wet climatic conditions and the influx of nutrient-rich freshwater. The mainly aquatic origin of their organic matter accords with an environmental setting that receives no fluvial input, most likely only minor surface runoff from the surrounding dunes, and a minor predominantly aeolian terrestrial contribution

At the north of the ephemeral Coorong lagoon, the 'sapropel event' at NSL coincides with a prolonged warm period and a maximum in effective precipitation (EP) that prevailed across southeastern Australia between 7000 and 5000 yr BP. A significant shift toward aridity, commencing at ~5000 yr BP, appears to have halted deposition of organic-rich sediments in NSL. This EP decline, in combination with the intense photosynthetic drawdown of bicarbonate by algal blooms that were eventually preserved as sapropel, is thought to have increased the pH of perennial NSL to such an extent that it was transformed into a poorly productive system dominated by carbonate precipitation.

Regardless of this shift to aridity, subsequent 'sapropel events' are recorded in the sedimentary successions of OML and LA. The different timing of sapropel deposition in the three lakes of the present study is here suggested to be evidence for a latitudinal influence on the timing of an EP decline and the resultant shift toward aridity across southeastern Australia. Alternatively, rather than reflecting a somewhat belated shift to aridity at OML and LA, the sapropels in these two southern lakes may have been deposited during relatively arid times. Indeed, these 'sapropel events' coincide with a regional period of aridity indicated by low and rapidly fluctuating water levels at Lake Keilambete, as well as a low water stand at nearby Lake Leake. Moreover, the 'sapropel events' in all three lakes each also coincide remarkably closely with periods of enhanced aeolian input to Blue Lake in the Snowy Mountains of southeastern Australia and with global periods of rapid climate change toward arid conditions. This correspondence of the Coorong lacustrine 'sapropel events' with periods of aridification points toward aeolian dust as a possible trigger for sapropel formation, provided that the lake in question is capable of supporting high levels of aquatic primary productivity. Indeed, the halt to sapropel deposition in the three lakes of the present study is here tentatively attributed to a combination of conditions that are simultaneously less conducive to primary production and more conducive to organic matter degradation. Significantly, and in contrast to sapropels in marine and deep-lake settings across the globe, those in these shallow, alkaline, coastal lakes are not necessarily indicative of a stable climate and relatively warm, wet environmental conditions.

11.5 Suggestions for future research

Unfortunately, the sedimentary successions of OML and LA did not extend back to the same point in time as the core retrieved from NSL. Deeper core extraction from OML is unlikely to have provided information on lacustrine conditions contemporaneous with sapropel deposition at NSL since the lower half of the OML1 core is made up purely of lagoonal sediments. At LA, lacustrine sediments likely extend below the thick calcitic hardpan at ~240 cm depth, but could not be retrieved with the D-section corer employed in the present investigation. Use of a different coring technique at LA could allow retrieval of a thicker lacustrine sequence that may extend back to, and thus allow comparison with, the period of sapropel deposition at NSL. While the D-section corer has the unusual benefit of retrieving uncompacted sediment, the technique only collects a half (semi-circular) core. This artefact of the sampling process meant that it was difficult to obtain both organic and inorganic isotopic data from the same depth in any given core. Use of a technique that collects a whole (and perhaps larger diameter) core would enable a more precise comparison of the organic and inorganic isotope profiles of the Holocene succession in each lake.

As with any palaeoenvironmental investigation, further information could have been obtained through the analysis of additional proxies. Thus, while the present study utilised bulk geochemical parameters, it would have benefited from access to more refined techniques such as compound-specific isotope or biomarker analysis (e.g. Wilkes et al., 1999; Hollander and Smith, 2001). More simply, the preparation and palynological analysis of smear slides may have aided the identification of the dispersed organic matter and its stratigraphic variability (Tyson, 1995). Diatom analysis is another source of independent information on lacustrine salinity. However, as diatomaceous silica readily dissolves in alkaline pore water, the complete diatom assemblage needed to accurately infer lacustrine conditions is unlikely to be preserved in these cores (cf. Edwards et al., 2006). Finally, the careful extraction and analysis of mineral matter from these carbonate sediments (cf. Stanley and De Deckker, 2002) is urgently needed to further assess the feasibility of dust influx as a trigger of sapropel formation. Such information would greatly enhance the palaeoenvironmental interpretation presented herein.

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GLOSSARY

Aeolian transport: delivery of fine particles (e.g. dust, pollen) by wind activity. Can operate over long (e.g. intercontinental) distances.

Allochthonous: minerogenic and/or organic material transported from its place of origin to form a sedimentary constituent at another locality (cf. autochthonous).

Anoxia: strictly speaking, the complete absence of molecular oxygen. Anoxic waters contain no dissolved oxygen.

Autochthonous: a material (e.g. mineral, fossil, organic matter) formed in the basin or water body where it is found today (cf. allochthonous).

Autotrophs: organisms that produce organic compounds using carbon dioxide as a carbon carbon source and either light or reactions of inorganic chemical compounds as an energy source. Plants and other organisms using photosynthesis are photoautotrophs; bacteria that utilize the oxidation of inorganic compounds such as hydrogen sulfide as an energy source are chemoautotrophs.

Bioturbation: mixing of sediment by biological activity (e.g. burrowing, grazing). Occurs in some oxygenated bottom waters, but typically absent in anoxic waters.

Chemotrophs: producers, including algae and bacteria, which convert energy from inorganic chemical compounds into more complex energy, without the use of sunlight.

Denitrification: bacterial reduction of dissolved nitrate (NO_3^-) to gaseous nitrogen (N_2). Typically occurs under anoxic conditions in subsurface lake sediments and hypolimnions of strongly stratified lakes.

Epilimnion: warm, oxygenated and less dense upper water layer.

Euphotic zone: surface layer of water in which light intensity is sufficient for photosynthesis.

Eutrophication: whereby a body of water becomes highly productive of aquatic plants, such as algae, due to the input of large quantities of nutrients.

Eutrophic lakes: characterised by an abundance of nutrients and by seasonal oxygen deficiency in bottom waters. Sediments are typically rich in organic matter.

Heterotrophs: organisms that, unlike autotrophs, cannot derive energy directly from light or from inorganic chemicals, and thus require organic substrates to get carbon for growth and development. They obtain chemical energy by breaking down the organic molecules they consume.

Holocene: (time) the last epoch of the Quaternary Period, equivalent to Oxygen Isotope Stage 2. Traditionally defined as beginning at 10 ka.

Hypolimnion: lower layer of colder, denser water. May become depleted in oxygen.

Nitrate assimilation: use of nitrate (NO_3^-) as a source of dissolved nitrogen.

Nitrification: aerobic bacterial oxidation of ammonium (NH_4^+) to nitrate or nitrite (NO_2^-).

Nitrogen fixation: incorporation of molecular nitrogen (N_2) into living biological matter. Restricted to a number of specialised bacteria and algae, notably cyanobacteria.

Oligotrophic lakes: characterised by a deficiency in plant nutrients and usually an abundance of dissolved oxygen in bottom waters. Sediments are typically organically-lean.

Ostracod: millimetre-sized crustacean with a soft body enclosed in a pair of shells made of chitin and low-Mg calcite.

Phytoplankton: microscopic floating plants, mainly algae that live suspended in bodies of water. These drift about because they cannot move by themselves or because they are too small or too weak to swim effectively against a current.

Playa: a shallow lake that exists intermittently, in wet seasons or especially wet years.

Schizohaline: (environment) one that alternates between hypersaline and freshwater conditions.

Vascular plants: have systems that allow fluid movement between organs (e.g. roots, leaves, flowers). Most land plants are vascular; algae are not.

APPENDICES

APPENDIX I Summary of previous studies on sapropels and associated sediments in lakes from the Coorong region, South Australia

Lake	Unit	Information
NSL	Massive	Type II-III protokerogen (hydrogen index = 180–305 mg HC/g TOC) Combined algal (coccoid cyanobacterial) and terrestrial plant input Terrestrial organic matter comprises cutinite from the grass-like metaphyte *Ruppia sp.* and inertinite Diverse carbonate assemblage (aragonite, hydromagnesite, calcite with minor dolomite at top)
	Laminated	Upper part: Type III-IV protokerogen (hydrogen index = 77–102 mg HC/g TOC) Lower part: Type II-III protokerogen (hydrogen index = 110–387 mg HC/g TOC) Predominance of inertinitic material and coccoid cyanobacteria Darker coloured laminae tend to contain more organic debris (abundant algal filaments and occasional *Ruppia* rhizomes) Largely unaffected by bioturbation or desiccation, probably due to the protective binding of benthic algae Mineralogy is entirely carbonate (aragonite, hydromagnesite)
	Sapropel	Sapropel B: Type II protokerogen (hydrogen index = 323–524 mg HC/g TOC) Sapropel A: Type I-II protokerogen (hydrogen index = 466–925 mg HC/g TOC) Largely amorphous organic matter; variably degraded algal and cyanobacterial (filamentous and coccoid) remains Colonial algae *(Botryococcus braunii)* abundant in Sapropel A, rare in Sapropel B Higher plant remains recognised exclusively in Sapropel B Highly branched isoprenoid (HBI) alkane (C_{20}) and alkene (C_{25}) biomarkers indicate significant diatom inputs Complete biomarker assemblage (C_{20} and C_{25} HBIs, C_{21}-C_{33} *n*-alkanes with a marked odd/even predominance, C_{27}-C_{31} hopanoid triterpenes and Δ^2-sterenes) is consistent with contribution of eukaryotic algae, vascular plants, bacteria and/or cyanobacteria to the preserved organic matter Carbonate (aragonite, calcite) in part inherited from skeletal remains of benthic ostracods and dwarf molluscs and gastropods; quartz probably allochthonous (aeolian or reworked from underlying unit)
	Basal	Type IV protokerogen (hydrogen index = 79 mg HC/g TOC) *n*-Alkane distribution is skewed toward high carbon numbers, signifying terrestrial organic matter UV petrography shows a low content of *B. braunii* and filamentous algae within a moderately amorphous groundmass Mineralogy varies dependent on relative proportions of quartz sand, bioclasts (whole pelecypod and gastropod shells) and micrite; carbonate is typically calcite with minor dolomite cement

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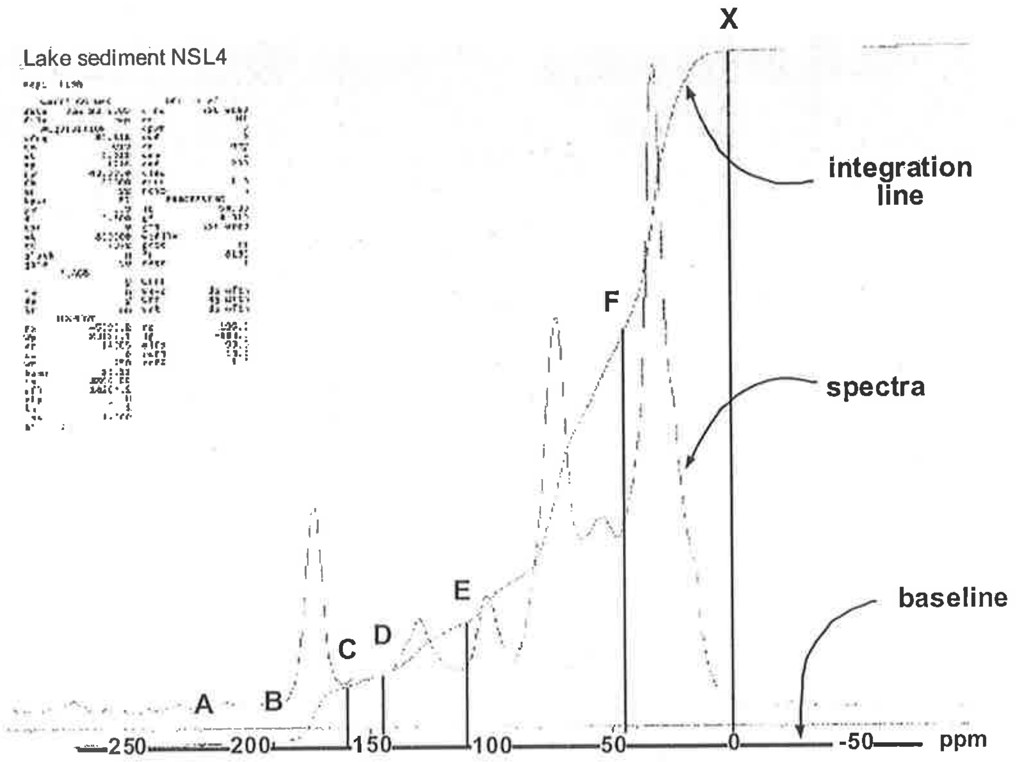
Lake	Unit	Information
OML	Massive	Pale, bioturbated, pelletal (predominantly aragonite) mud with minor to abundant remains of *Coxiella striata*
	Lacustrine (containing sapropel)	Type II-III protokerogen (hydrogen index = 280–800 HC/g TOC) Bimodal *n*-alkane profile with marked predominance of odd-carbon-numbered homologues Complete biomarker assemblage comprises C_{27}-C_{29} sterenes and Δ^2-sterenes, C_{30} sterane, various pentacyclic triterpanes and a high relative abundance of C_{20} and C_{25} HBIs Dominant aliphatic hydrocarbons are pristane and 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane ($C_{21:0}$ HBI) Sapropel layers are dominated by a single diatom species, *Campylodiscus sp.*; *Pinnularia sp.* also present $\delta^{13}C_{PDB}$ of bulk sapropelic organic matter ranges from -21.9 to -16.9‰ $\delta^{13}C_{PDB}$ of $C_{25:1}$ HBI is relatively constant: -25.8 to -23.1‰
	Lagoonal	Shallow marine molluscan, foraminiferal and ostracod faunas
	Humic	Type III-IV protokerogen (hydrogen index = 100–210 HC/g TOC) $\delta^{13}C_{PDB}$ of bulk organic matter ranges from -26.7 to -24.4‰
LA		Gelatinous benthic microbial community present across entire lake floor $\delta^{13}C_{PDB}$ of bulk organic matter increases from -23 to -20‰ in the lower laminated unit to -18 to -16‰ in the upper laminated unit Ostracod biostratigraphy suggests there was a major salinity increase associated with sapropel formation

Source: Warren 1988, 1990; Hayball, 1990; Hayball et al., 1991; Mazzoleni, 1993; Hepplewhite, 1994; McKirdy et al., 1995, 1999, 2002, 2005; Edwards et al., 2006

Other Coorong Sapropels

Cooke Plains Embayment (von der Borch and Altmann, 1979)	Greenish-black in colour; rubbery texture with cheese-like fracture; up to 40 cm thick Dominated by remains of blue-green algae; significant quantities of diatom frustles throughout Predominantly terrestrial fossil pollen assemblage (Chenopodiaceae, Myrtaceae and *Casuarina sp.*); freshwater aquatic plant pollen (*Myriophyllum sp.* and *Haloragis sp.*) and colonial algae (*B. braunii*) are also present in significant quantities
South South Stromatolite Lake (Macdonald. 1991)	Type II protokerogen (hydrogen index = 300–600 HC/g TOC) Variably degraded remains of *B. braunii*, filamentous algae and coccoid cyanobacteria within an amorphous groundmass High relative abundance of C_{20} and C_{25} HBIs

APPENDIX II Integration method used to determine percent carbon type from ^{13}C-NMR spectra



Method

- Vertical lines (A-X) are dropped from the spectral integration line to the horizontal baseline and measured
- The difference between the height of the lines that bound each chemical range are calculated
- These values are integrated with respect to the full height of the integration line (X) to determine percent carbon reflected in each chemical shift range

chemical shift range (ppm)	carbon type	lines	(mm)	height	percent carbon
200 - 190	aldehyde/keytone	B - A	= (1.5 - 0.8) =	0.7	0.4
190 - 160	carbonyl	C - B	= (15.5 - 1.5) =	14	8.1
160 - 145	O-aryl	D - C	= (18.5 - 15.5) =	3	1.6
145 - 110	aryl	E - D	= (32.0 - 18.5) =	13.5	7.6
110 - 46	O-alkyl	F - E	= (106.0 - 32.0) =	86	40.4
46 - 0	alkyl	X - F	= (184.5 - 106) =	78.5	42.4

APPENDIX III Results of X-ray diffraction analysis of sediment samples from NSL, OML and LA

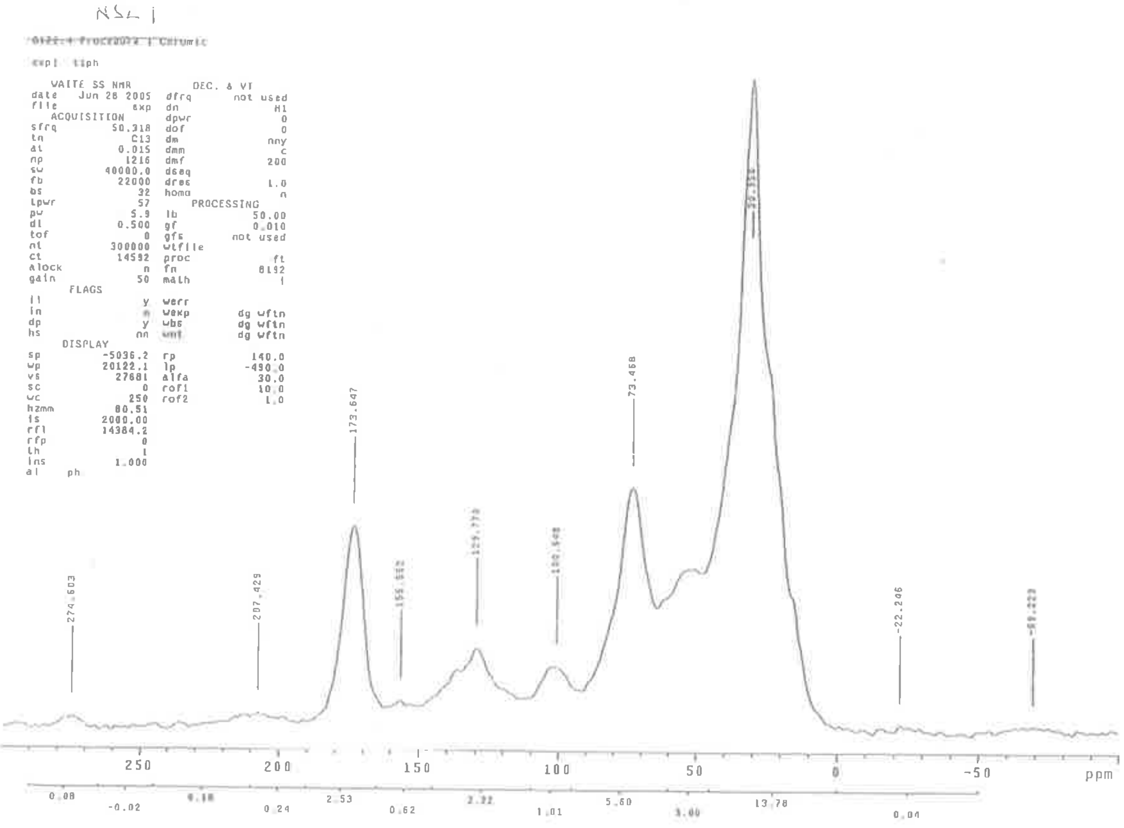
CSIRO Number	Sample Label	Depth (cm)	Quartz (SiO_2)	Calcite ($CaCO_3$)	Mg-Calcite ($[Ca,Mg]CO_3$)	Magnesite ($MgCO_3$)	Dolomite ($CaMg[CO_3]_2$)	Ca-Dolomite ($Ca[Ca,Mg][CO_3]_2$)	Aragonite ($CaCO_3$)	Halite ($NaCl$)	Bassanite ($CaSO_4.0.5H_2O$)	Hydromagnesite ($Mg_5[CO_3]_4[OH]_2 \cdot 4H_2O$)	Albite	Orthoclase	Mica	Kaolin	Smectite
21008	NSL1	7	10	3	-	-	-	-	55	8	1	23	-	-	-	-	-
21009	NSL2	40	2	1	-	-	-	-	74	8	1	14	-	-	-	-	-
21010	NSL3	52	2	1	-	-	-	-	64	9	1	23	-	-	-	-	-
21011	NSL4	76	-	<1	-	-	-	-	48	12	1	38	-	-	-	-	-
21012	NSL5	95	4	1	-	-	-	-	60	8	1	26	-	-	-	-	-
21013	NSL6	124	20	3	-	5	-	-	51	6	<1	14	<1	1	-	-	-
21014	NSL7	143	55	3	-	8	-	-	19	5	<1	2	1	6	-	-	-
21015	NSL8	155	8	2	-	22	-	-	46	10	<1	11	<1	<1	-	-	-
21016	NSL9	166	36	4	-	<1	-	-	41	7	<1	8	1	3	-	-	-
21017	NSL10	179	13	4	-	-	-	-	68	14	<1	-	<1	<1	-	-	-
21018	NSL11	190	24	4	6	-	-	-	47	17	1	-	<1	2	-	-	-
21019	NSL12	214	15	7	9	-	-	-	40	17	2	-	<1	4	6	-	-
21020	NSL13	238	4	6	9	-	-	-	58	21	2	-	-	-	-	-	-
21021	NSL14	260	40	7	5	-	-	-	32	11	2	-	<1	3	-	-	-
21022	NSL15	283	25	9	2	-	-	-	16	26	4	-	4	1	4	-	9
21023	NSL16	293	21	8	2	-	4	-	11	35	<1	-	2	1	-	8	7
21024	OML1	4.5	<1	-	55	-	-	-	42	2	-	-	-	-	-	-	-
21025	OML2	19.5	<1	-	79	-	-	-	11	10	<1	-	-	-	-	-	-
21026	OML3	28	<1	7	37	-	-	-	43	11	2	-	-	-	-	-	-
21027	OML4	39	1	6	17	-	-	-	38	32	6	-	-	-	-	-	-
21028	OML5	52.5	-	11	51	-	-	-	19	17	2	-	-	-	-	-	-
21029	OML6	59.5	5	19	28	-	-	-	21	23	4	-	-	-	-	-	-
21030	OML7	65	<1	85	5	-	-	-	<1	8	2	-	-	-	-	-	-
21031	OML8	74.5	<1	9	69	-	-	-	14	7	<1	-	-	-	-	-	-
21032	OML9	84.5	2	26	28	-	-	-	18	25	<1	-	-	-	-	-	-
21033	OML10	88	4	10	39	-	-	-	24	20	2	-	-	-	-	-	-
21034	OML11	94.5	2	20	50	-	-	-	9	17	1	-	-	-	-	-	-
21035	OML12	101.5	1	-	94	-	-	-	<1	4	-	-	-	-	-	-	-
21036	OML13	105.5	3	5	6	-	-	-	85	1	-	-	-	-	-	-	-
21037	OML14	123.5	18	46	8	-	-	-	24	<1	-	-	3	<1	-	-	-

Results of X-ray diffraction analysis (continued)

CSIRO Number	Sample Label	Depth (cm)	Quartz (SiO_2)	Calcite ($CaCO_3$)	Mg-Calcite ($[Ca,Mg]CO_3$)	Magnesite ($MgCO_3$)	Dolomite ($CaMg[CO_3]_2$)	Ca-Dolomite ($Ca[Ca,Mg][CO_3]_2$)	Aragonite ($CaCO_3$)	Halite ($NaCl$)	Bassanite ($CaSO_4.0.5H_2O$)	Hydromagnesite ($Mg_5[CO_3]_4[OH]_2 \cdot 4H_2O$)	Albite	Orthoclase	Mica	Kaolin	Smectite
20988	LA1	12.5	3	2	-	-	-	88	1	6	-	-	-	-	-	-	-
20989	LA2	32	1	2	-	-	-	93	1	3	-	-	-	-	-	-	-
20990	LA3	54	1	3	-	-	-	51	26	16	3	-	-	-	-	-	-
20991	LA4	70.5	<1	3	-	-	-	71	4	19	3	-	-	-	-	-	-
20992	LA5	85.5	-	4	-	-	-	52	18	22	4	-	-	-	-	-	-
20993	LA6	97	2	-	15	-	-	45	8	27	4	-	-	-	-	-	-
20994	LA7	103.5	1	-	29	-	-	15	28	24	4	-	-	-	-	-	-
20995	LA8	109.5	2	-	25	-	-	14	21	33	5	-	-	-	-	-	-
20996	LA9	120.5	1	-	13	-	-	39	7	35	5	-	-	-	-	-	-
20997	LA10	136.5	1	-	10	-	-	25	32	27	4	-	-	-	-	-	-
20998	LA11	152.5	1	-	16	-	-	46	19	17	<1	-	-	-	-	-	-
20999	LA12	173	<1	-	13	-	-	52	18	14	2	-	-	-	-	-	-
21000	LA13	187.5	1	-	14	-	-	47	22	16	-	-	-	-	-	-	-
21001	LA14	201.5	<1	-	9	-	-	43	36	12	-	-	-	-	-	-	-
21002	LA15	210.5	<1	-	12	-	-	63	12	12	-	-	-	-	-	-	-
21003	LA16	222	2	-	17	-	-	33	34	14	<1	-	-	-	-	-	-
21004	LA17	225	3	-	16	-	-	9	55	17	-	-	-	-	-	-	-
21005	LA18	236.5	2	-	23	-	-	22	33	19	-	-	-	-	-	-	-
21006	LA19	244	6	-	27	-	-	43	13	12	-	-	-	-	-	-	-
21007	LA20	249	9	-	59	-	-	11	8	12	-	-	-	-	-	-	-

Mineralogical and Geochemical Services
Environmental Contaminants Directorate
CSIRO Land and Water
Waite Rd, Urrbrae, SA, 5064
Ph: +61 (08) 8303 8497
Fax: +61 (08) 8303 8550
Email: Mark.Raven@csiro.au

APPENDIX IV A ^{13}C-NMR spectra for NSL


NSL 1

~~[illegible]~~

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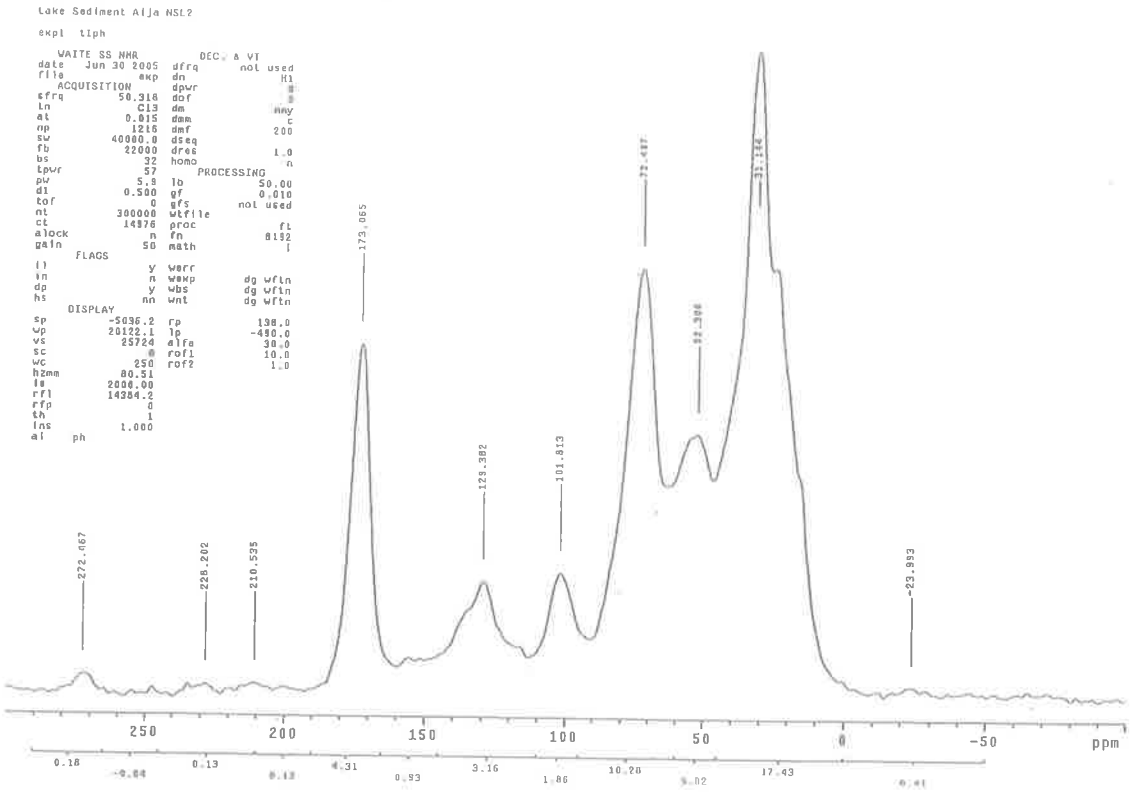
sfrq         50.318  dof                0
tn              C13  dm               nny
at            0.015  dmm                c
np             1216  dmf              200
sw          40000.0  dseq
fb            22000  dres             1.0
bs               32  homo               n
tpwr             57      PROCESSING
pw              5.9  lb             50.00
d1            0.500  gf             0.010
tof               0  gfs         not used
nt           300000  wtfile
ct            14592  proc              ft
alock             n  fn              8192
gain             50  math               f
       FLAGS
il                y  werr
in                n  wexp        dg wftn
dp                y  wbs         dg wftn
hs               nn  wnt         dg wftn
      DISPLAY
sp          -5036.2  rp             140.0
wp          20122.1  lp            -490.0
vs            27681  alfa            30.0
sc                0  rof1            10.0
wc              250  rof2             1.0
hzmm          80.51
is          2000.00
rfl         14384.2
rfp               0
th                1
ins           1.000
ai     ph
```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Lake Sediment Alja NSL2

expl   tiph

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file            exp  dn                H1
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sfrq         50.318  dof                0
tn              C13  dm               nny
at            0.015  dmm                c
np             1216  dmf              200
sw          40000.0  dseq
fb            22000  dres             1.0
bs               32  homo               n
tpwr             57      PROCESSING
pw              5.9  lb             50.00
d1            0.500  gf             0.010
tof               0  gfs         not used
nt           300000  wtfile
ct            14976  proc              ft
alock             n  fn              8192
gain             50  math               f
       FLAGS
il                y  werr
in                n  wexp        dg wftn
dp                y  wbs         dg wftn
hs               nn  wnt         dg wftn
      DISPLAY
sp          -5036.2  rp             138.0
wp          20122.1  lp            -490.0
vs            25724  alfa            30.0
sc                0  rof1            10.0
wc              250  rof2             1.0
hzmm          80.51
is          2000.00
rfl         14384.2
rfp               0
th                1
ins           1.000
ai     ph
```

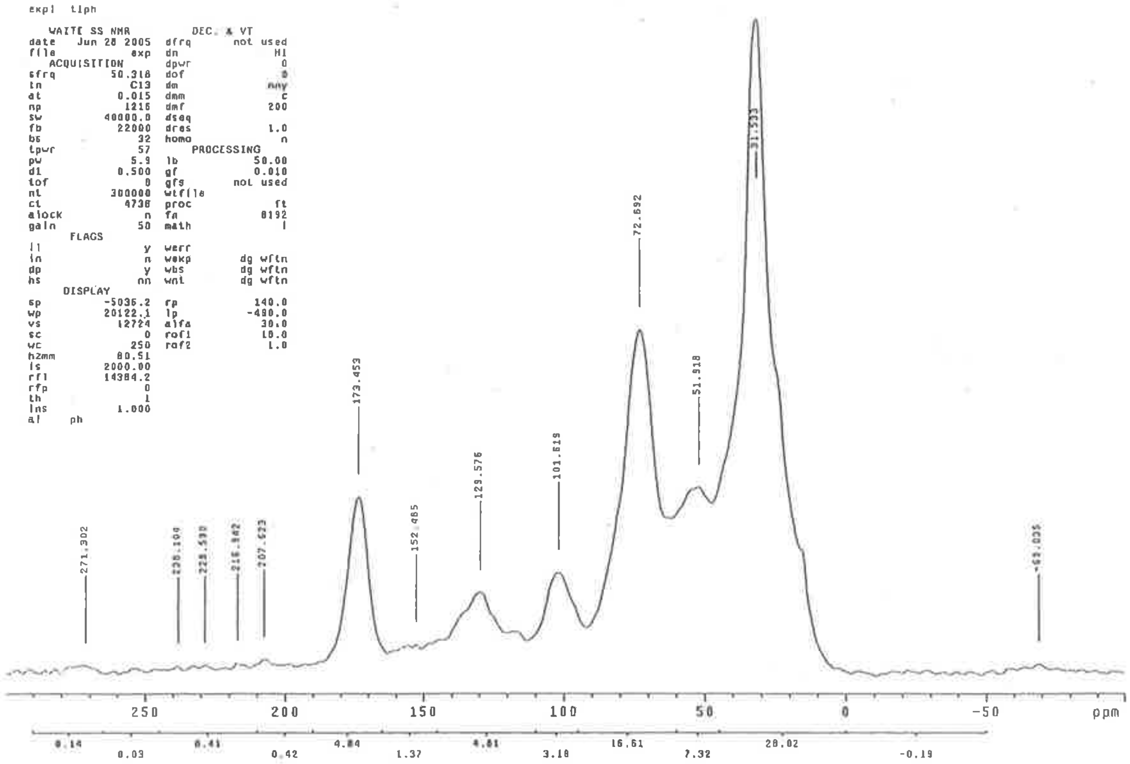

```
Lake Sediment, NSL3, Alja

expl  tlph

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file           exp  dn                H1
   ACQUISITION      dpwr               0
sfrq        50.318  dof                0
tn             C13  dm               nny
at           0.015  dmm                c
np            1216  dmf              200
sw         40000.0  dseq
fb           22000  dres             1.0
bs              32  homo               n
tpwr            57      PROCESSING
pw             5.9  lb             50.00
d1           0.500  gf             0.010
tof              0  gfs         not used
nt          300000  wtfile
ct            4738  proc              ft
alock            n  fn              8192
gain            50  math               l
       FLAGS
il               y  werr
in               n  wexp         dg wftn
dp               y  wbs          dg wftn
hs              nn  wnt          dg wftn
      DISPLAY
sp         -5036.2  rp             140.0
wp         20122.1  lp            -480.0
vs           12724  alfa            30.0
sc               0  rofl            10.0
wc             250  rof2             1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
al     ph
```

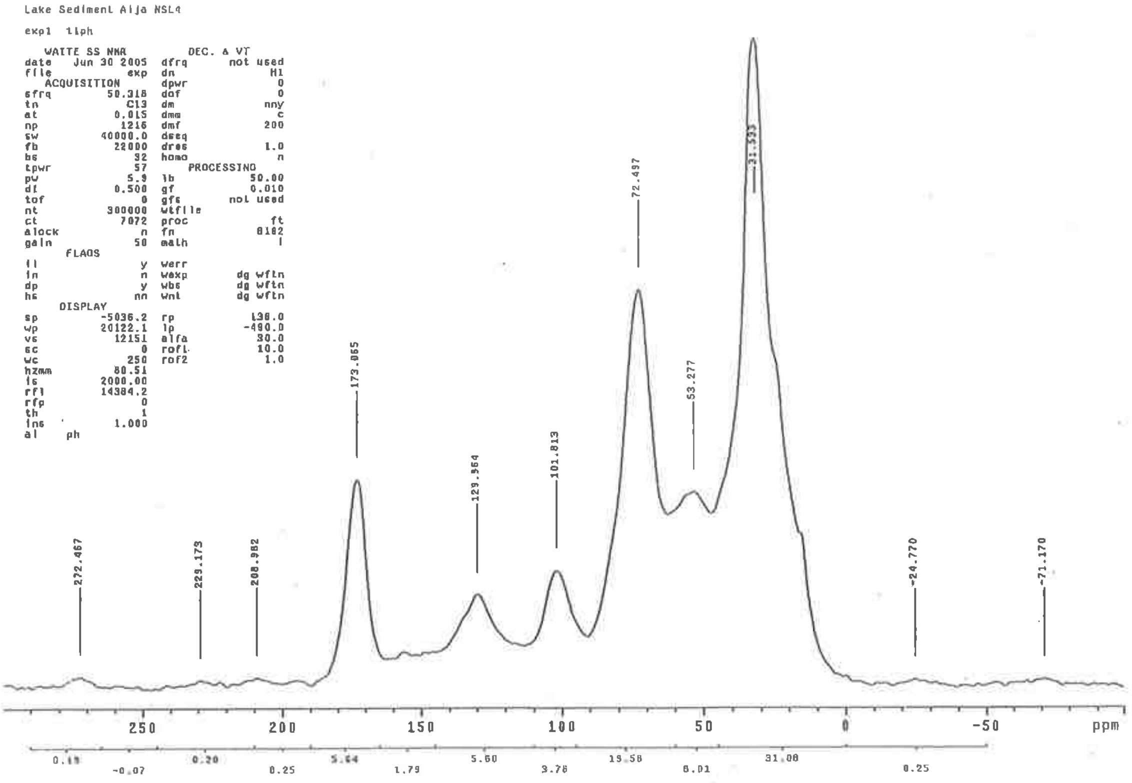

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Lake Sediment Alja NSL4

expl  tlph

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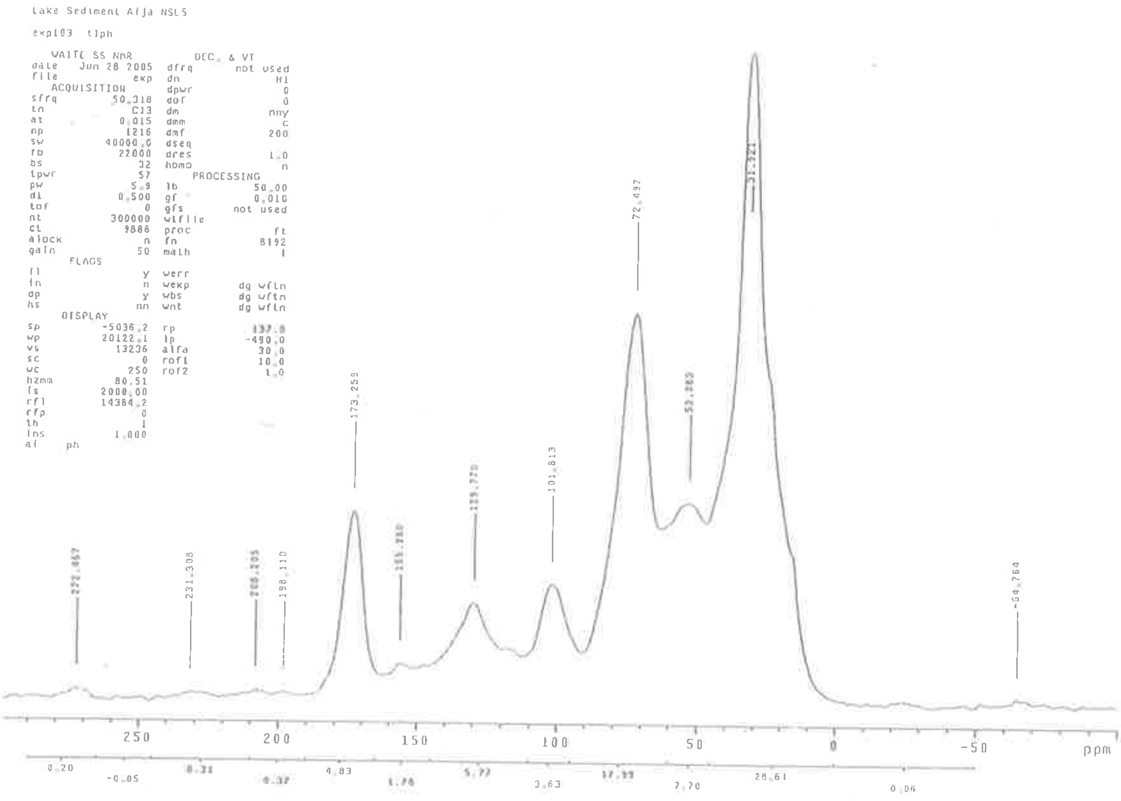
file           exp  dn                H1
   ACQUISITION      dpwr               0
sfrq        50.318  dof                0
tn             C13  dm               nny
at           0.015  dmm                c
np            1216  dmf              200
sw         40000.0  dseq
fb           22000  dres             1.0
bs              32  homo               n
tpwr            57      PROCESSING
pw             5.9  lb             50.00
dl           0.500  gf             0.010
tof              0  gfs         not used
nt          300000  wtfile
ct            7072  proc              ft
alock            n  fn              8182
gain            50  math               l
       FLAGS
il               y  werr
in               n  wexp         dg wftn
dp               y  wbs          dg wftn
hs              nn  wnt          dg wftn
      DISPLAY
sp         -5036.2  rp             138.0
wp         20122.1  lp            -480.0
vs           12151  alfa            30.0
sc               0  rofl            10.0
wc             250  rof2             1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
al     ph
```



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Lake Sediment Aija NSL5

exp103  t1ph

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date   Jun 28 2005  dfrq       not used
file           exp  dn               H1
   ACQUISITION      dpwr              0
sfrq        50.318  dof               0
tn             C13  dm              nny
at           0.015  dmm               c
np            1216  dmf             200
sw         40000.0  dseq
fb           22000  dres            1.0
bs              32  homo              n
tpwr            57       PROCESSING
pw             5.9  lb            50.00
d1           0.500  gf            0.010
tof              0  gfs        not used
nt          300000  wtfile
ct            9888  proc             ft
alock            n  fn             8192
gain            50  math              f
      FLAGS
il               y  werr
in               n  wexp        dg wfln
dp               y  wbs         dg wftn
hs              nn  wnt         dg wfln
     DISPLAY
sp         -5036.2  rp            137.0
wp         20122.1  lp           -490.0
vs           13236  alfa           30.0
sc               0  rofl           10.0
wc             250  rof2            1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
```
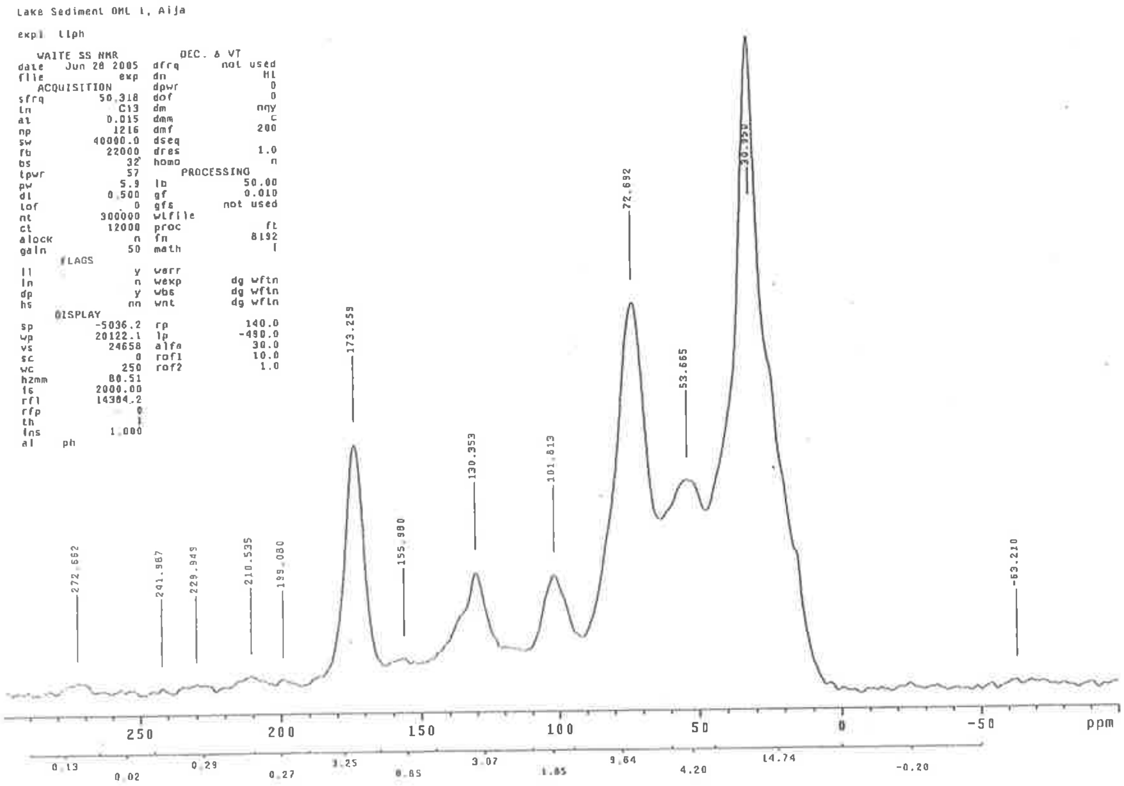

APPENDIX IV B ^{13}C-NMR spectra for OML



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Lake Sediment OML 1, Aija

expl  tlph

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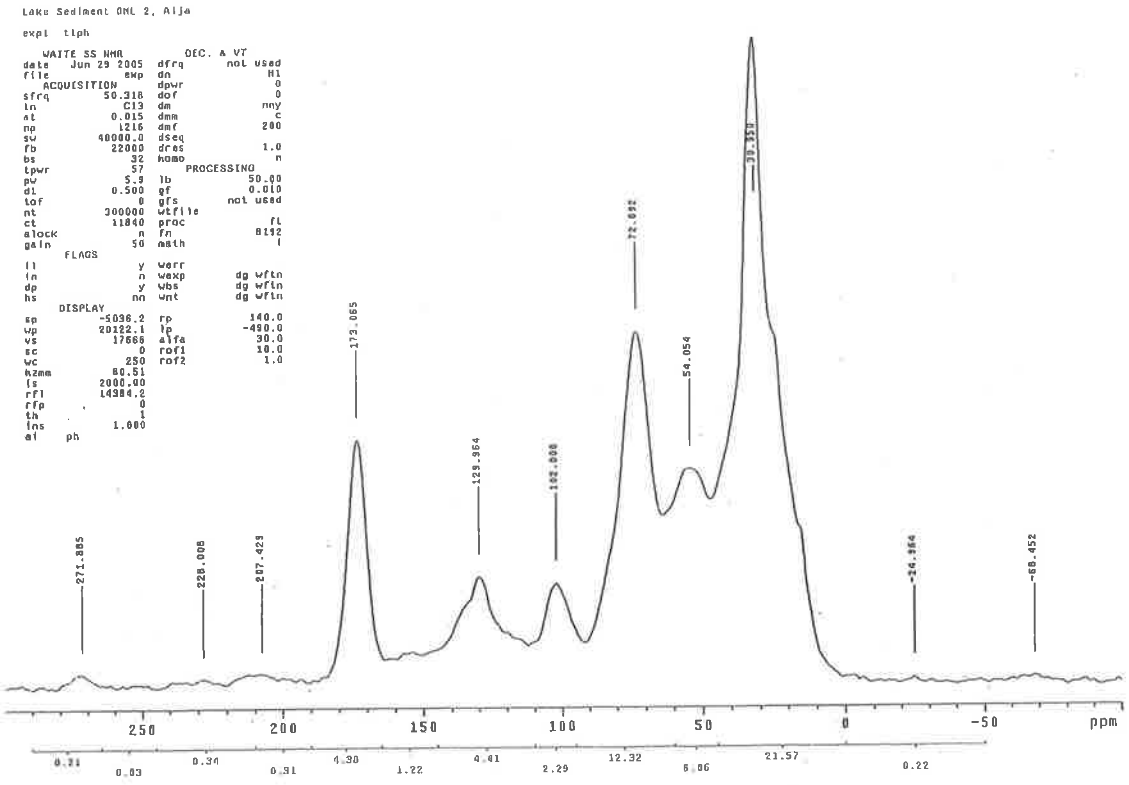
file           exp  dn               H1
  ACQUISITION       dpwr              0
sfrq        50.318  dof               0
tn             C13  dm              nny
at           0.015  dmm               c
np            1216  dmf             200
sw         40000.0  dseq
fb           22000  dres            1.0
bs              32  homo              n
tpwr            57     PROCESSING
pw             5.9  lb            50.00
d1           0.500  gf            0.010
tof              0  gfs        not used
nt          300000  wtfile
ct           12000  proc             ft
alock            n  fn             8192
gain            50  math              f
      FLAGS
il               y  werr
in               n  wexp        dg wftn
dp               y  wbs         dg wftn
hs              nn  wnt         dg wftn
      DISPLAY
sp         -5036.2  rp            140.0
wp         20122.1  lp           -490.0
vs           24658  alfa           30.0
sc               0  rof1           10.0
wc             250  rof2            1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
```



```
Lake Sediment OML 2, Aija

expl  tlph

  WAITE SS NMR           DEC. & VT
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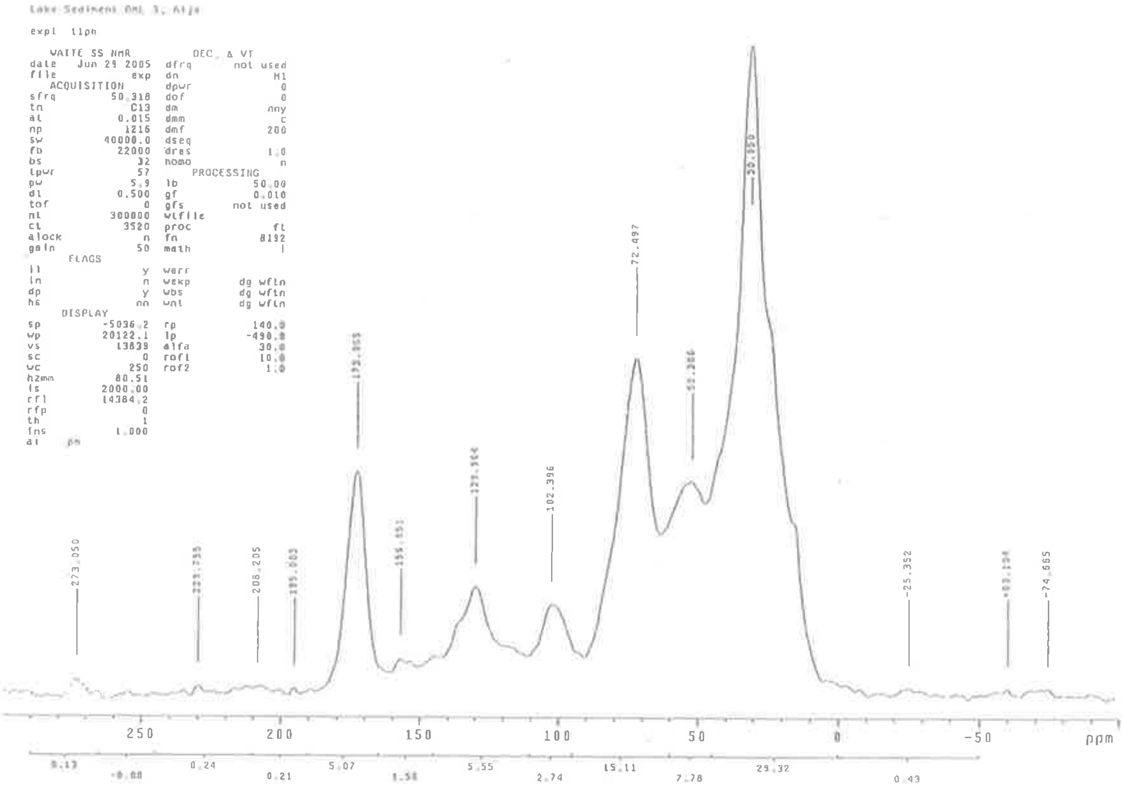
file           exp  dn               H1
  ACQUISITION       dpwr              0
sfrq        50.318  dof               0
tn             C13  dm              nny
at           0.015  dmm               c
np            1216  dmf             200
sw         40000.0  dseq
fb           22000  dres            1.0
bs              32  homo              n
tpwr            57     PROCESSING
pw             5.9  lb            50.00
d1           0.500  gf            0.010
tof              0  gfs        not used
nt          300000  wtfile
ct           11840  proc             ft
alock            n  fn             8192
gain            50  math              f
      FLAGS
il               y  werr
in               n  wexp        dg wftn
dp               y  wbs         dg wftn
hs              nn  wnt         dg wftn
      DISPLAY
sp         -5036.2  rp            140.0
wp         20122.1  lp           -490.0
vs           17666  alfa           30.0
sc               0  rof1           10.0
wc             250  rof2            1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
```



```
Lake Sediment DML 3, Aija

expl  tlph

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file           exp  dn                H1
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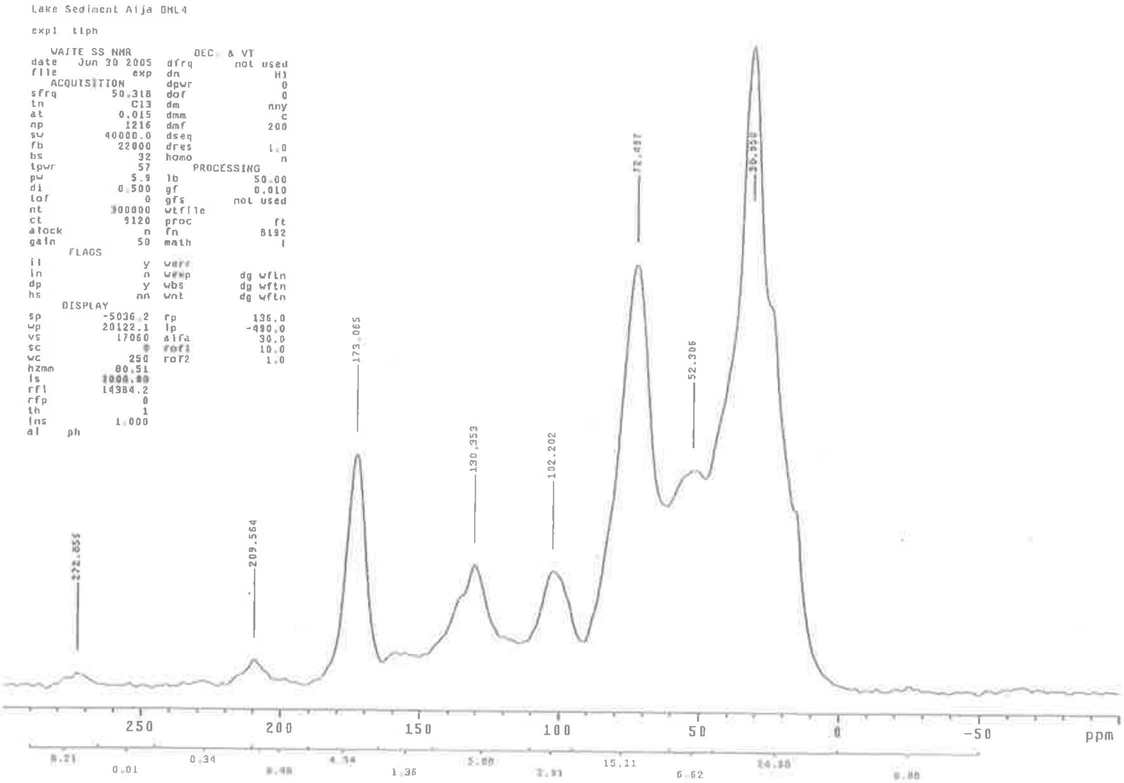
sfrq        50.318  dof                0
tn             C13  dm               nny
at           0.015  dmm                c
np            1216  dmf              200
sw         40000.0  dseq
fb           22000  dres             1.0
bs              32  homo               n
tpwr            57       PROCESSING
pw             5.9  lb             50.00
d1           0.500  gf             0.010
tof              0  gfs         not used
nt          300000  wtfile
ct            3520  proc              ft
alock            n  fn              8192
gain            50  math               f
      FLAGS
il               y  werr
in               n  wexp         dg wftn
dp               y  wbs          dg wftn
hs              nn  wnt          dg wftn
     DISPLAY
sp         -5036.2  rp             140.0
wp         20122.1  lp            -490.0
vs           13839  alfa            30.0
sc               0  rofl            10.0
wc             250  rof2             1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
```



```
Lake Sediment Aija DML4

expl  tlph

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file           exp  dn                H1
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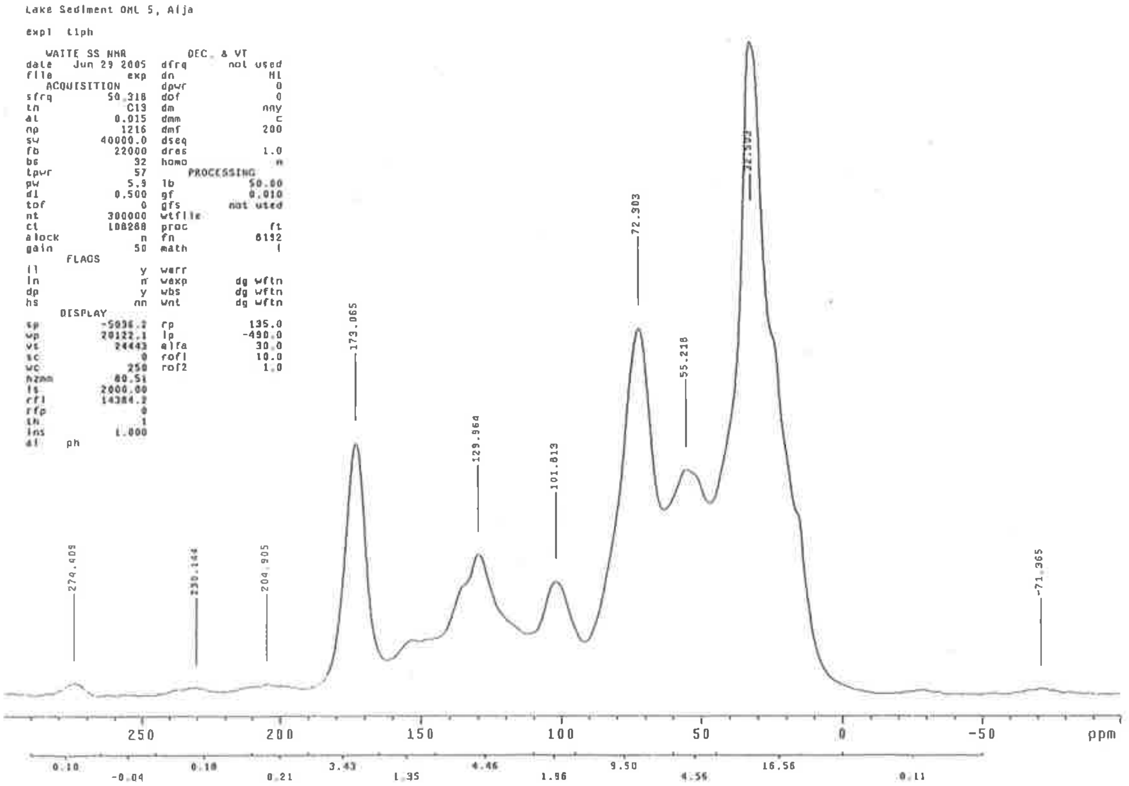
sfrq        50.318  dof                0
tn             C13  dm               nny
at           0.015  dmm                c
np            1216  dmf              200
sw         40000.0  dseq
fb           22000  dres             1.0
bs              32  homo               n
tpwr            57       PROCESSING
pw             5.9  lb             50.00
d1           0.500  gf             0.010
tof              0  gfs         not used
nt          300000  wtfile
ct            9120  proc              ft
alock            n  fn              8192
gain            50  math               f
      FLAGS
il               y  werr
in               n  wexp         dg wftn
dp               y  wbs          dg wftn
hs              nn  wnt          dg wftn
     DISPLAY
sp         -5036.2  rp             136.0
wp         20122.1  lp            -490.0
vs           17060  alfa            30.0
sc               0  rofl            10.0
wc             250  rof2             1.0
hzmm         80.51
is         1000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
```



```
Lake Sediment OML 5, Alja

expl  tlph

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file           exp   dn                H1
   ACQUISITION       dpwr               0
sfrq        50.318   dof                0
tn             C13   dm               nny
at           0.015   dmm                c
np            1216   dmf              200
sw         40000.0   dseq
fb           22000   dres             1.0
bs              32   homo               n
tpwr            57      PROCESSING
pw             5.9   lb             50.00
d1           0.500   gf             0.010
tof              0   gfs         not used
nt          300000   wtfile
ct          108288   proc              ft
alock            n   fn              8192
gain            50   math               f
      FLAGS
il               y   werr
in               n   wexp         dg wftn
dp               y   wbs          dg wftn
hs              nn   wnt          dg wftn
     DISPLAY
sp         -5036.2   rp             135.0
wp         20122.1   lp            -490.0
vs           24443   alfa            30.0
sc               0   rof1            10.0
wc             250   rof2             1.0
hzmm         80.51
is         2000.00
rfl        14384.2
rfp              0
th               1
ins          1.000
ai    ph
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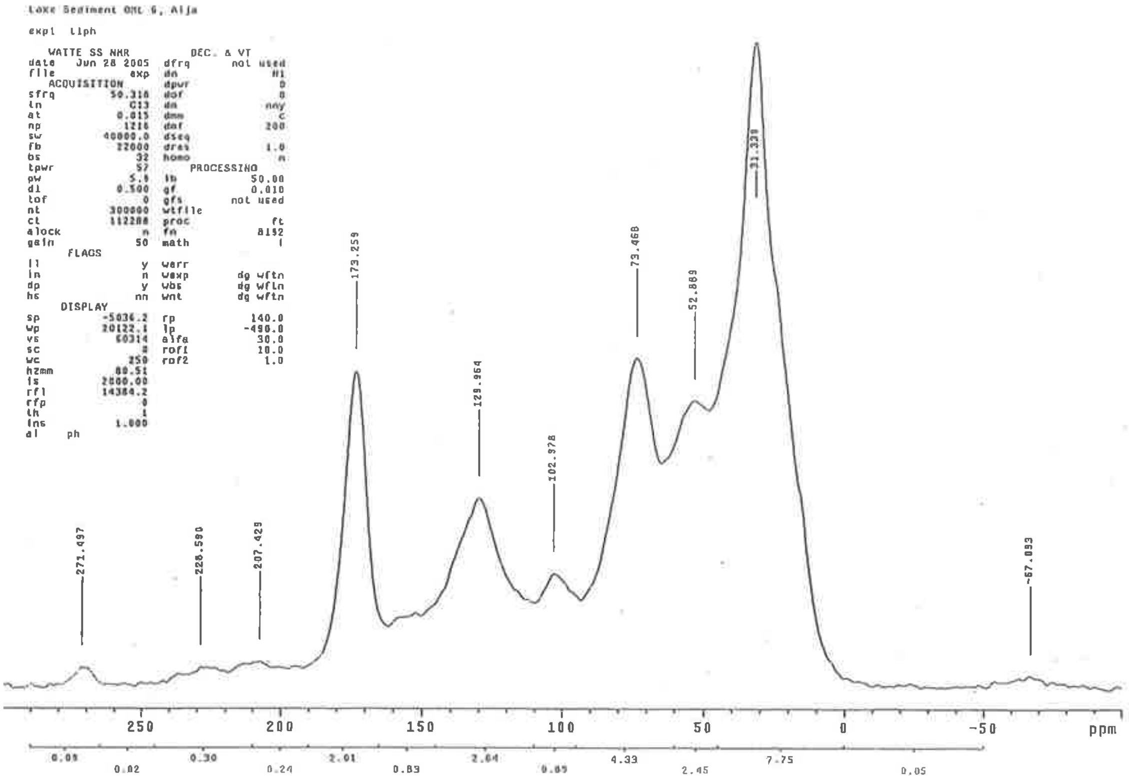

```
Lake Sediment OML 6, Alja

expl  tlph

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hzmm         80.51
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ins          1.000
ai    ph
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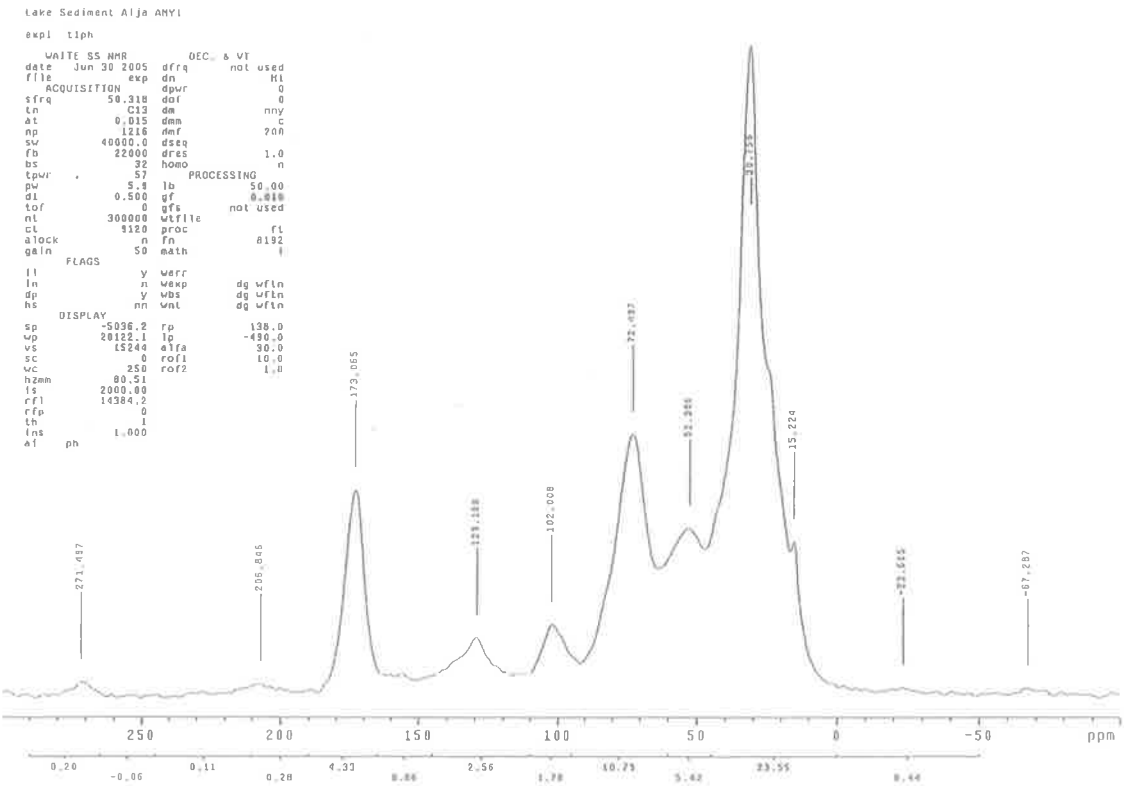
APPENDIX IV C ^{13}C-NMR spectra for LA



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Lake Sediment Alja ANYl

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ai     ph
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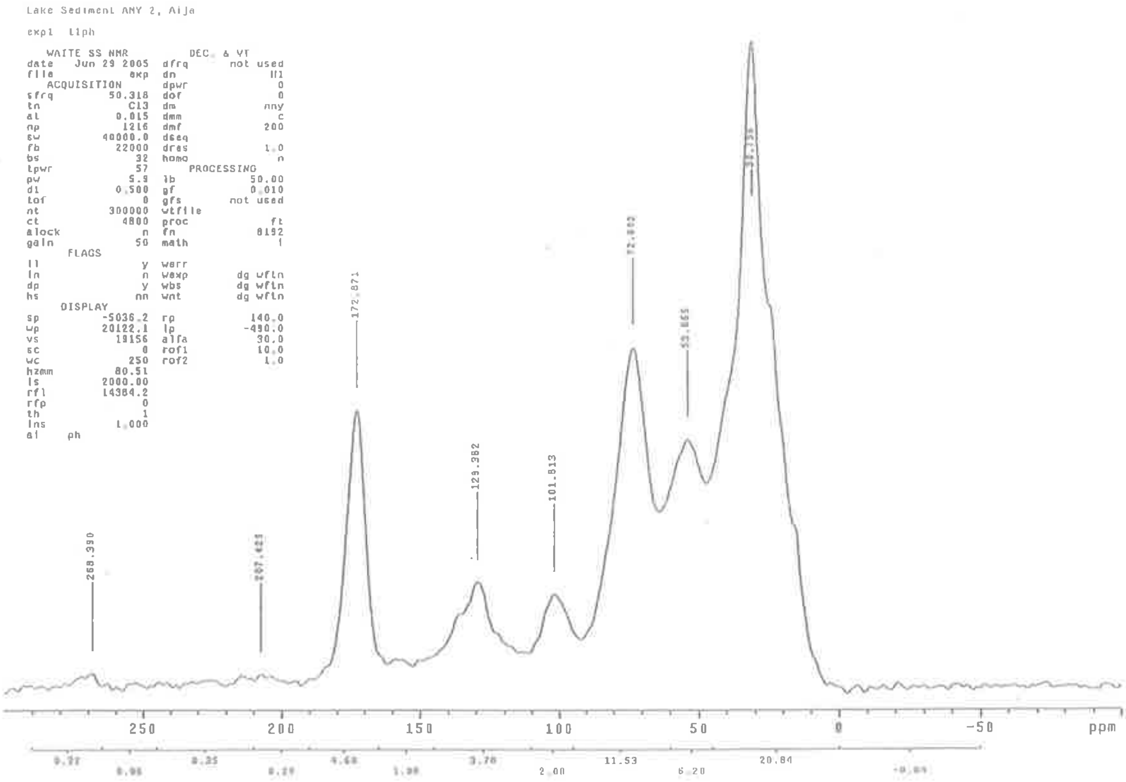

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np            1216  dmf            200
sw         40000.0  dseq
fb           22000  dres           1.0
bs              32  homo             n
tpwr            57       PROCESSING
pw             5.9  lb           50.00
d1           0.500  gf           0.010
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rfl        14384.2
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th               1
ins          1.000
ai     ph
```

Lake-sediment AMY 3, Alja

expl tlph

```
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tn              C13   dm               nny
at            0.015   dmm                c
np             1216   dmf              200
sw          40000.0   dseq
fb            22000   dres             1.0
bs               32   homo               n
tpwr             57        PROCESSING
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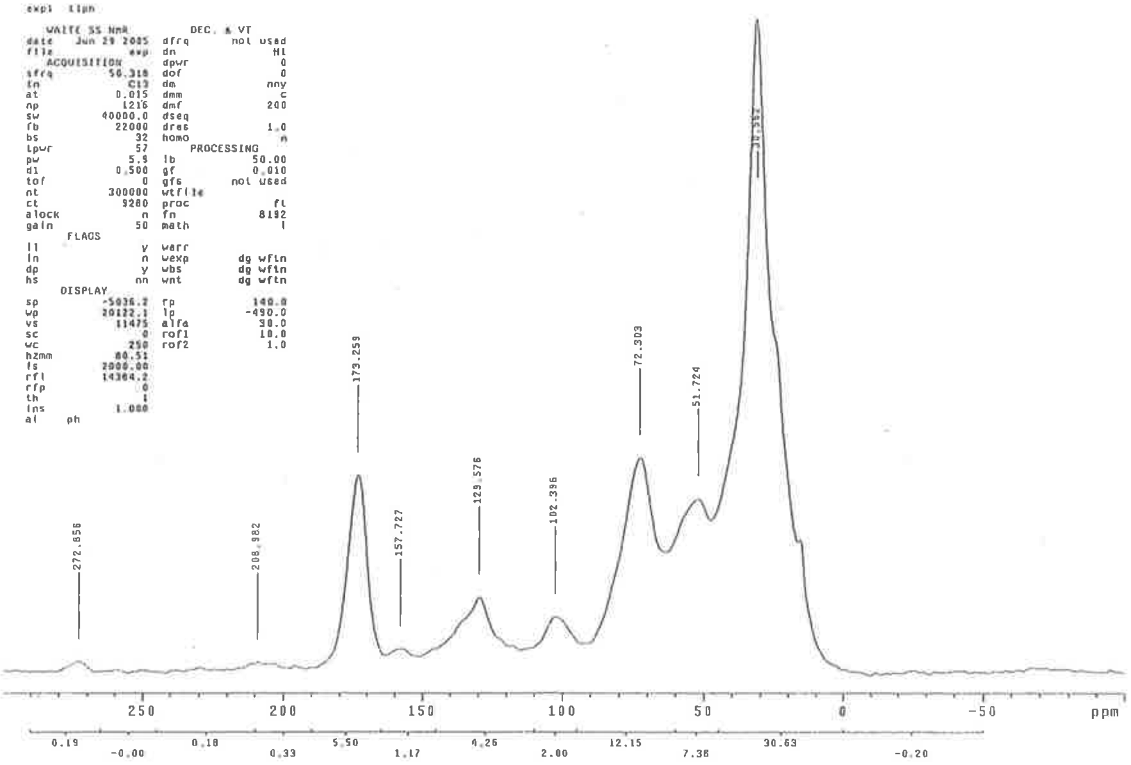

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Lake Sediment AMY ~~8~~, Alja

expl tlph

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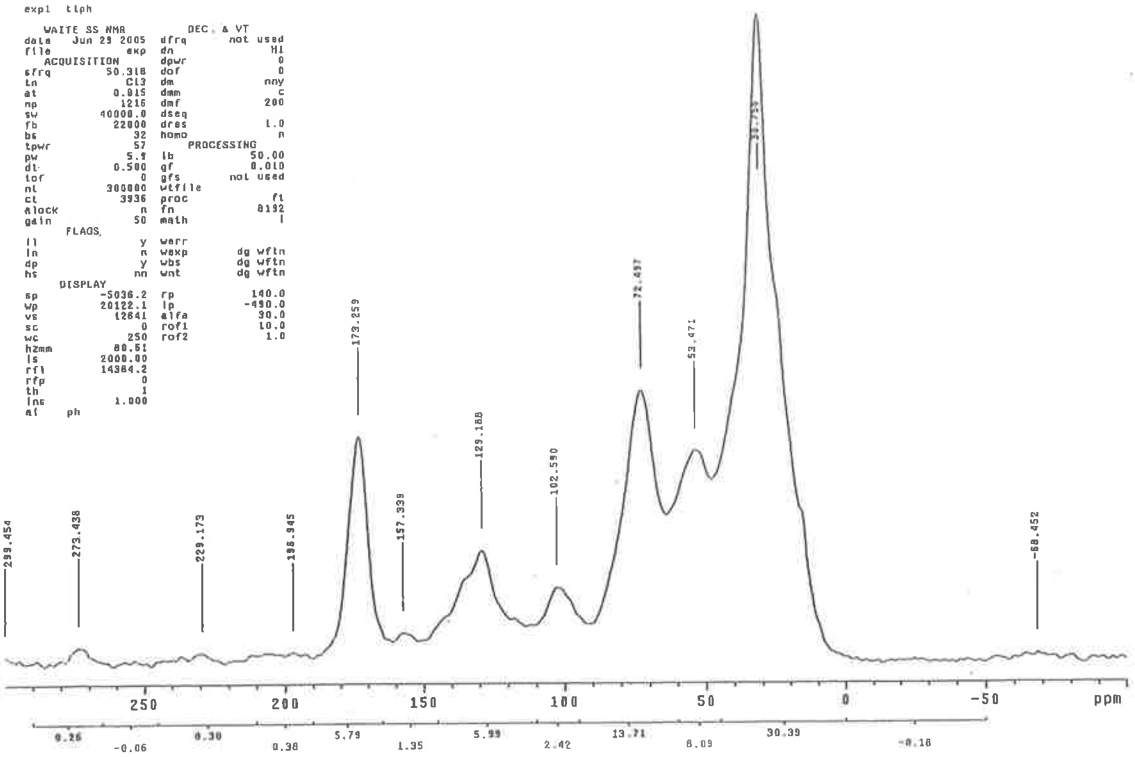

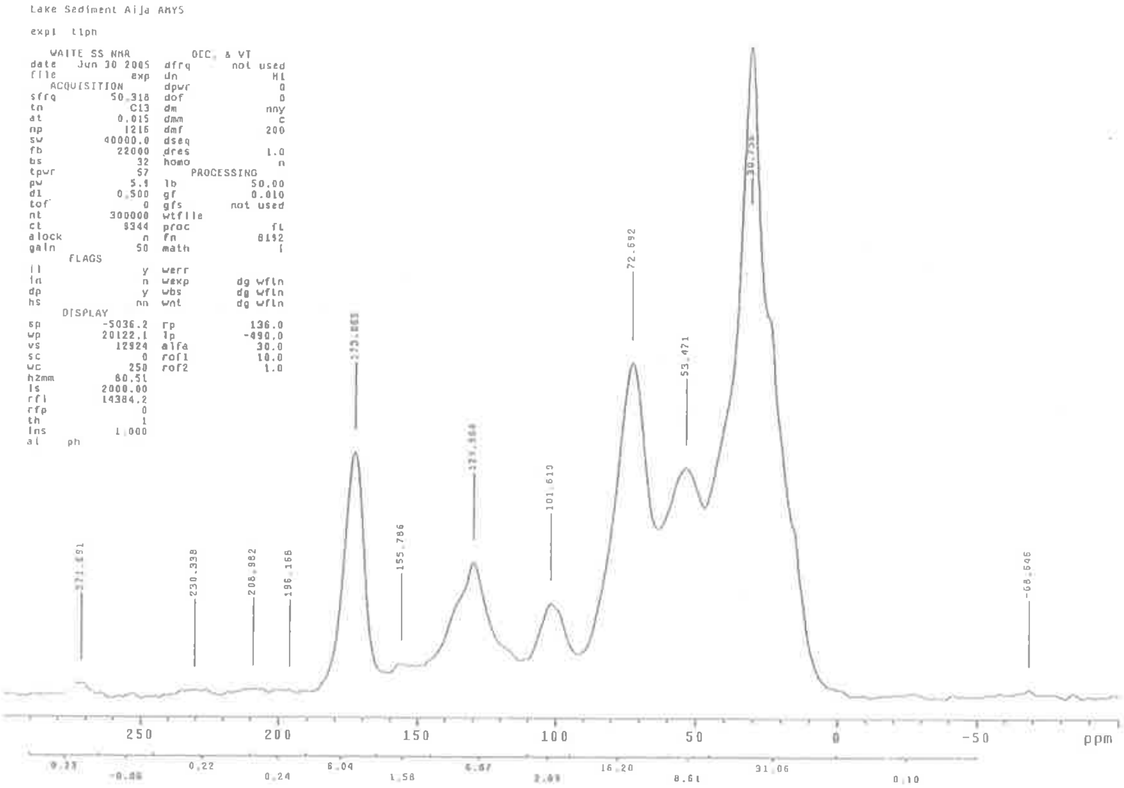

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Lake Sediment Aija AMYS

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np             1216  dmf              200
sw          40000.0  dseq
fb            22000  dres             1.0
bs               32  homo               n
tpwr             57       PROCESSING
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ai     ph
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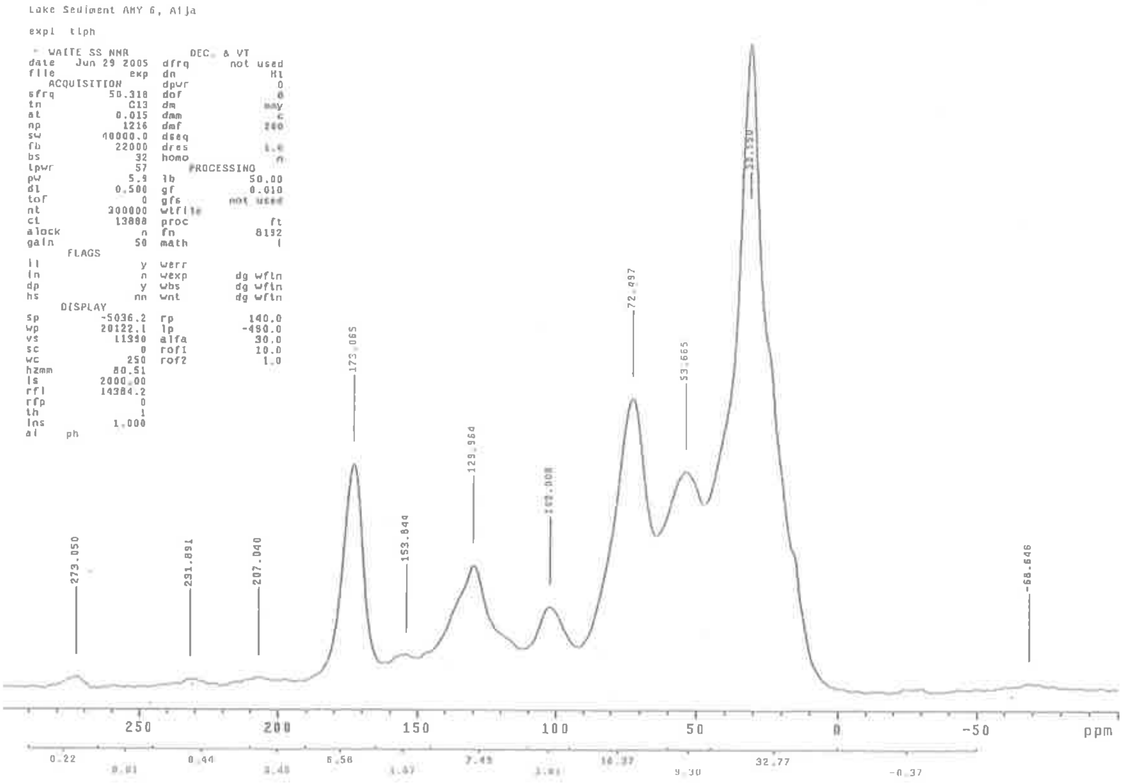

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bs               32  homo               n
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is          2000.00
rfl         14384.2
rfp               0
th                1
ins           1.000
ai     ph
```

APPENDIX V OxCal output showing the multiple age ranges (and associated statistical probabilities) produced by calibration of conventional radiocarbon ages

Lake	ANSTO code	Depth (cm)	Conventional ^{14}C Age (yr BP)		(1σ error)	Calibrated ^{14}C Age (Cal yrs BP) (1σ error) age range	prob.	(2σ error) age range	prob.
NSL	OZH369	118	5470	+/-	180	6400 - 5990	1	6650 - 5750	1
	OZH213	152	5050	+/-	50	5880 - 5820	0.27	5900 - 5600	1
						5760 - 5650	0.73		
	OZH214	183	4930	+/-	50	5660 - 5580	0.92	5740 - 5570	0.83
						5510 - 5480	0.08	5550 - 5470	0.17
	OZH215	237	5930	+/-	50	6780 - 6760	0.05	6850 - 6810	0.03
						6750 - 6630	0.95	6800 - 6530	0.97
	OZH216	282	6280	+/-	50	7250 - 7190	0.28	7270 - 6980	1
						7180 - 7150	0.17		
						7120 - 7020	0.55		
	OZH370	297	6150	+/-	90	7160 - 7110	0.16	7250 - 6700	1
						7100 - 7040	0.11		
						7030 - 6850	0.71		
						6820 - 6800	0.02		
	OZH371	297	6210	+/-	60	7160 - 6970	1	7250 - 6880	1
OML	OZH204	52	3090	+/-	50	3340 - 3200	0.89	3370 - 3070	1
						3190 - 3160	0.11		
	OZH365	69	3830	+/-	50	4240 - 4080	0.93	4410 - 4320	0.04
						4030 - 4010	0.07	4300 - 3970	0.96
	OZH205	85	4380	+/-	50	4970 - 4840	1	5050 - 4820	1
	OZH366	104	4330	+/-	50	4960 - 4930	0.09	4980 - 4780	0.75
						4890 - 4810	0.71	4770 - 4620	0.25
						4760 - 4700	0.20		
	OZH206	105	4150	+/-	50	4810 - 4760	0.22	4830 - 4500	0.91
						4700 - 4670	0.10	4490 - 4440	0.09
						4650 - 4520	0.67		
						4460 - 4450	0.01		
	OZH367	131	4250	+/-	80	4850 - 4780	0.28	5000 - 4400	1
						4770 - 4610	0.72		
	OZH368	131	4290	+/-	55	4870 - 4800	0.43	4960 - 4930	0.02
						4770 - 4640	0.57	4890 - 4570	0.98
	OZH207	182	4550	+/-	160	5320 - 4950	0.88	5600 - 4700	1
						4940 - 4870	0.12		
	OZH208	182	6890	+/-	50	7710 - 7600	1	7790 - 7580	1
AMY	OZH360	66	2430	+/-	40	2470 - 2340	1	2700 - 2630	0.10
								2620 - 2590	0.03
								2540 - 2320	0.87
	OZH361	76	2640	+/-	40	2770 - 2700	0.79	2790 - 2680	0.64
						2640 - 2610	0.14	2650 - 2610	0.12
						2560 - 2540	0.07	2600 - 2490	0.24
	OZH362	101	3060	+/-	50	3330 - 3290	0.14	3360 - 3000	1
						3270 - 3140	0.74		
						3130 - 3110	0.06		
						3100 - 3080	0.06		
	OZH209	109	3060	+/-	50	3330 - 3290	0.14	3360 - 3000	1
						3270 - 3140	0.74		
						3130 - 3110	0.06		
						3100 - 3080	0.06		
	OZH363	146	3340	+/-	50	3580 - 3440	1	3640 - 3390	1
	OZH364	197	3620	+/-	40	3960 - 3940	0.05	3980 - 3710	1
						3930 - 3820	0.81		
						3790 - 3770	0.08		
						3750 - 3730	0.06		
	OZH210	211	4020	+/-	50	4520 - 4380	0.79	4570 - 4240	1
						4370 - 4350	0.07		
						4330 - 4290	0.13		
	OZH211	223	4140	+/-	50	4810 - 4760	0.19	4820 - 4750	0.19
						4700 - 4670	0.07	4730 - 4430	0.81
						4650 - 4510	0.66		
						4470 - 4440	0.08		
	OZH212	245	4140	+/-	50	4810 - 4760	0.19	4820 - 4750	0.19
						4700 - 4670	0.07	4730 - 4430	0.81
						4650 - 4510	0.66		
						4470 - 4440	0.08		

APPENDIX VI

Geochemical and carbon and nitrogen isotope values for vegetation samples collected from within and around NSL, OML and LA

Sample ID	Vegetation	Lakes	N %	C %	C/N (mass)	C/N (atomic)	$\delta^{15}N$ ‰	$\delta^{13}C$ ‰
1	*Salicornia sp.*	NSL, OML, LA	1.8	39.1	22.0	25.6	13.5	-28.7
2	Submerged reed (roots)	OML	4.5	47.3	10.6	12.3	5.3	-20.2
3	*Ruppia sp.*	OML	1.5	28.7	19.3	22.5	13.4	-16.2
4	Submerged reed (leaves)	OML	1.5	35.8	23.1	27.0	13.7	-15.5
5	*Pimlea serpylifolia*	LA	1.4	41.6	29.7	34.6	5.3	-30.0
5b			0.5	40.5	76.5	89.3	6.2	-30.2
7	*Melaleuca halamaturm*	NSL, LA	0.8	44.6	55.1	64.3	3.6	-25.9
7b			0.6	47.3	74.4	86.8	0.7	-25.3
8	*Rhagodia sp.*	NSL	1.0	37.1	35.9	41.9	3.7	-28.1
8b			0.8	40.7	48.4	56.5	10.8	-26.8
9	*Eucalyptus diversifolia*	NSL	0.7	50.5	76.1	88.8	154.2	-26.6
9b			0.4	50.9	128.2	149.6	480.2	-25.1
10	*Thomasia petalocalyx*	NSL	0.9	48.6	53.0	61.8	-1.0	-26.3
11	*Banksia marginata*	NSL	0.6	51.7	84.9	99.1	13.3	-25.6
11b			0.2	46.3	292.1	340.8	7.8	-25.6
12	*Olearia axcillaris*	NSL	0.9	45.2	48.7	56.8	3.7	-26.0
13	*Salicornia quinquefolia*	NSL	0.9	30.3	35.1	41.0	5.6	-25.3
14	*Halosarcia sp.*	NSL	1.0	29.7	28.3	33.1	3.7	-27.3
15	*Melaleuca laceolata*	OML	1.4	49.1	35.3	41.3	2.6	-28.6
15b			0.6	46.5	74.7	87.1	13.0	-27.0
16	*Tetragonia implexicoma*	OML	0.9	27.8	30.8	35.9	3.6	-25.7
18	*Acacia longifolia*	OML	1.6	45.4	27.6	32.3	-16.8	-28.1
18b			0.9	42.7	46.0	53.7	-15.6	-26.3
19	*Leucopogon sp.*	OML	0.5	29.0	68.0	79.4	-0.8	-29.2
19b			0.4	48.1	133.3	155.5	-6.5	-28.3
X1	Unidentified reed/sedge	NSL, OML, LA	0.7	45.2	62.0	72.3	8.9	-25.9
X2	Unidentified reed/sedge	NSL, OML, LA	0.6	34.4	58.1	67.8	6.9	-30.5
X3	Unidentified reed/sedge	NSL, OML, LA	1.2	39.7	34.1	39.8	0.3	-27.0
X4	Unidentified reed/sedge	NSL, OML, LA	0.7	43.0	60.7	70.8	-0.6	-28.2

PUBLICATIONS

PUBLICATIONS ARISING FROM THESIS

Mee, A.C., McKirdy D.M., Krull, E.S., Williams, M.A.J., 2004. 'Geochemical analysis of organic-rich lacustrine sediments as a tool for reconstructing Holocene environmental conditions along the Coorong coastal plain, southeastern Australia.' *In:* Roach I.C. (Ed.) Regolith 2004. CRC LEME, Australia. pp 247-251.

Mee, A.C., McKirdy, D.M., Krull, E.S., Williams, M.A.J., 2006. 'Holocene environmental change recorded in shallow lakes of the Coorong region, southeastern Australia.' Australian Earth Sciences Convention Extended Abstracts. Online at www.earth2006.org.au

Mee, A.C., McKirdy, D.M., Williams, M.A.J., Krull, E.S., 2007. 'New radiocarbon dates from sapropels in three Holocene lakes of the Coorong coastal plain, southeastern Australia.' Australian Journal of Earth Sciences 54: 1-11.

Australian Journal of Earth Sciences (2007) **54**, (825–835)

New radiocarbon dates from sapropels in three Holocene lakes of the Coorong coastal plain, southeastern Australia

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[2]*Geographical & Environmental Studies and CRC for Landscape, Environments & Mineral Exploration, University of Adelaide, SA 5005, Australia.*
[3]*CSIRO Land and Water and CRC for Greenhouse Accounting, PMB2, Glen Osmond, SA 5064, Australia.*

The Holocene calcareous mudstone successions of numerous shallow coastal lakes in the Coorong region of southeastern South Australia include prominent organic-rich intervals (0.01–1 m thick; total organic carbon $>2\%$), herein termed sapropels. New radiocarbon dates ($n = 25$) on bulk organic matter in single cores from three such lakes indicate that these sapropels are older in North Stromatolite Lake, part of the Salt Creek lake chain, than 100 km further south in the Robe Range at Old Man Lake and Lake Amy. The onset of sapropel deposition in North Stromatolite Lake at *ca* 6400 cal y BP marked its isolation from the open Coorong Lagoon, whereas in Old Man Lake, the onset of sapropel formation at *ca* 4000 cal y BP coincided with the transition from lagoonal to perennial lacustrine conditions as the sea withdrew from the interdunal Robe–Woakwine corridor. In contrast, the depocentre at Lake Amy was never directly connected to the marine system. Here, organic matter from near the base of the lowermost sapropel, dated at *ca* 4100 cal y BP, provides a minimum age for the onset of lacustrine conditions. Sapropel deposition recorded thus far in these lacustrine sequences ceased earlier in North Stromatolite Lake (*ca* 5000 cal y BP) than in Old Man Lake (*ca* 2600 cal y BP) and Lake Amy (*ca* 1900 cal y BP). This may simply reflect a marked local climatic gradient (drier in the north, wetter in the south). Alternatively, it may indicate that these shallow lacustrine sapropels, unlike their marine and deep-lake counterparts, do not form only during times of high precipitation but may be triggered by other processes such as the enhanced aeolianite influx associated with aridification.

KEY WORDS: coastal lakes, Coorong, Holocene, radiocarbon age, sapropel, South Australia.

INTRODUCTION

The Holocene successions of many shallow perennial and ephemeral lakes along the Coorong coastal plain are notable for their content of one or more organic-rich units or sapropels (von der Borch & Altmann 1979; Warren 1990; Mee *et al.* 2004, 2005). Sapropels are marine or lacustrine sediments >0.01 m thick and containing $>2\%$ by dry weight of total organic carbon (TOC) (Kidd *et al.* 1978). In the three lakes of the present study (North Stromatolite Lake, Old Man Lake, Lake Amy: Figure 1), sapropels are gelatinous calcareous mudstones up to 1 m thick and rich in organic matter of predominantly algal and bacterial origin (TOC $= 2$–23%; hydrogen index, HI >300 mg hydrocarbons/g TOC: Hayball *et al.* 1991; Mee *et al.* 2004). Previous studies of the microfossil and molecular fossil assemblages of these sapropels have identified diatoms as major sources of their organic matter (McKirdy *et al.* 1995, 1999, 2002; Edwards *et al.* 2006).

Comparison with other sapropels

Across the globe, the deposition of similar organic-rich sediments in marine and deep-lake settings has been linked to abrupt environmental change, particularly increased precipitation and river discharge (Bouloubassi *et al.* 1999; Meyers & Lallier-Verges 1999; Tolun *et al.* 2002; Meyers 2003). The resulting riverine influx of nutrients boosts primary productivity leading to enrichment of the sediments in autochthonous organic matter. Restricted circulation and bottom water anoxia enhance the preservation of the sapropel but are not prerequisites for its formation (Pedersen & Calvert 1990; Calvert *et al.* 1992), as also recently demonstrated for North Stromatolite Lake (Edwards *et al.* 2006). Accordingly, McKirdy *et al.* (2002) were the first to suggest that the lacustrine sapropels of the Coorong region may be proxies for Holocene climate change across southeastern Australia. However, the exact trigger(s) of the enhanced productivity required for

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ISSN 0812-0099 print/ISSN 1440-0952 online © 2007 Geological Society of Australia
DOI: 10.1080/08120090701392697

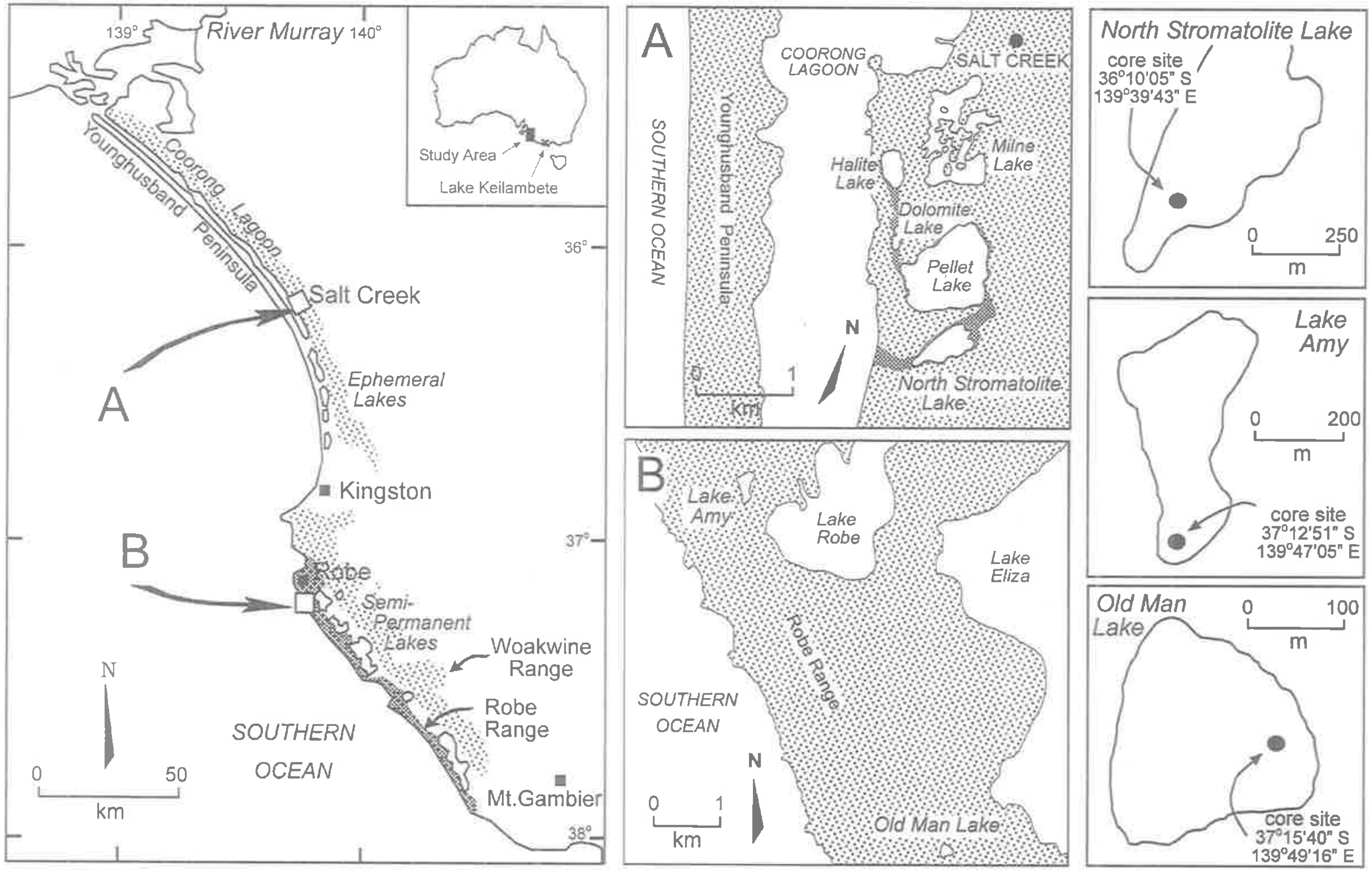

Figure 1 Map of the Coorong coastal plain, southeastern Australia, showing the locations of North Stromatolite Lake, Old Man Lake and Lake Amy, and the core sites within them.

sapropel formation in these relatively shallow coastal lakes have yet to be identified. This is especially true of those in the Salt Creek lake chain and the Robe Range (Figure 1), none of which are fed by streams or rivers. Rather, North Stromatolite Lake and Old Man Lake are charged by westward-flowing saline continental groundwater (Holmes & Waterhouse 1983; Warren 1990) augmented by seasonal precipitation, whereas the more elevated Lake Amy is the surface expression of a local perched water-table high in the Robe Range (A. J. Brenchley pers. comm. 2005). The regional water-table has remained nearly static throughout the history of these coastal lakes, reflecting the near constancy of mid- to Late Holocene sea-level. Maximum annual rainfall is 600 mm near Kingston (Figure 1) where precipitation exceeds evaporation for 3–4 months of the year, while around Salt Creek it is 400 mm, and evaporation exceeds precipitation for all but a few weeks in mid-winter (Warren 1990). The hypolimnion of North Stromatolite Lake during deposition of its sapropel unit, as inferred from key indicator diatom species and oxygen isotope measurements on benthic ostracods, increased erratically from oligosaline to eusaline (Edwards *et al.* 2006). These authors interpreted the biostratigraphy and chemostratigraphy of this sapropel to indicate variable climate during its deposition.

Holocene climatic variability

A growing body of evidence shows that there were frequent and often rapid climatic variations across the globe throughout the Holocene (Bond *et al.* 2001; Mayewski *et al.* 2004; Turney *et al.* 2004). In southeastern Australia, the expansion of woody vegetation (Kershaw *et al.* 1991) and rising lake levels (Dodson 1977; Bowler 1981; Edney *et al.* 1990) are evidence of an absolute increase in precipitation and a general climatic amelioration beginning *ca* 10 000 y BP. The early to mid Holocene (8000–6000 y BP) is considered by numerous authors (Chivas *et al.* 1993; Dodson & Ono 1997) to be a time of prolonged regional warming when rainfall was possibly 5–10% higher and temperatures 1–2°C warmer than today (McGlone *et al.* 1996). In western Victoria, at Lake Keilambete, the water level rose by 35 m between 11 000 and 7500 y BP before beginning a slow decline toward its mid-Holocene level *ca* 6500 y BP (Bowler 1981) (Figure 2). Palynological studies at nearby Lakes Terang and Bullenmerri indicate the development of wetter conditions between 8000 and 6200 y BP (D'Costa & Kershaw 1995) and 8000 and 5500 y BP (Dodson 1979), respectively. In southern South Australia, the 50 000 year-old Lake Leake was at its deepest between 8000 and 3000 y BP (Dodson 1975).

Since the peak of the Holocene marine transgression at *ca* 6000 y BP (Belperio 1995), there has been a shift toward generally cooler and drier conditions across the region. Vegetation change recorded in the sediments of Lake Frome suggests that summer precipitation in eastern South Australia had significantly decreased by *ca* 4500 y BP (Singh & Luly 1991). Playa conditions were re-established at Lake Frome by 3000 y BP (Bowler & Teller 1986). A similar two-phase drying is recorded at Chapple Vale Swamp, 30 km northwest of Cape Otway, where pollen analysis suggests that a reduction in effective precipitation began at 4600 y BP and was further accentuated some 800 years later (McKenzie & Kershaw 1997). A simultaneous shift to drier conditions in the Mt Lofty Ranges is implied by a reduction in

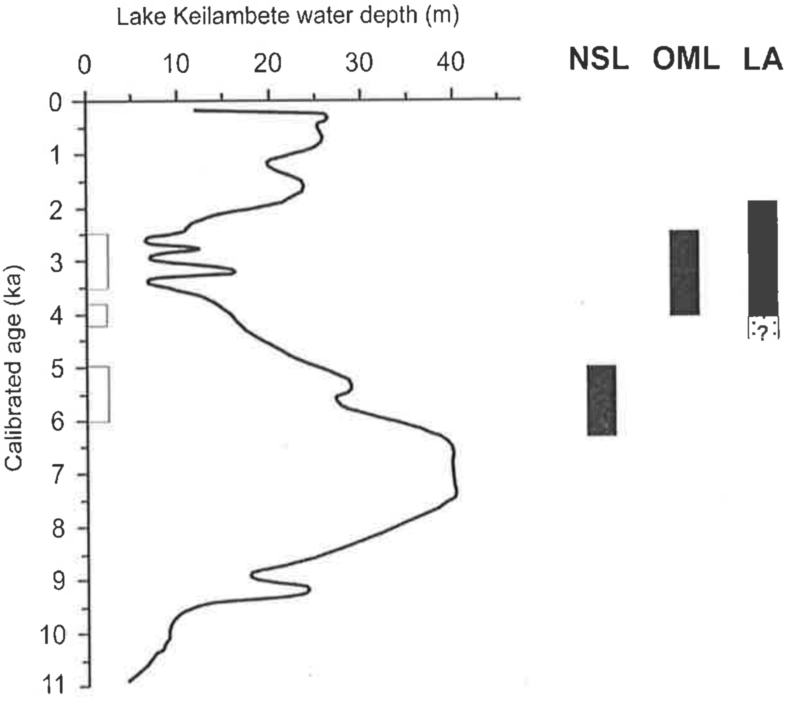

Figure 2 Water-level curve for Lake Keilambete in western Victoria (after Bowler 1981). The black bars indicate periods of sapropel deposition in North Stromatolite Lake, Old Man Lake and Lake Amy (this study). The paler bars represent periods of rapid global climate change (after Mayewski *et al.* 2004).

organic content and humification of the sediments in Boat Harbour Creek (Bickford & Gell 2005). Minimum effective precipitation seems to have occurred slightly later at Lake Keilambete, which was at its lowest Holocene levels between 3500 and 2500 y BP and has since returned to a somewhat wetter climatic regime (Bowler 1981) (Figure 2). There has been no such return to wetter conditions in semiarid northwestern Victoria, where permanent Lake Tyrrell dried to a playa at *ca* 2200 y BP (Luly 1993).

Sapropel deposition in the lakes of the Coorong region may be a manifestation of the regional Holocene climatic changes documented in the aforementioned studies. The radiocarbon ages reported herein define the onset and cessation of sapropel deposition recorded thus far in these three lakes. These data are a fundamental addition to the fragmentary radiocarbon database for Holocene sediments of southeastern South Australia (von der Borch & Altmann 1979; Barnett 1994; Cann *et al.* 1999; Mee *et al.* 2004; Edwards *et al.* 2006).

Geology of the Coorong coastal plain

The modern coastal Robe Range and adjacent Woakwine Range, situated 10–15 km inland, are the youngest of a sequence of 13 subparallel northwest–southeast-trending beach-dune ridges preserved along the coastal plain of southeastern Australia (Figure 1). The ridges are each related to specific Pleistocene sea-level highstands with the Woakwine Range being associated with the last interglacial at *ca* 125 000 y BP (Schwebel 1983; Huntley *et al.* 1993; Belperio 1995). In the early Holocene (prior to *ca* 7000 y BP), the postglacial marine transgression flooded the Robe–Woakwine corridor resulting in the formation of a shallow back-barrier lagoon, which was open to the Southern Ocean near the present towns of Robe and Beachport (Cann *et al.* 1999). Sea-level stabilised close to its present position at *ca* 6700 y BP (Belperio 1995). Since this time, sand transport associated with a combination of ocean swell, wave action and tidal movement has isolated the Robe–Woakwine backbarrier lagoon from the open ocean. To the north lies the Coorong Lagoon itself. At the peak of the marine transgression, this water body extended continuously for more than 200 km from the Murray mouth to Kingston. Subsequent landward migration of the coastal dunes of the Younghusband Peninsula has broken the lagoon south of Salt Creek into a series of ephemeral lakes (Warren 1990). Evidence of rapid change from marine to lacustrine conditions is evident in sediment cores retrieved from these modern lakes. For example, beds of fossil marine fauna, such as oysters, are present in the lacustrine sedimentary sequence of lakes Eliza (Burne & Ferguson 1983) and Robe (Cann *et al.* 1991).

Evolution of three small Coorong lakes

North Stromatolite Lake is part of the Salt Creek lake chain, situated at the northern end of the ephemeral Coorong Lagoon and within the Coorong National Park, ~230 km south-southeast of Adelaide (Figure 1). During the early Holocene, this group of four lakes existed as a narrow extension of the Coorong Lagoon, connected via the southern end of North Stromatolite Lake. Dune migration and sediment deposition eventually blocked this access corridor and isolated the embayment from the Coorong Lagoon. The resulting restriction of water movement led to the buildup of sandy estuarine sediments in the inter-lake corridors effectively converting the water body from an estuarine/marine environment into the chain of isolated schizosaline lakes that exists today. They are designated Type 2 lakes by Warren (1990) to distinguish them from others like Milne Lake (Type 1) that initially were not connected to the Coorong Lagoon. The subsequent evolution of water chemistry and therefore sedimentology is unique to each lake and has been well documented by Rosen *et al.* (1988) and Warren (1990). The upward-shoaling calcareous mudstone succession of the Salt Creek lake chain typically contains three distinct Holocene lacustrine carbonate units (Figure 3)—(i) organic-rich mudstone (sapropel); (ii) laminated pelletal mudstone; and (iii) massive pelletal mudstone/packstone—that overlie Pleistocene siliciclastic–carbonate grainstone to wackestone and beach-dune sands. This textural transition from laminated to massive sedimentary units has been interpreted as a change from perennial to ephemeral aquatic conditions in a setting of relatively low energy (Warren 1990).

Old Man Lake and Lake Amy are both shallow (<4 m water depth) perennial lakes located near the township of Robe and nestled in topographic lows of the Robe Range, ~100 km south of North Stromatolite Lake (Figure 1). As a result of differential neotectonic uplift, the coastal barrier deposits of the Last Glacial Maximum in this area are now ~2 m higher than those at Salt Creek (Murray-Wallace & Belperio 1991). Old Man Lake existed as a restricted embayment of a local back-barrier lagoon during the early Holocene and has evolved in a manner similar to that described above for North Stromatolite Lake. A siliciclastic–carbonate lagoonal unit containing humic organic matter is associated with the rising groundwater-table that preceded the early Holocene transgressive marine flooding and was deposited unconformably on the basal Pleistocene aeolianite. The upward-shoaling transition from marine to lacustrine conditions is apparent in the three subsequent and distinct carbonate units (Figure 3): lagoonal silts and muds with abundant remains of shallow marine fauna; laminated lacustrine mudstone with sapropel intervals; and massive pelletal mud with abundant remains of the gastropod *Coxiella striata* (McKirdy *et al.* 1999).

As Lake Amy was never directly connected to the marine system, its sediments are an expression of changes in the local perched groundwater-table. A massive bioturbated pelletal carbonate mudstone overlies a laminated lacustrine mudstone with sapropel intervals, hardpans and variable amounts of ostracod and gastropod remains (Figure 3). This sequence represents an upward-shoaling lacustrine system analogous to the Type 1 lakes near Salt Creek. In the absence of an estuarine connection to the ocean, there is no lagoonal unit. Previous workers have observed a humic transgressive unit similar to that observed in Old Man

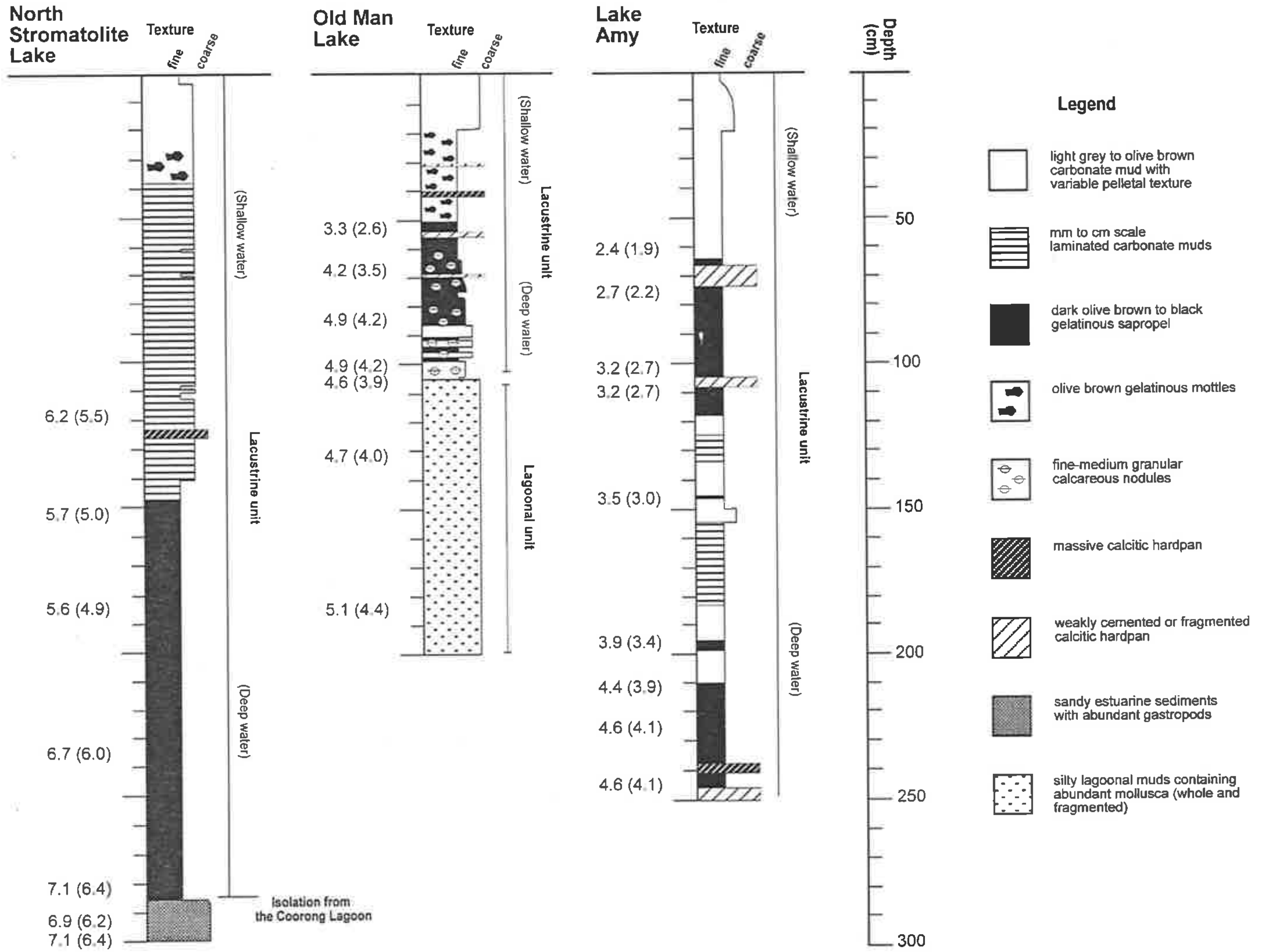

Figure 3 Stratigraphic logs for the uncompacted sediment cores from North Stromatolite Lake, Old Man Lake and Lake Amy. ^{14}C ages of dated intervals are in calibrated years BP × 1000. Those in brackets are reservoir-corrected ages.

Lake overlying the basal Pleistocene aeolianite and dated at 7870 ± 210 y BP (Cann *et al.* 1999; McKirdy *et al.* 2005). However, the core analysed in the present study ended short of the base of the lowermost sapropel interval and thus did not reach these older units.

The data presented herein are part of ongoing geochemical investigations of sediment cores from North Stromatolite Lake, Old Man Lake and Lake Amy (Mee *et al.* 2004, 2005, 2006; McKirdy *et al.* 2005; Edwards *et al.* 2006) aimed at establishing the nature and extent of Holocene environmental change throughout the Coorong region. This suite of 25 new radiocarbon dates on organic matter from three separate localities and on two modern water samples provides a robust geochronological framework for assessing the timing and duration of Holocene lacustrine sapropel events in southeastern South Australia and hence their possible paleoclimatic implications.

METHODS

A single sediment core was collected from each lake during December 2003 using a D-section (Russian peat) corer. This technique retrieves only a semicircular (half) core of 50 mm diameter, yet is superior to other soft-sediment coring methods because it does not compact the collected sediment. Upon return from the field core stratigraphy was described in detail and the cores stored at 4°C in the Geographical and Environmental Studies Core Store at the University of Adelaide. To determine total organic carbon (TOC) content, subsamples (1 cm thick) were treated with 5% w/w sulfurous acid (H_2SO_3) prior to incineration in a LECO C 144 carbon analyser. Sulfurous acid was used in the pretreatment process to remove the carbonate fraction while minimising the loss of labile organic carbon components. One in five samples were duplicated with results differing by <0.5%. Radiocarbon dating and carbon isotopic analysis of the bulk organic matter ($n = 24$) plus one charcoal sample were undertaken at the ANSTO AMS facility (Fink *et al.* 2004). Two samples from Old Man Lake (OZH366, OZH368) plus a sample from the basal unit of North Stromatolite Lake (OZH371) were initially submitted for radiocarbon analysis of the charcoal fraction for comparison with bulk organic matter from the same depth. Unfortunately, there was insufficient charcoal in the sedimentary samples so the three paired dates are all from bulk organic matter only. While the absence of macroscopic charcoal or macrofossil dates is regrettable, it is encouraging to see that all paired samples returned comparable radiocarbon dates. Subsequently, in June 2005, water samples were collected from two of the lakes (Old Man Lake and Lake Amy) for dating of their dissolved carbonate. All radiocarbon dates were converted to calendar years by calibration against the atmospheric ^{14}C curve for the Southern Hemisphere (McCormac *et al.* 2004) using the internationally ratified online calibration program, OxCal (version 3.10: Bronk Ramsey 1995, 2001). Carbon isotopic values are reported as $\delta^{13}C‰$ relative to the PDB standard. Replicate analyses of laboratory standards typically showed a precision of ±0.1‰.

RESULTS

Total organic carbon

The TOC contents of samples taken from depths adjacent to the radiocarbon samples are shown in Table 1. These values are representative of the major sedimentary units in each lake (Mee *et al.* 2004, 2005).

The basal estuarine sandy unit of North Stromatolite Lake is relatively low in TOC (<1%). The overlying organic-rich lacustrine unit may be subdivided into a lower dark olive-grey sapropel (~1 m thick, TOC = 6–16%) and an upper olive to dark-brown sapropel (~0.3 m, TOC ~4%). TOC decreases to <1% in the overlying laminated and massive units.

The lagoonal unit in the lower section of the Old Man Lake core has TOC values <0.5%. In the overlying lacustrine sapropelic unit, TOC fluctuates in the range 3–17%, the lower values coinciding with the presence of carbonate accumulations such as ostracods, gastropods and less commonly calcitic nodules and granular hardpans.

In the Lake Amy core TOC contents throughout the lacustrine laminated sapropelic mudstone remain above 10% (max. 21.5%). The sample relatively low in TOC at the top of this unit is from immediately above a weakly cemented hardpan.

Stable carbon isotopic composition

Organic matter in the dated sapropels (Figure 3) has carbon isotopic compositions ($\delta^{13}C$ of −23.7 to −16.9‰: Table 1) that are well within the range previously reported for these lakes (McKirdy *et al.* 1999, 2005; Mee *et al.* 2004, 2006). Similar $\delta^{13}C$ values were obtained for the organically lean sediments above and below the sapropel interval in North Stromatolite Lake (−19.0‰, shallow lacustrine; −17.6 and −19.5‰, estuarine) and below it in Old Man Lake (−17.7 and −19.2‰, lagoonal). In contrast, the dispersed organic matter and charcoal from lower in the lagoonal unit at Old Man Lake is more depleted in ^{13}C ($\delta^{13}C = -25.0$ and −24.0‰, respectively).

Radiocarbon

Conventional and calibrated radiocarbon ages for samples of the bulk organic matter preserved in the Holocene sediments of all three lakes are shown in Table 1, along with similar data on inorganic carbon in contemporary water samples from Old Man Lake and Lake Amy. The latter help constrain the magnitude of the ^{14}C reservoir effect (previously known as the 'hard water effect') on the groundwater entering these lakes and on the aquatic photosynthetic biomass that used its dissolved carbonate as a carbon source (Geyh *et al.* 1998).

The radiocarbon dates discussed below are the calibrated ages (expressed as calendar years BP). The maximum ages (y BP) on bulk organic matter (sapropel) are 7070 ± 95 in North Stromatolite Lake, 5140 ± 185 in Old Man Lake and 4580 ± 70 in Lake Amy, whereas the age of the charcoal from low in the lagoonal unit in Old Man Lake is 7660 ± 55. Present-day water samples from

Table 1 Carbon isotope values ($\delta^{13}C$ relative to PDB), and conventional and calibrated radiocarbon ages for bulk organic matter and dissolved carbonate carbon in water samples from North Stromatolite Lake, Old Man Lake and Lake Amy plus a 1 cm^3 piece of charcoal picked from the lagoonal unit of Old Man Lake.

ANSTO code	Depth (cm)	$\delta^{13}C$ (‰)	Conventional ^{14}C age (y BP)	Calibrated ^{14}C age (cal y BP)	TOC (%) at [depth (cm)]
North Stromatolite Lake					
OZH369	118	−19.0	5470 ± 180	6200 ± 205	0.7 [124]
OZH213	152	−17.1	5050 ± 50	5710 ± 55	3.9 [155]
OZH214	183	−18.6	4930 ± 50	5620 ± 40	4.1 [179]
OZH215	237	−18.6	5930 ± 50	6710 ± 75	16.4 [238]
OZH216	282	−21.1	6280 ± 50	7070 ± 50	9.5 [283]
OZH370	297	−19.5	6150 ± 90	6940 ± 90	0.7 [293]
OZH371	297	−17.6	6210 ± 60	7070 ± 95	0.7 [293]
Old Man Lake					
OZI264[a]	0	0.1	815 ± 40	700 ± 30	–
OZH204	52	−20.8	3090 ± 50	3270 ± 70	4.0 [52]
OZH365	69	−21.9	3830 ± 50	4160 ± 80	13.4 [65]
OZH205	85	−19.6	4380 ± 50	4910 ± 65	15.9 [85]
OZH366	104	−22.2	4330 ± 50	4850 ± 40	3.1 [105]
OZH206	105	−22.7	4150 ± 50	4610 ± 90	3.1 [105]
OZH367	131	−19.2	4250 ± 80	4690 ± 80	0.3 [124]
OZH368	131	−17.7	4290 ± 55	4710 ± 65	0.3 [124]
OZH207	182	−25.0	4550 ± 160	5140 ± 185	0.4 [183]
OZH208[b]	182	−24.0	6890 ± 50	7660 ± 55	–
Lake Amy					
OZI263[a]	0	1.1	475 ± 30	505 ± 20	–
OZH360	66	−17.7	2430 ± 40	2410 ± 65	8.1 [70]
OZH361	76	−16.9	2640 ± 40	2740 ± 35	8.1 [70]
OZH362	101	−18.5	3060 ± 50	3210 ± 65	16.8 [103]
OZH209	109	−18.0	3060 ± 50	3210 ± 65	16.3 [110]
OZH363	146	−19.3	3340 ± 50	3510 ± 70	10.4 [152]
OZH364	197	−17.6	3620 ± 40	3880 ± 55	10.4 [201]
OZH210	211	−19.2	4020 ± 50	4450 ± 70	14.3 [210]
OZH211	223	−20.9	4140 ± 50	4580 ± 70	20.6 [222]
OZH212	245	−23.0	4140 ± 50	4580 ± 70	17.4 [244]

Total organic carbon (TOC) values are for adjacent samples taken for geochemical analysis (Mee *et al.* 2004, 2005).
[a]Water sample; [b]charcoal fragment.

Lake Amy and Old Man Lake yielded apparent ages of 505 ± 20 and 700 ± 30 y BP, respectively.

DISCUSSION

Stable carbon isotopic signatures

The $\delta^{13}C$ values obtained for the dated sapropel samples in all three lakes, along with the elemental and ^{13}C-NMR data from our earlier studies (Mee *et al.* 2004, 2006), are indicative of organic matter derived largely from lacustrine photoautotrophs (algae and bacteria) that used bicarbonate as their source of dissolved inorganic carbon, augmented by minor inputs of allochthonous terrestrial biomass. Those of the dispersed organic matter and charcoal in the lagoonal unit at Old Man Lake are consistent with its likely origin from mostly terrestrial vegetation (C3 land plants).

Reservoir effect

From their inception, all three lakes have been shallow (<4 m), ensuring rapid equilibration of their dissolved inorganic carbon with atmospheric radiocarbon. However, given the permeable and calcareous nature of the Pleistocene beach ridge arenites (Bridgewater Formation) which dominate the surficial geology of the Coorong and Robe–Naracoorte coastal plains (Schwebel 1983; Cann *et al.* 1999), it is inevitable that some portion of the dissolved carbonate in the continental groundwaters that charge these lakes will be inert carbon entrained from the unconfined host aquifer. Photosynthetic incorporation of this inert carbon causes the apparent radiocarbon ages of aquatic organic matter to be somewhat older than the true ages. This 'reservoir effect' is confirmed by the fact that carbonate dissolved in the water from Lake Amy and Old Man Lake comprises <100% modern carbon (94.26 and 90.35 pMC, respectively), giving rise to the aforementioned apparent ages of 505 and 700 y BP. The older of these two ages reflects the larger catchment area for the groundwater entering Old Man Lake and North Stromatolite Lake from the coastal hinterland and hence its longer interaction with the Bridgewater Formation. The much smaller local catchment of the perched water-table at Lake Amy means that its water has had less contact with the calcarenite of the surrounding Robe Range.

Accordingly, a higher proportion of its dissolved carbonate is modern carbon.

Macroscopic terrestrial plant remains yield the most reliable radiocarbon dates on lacustrine sediments (Geyh *et al.* 1998). In the absence of such material in these cores, the apparent ages of contemporary water in Old Man Lake and Lake Amy provide the best available constraints on the magnitude of the hard-water effect on the ^{14}C dates obtained for the sapropels in this study. In applying this reservoir correction (Figures 2, 3), the following assumptions were made: (i) that there has been no significant secular change in the volume/surface ratio of each lake, and hence in the relative proportion of the two principal sources of ^{14}C entering its water column (viz. atmospheric CO_2 and dissolved inorganic carbon in groundwater and runoff) during growth of the aquatic biomass that was eventually deposited as sapropel; and (ii) that as North Stromatolite Lake and Old Man Lake are charged by the same westward-flowing saline continental groundwater, the same correction can be made to North Stromatolite Lake as to Old Man Lake.

North Stromatolite Lake

In North Stromatolite Lake, organic matter in both the basal estuarine unit and the sapropel immediately overlying it are dated at *ca* 6400 cal y BP. Such close similarity in ages cannot be attributed to the downward infiltration of organic matter from the sapropel into the basal sand, as the two units have different organic carbon isotope values (mean basal = −18.5‰, sapropel = −21.1‰: Table 1). Instead, the similarity exemplifies the recognised uncertainty associated with radiocarbon dating while also reflecting a rapid onset of sapropel deposition at this time. The commencement of sapropel deposition marks isolation of the Salt Creek lake chain from the Coorong Lagoon and its transition from an estuarine environment to a perennial lake system (Warren 1990).

For the purpose of discussing sedimentation rates in North Stromatolite Lake, sample OZH216 (sapropel), rather than OZH370 or OZH371 (basal), is chosen as representing the true onset of sapropel deposition (at *ca* 6400 cal y BP). Its cessation is marked by sample OZH213 (dated at *ca* 5000 cal y BP) where the base of the laminated unit indicates a transition to shallower and less productive lacustrine conditions. The two contiguous organic-rich sapropel units (total thickness 130 cm) were deposited in ~1400 years (9 cm/100 y) at three times the rate of the organic-poor laminated and massive units (150 cm in ~5000 y). This decrease in sedimentation rate is interpreted as a reflection of the decline in primary productivity of autochthonous organic matter (as opposed to increased decomposition) during the later Holocene, but is also due to the 'fill and spill' sedimentation process acting in the lake (Warren 1990). This may be summarised as follows. Once the surface connection with the Coorong lagoon was severed, vertical accretion of lacustrine sediments gradually filled deeper parts of the interdunal depression. At this stage, the lake was perennial, and carbonate mud was precipitated in response to summer evaporation. As the lake basin filled with sediment, the same volume of annual inflow (derived from direct rainfall, runoff, aerosols and groundwater: Warren 1990) was forced to spill out over the original lake margins, and the same amount of precipitated carbonate was spread over a wider area, thereby decreasing the vertical sedimentation rate.

The relatively large error (±205 y) in the age of sample OZH369 may be attributed to the low TOC content of the laminated unit. Even so, its organic matter appears to be appreciably older than that in the underlying sapropel, suggesting the possible existence of a greater reservoir effect during deposition of the laminated unit. This cannot be quantified from the data obtained thus far. As the focus of this study is on the sapropel units of these lacustrine successions, no radiocarbon sample was taken at the laminated/massive unit boundary, and hence the transition from perennial to ephemeral conditions in North Stromatolite Lake is not yet accurately dated.

The sapropel event in North Stromatolite Lake (6400 – 5000 y BP: Figure 2) occurred during a prolonged maximum in effective precipitation that prevailed across southeastern Australia between 7000 and 5000 y BP (Shulmeister 1999). A significant shift toward aridity commencing at *ca* 5000 y BP has been well documented in various paleolimnological studies across this region (von der Borch & Altmann 1979; Bowler 1981; Ahmad 1996; Dodson & Ono 1997; Stanley & De Deckker 2002). It was this decline in effective precipitation, also reflected in the level of Lake Keilambete in western Victoria (Figures 1, 2), which we interpret as having halted deposition of organic-rich sediments in North Stromatolite Lake. This local sapropel event in the Salt Creek lake chain happens to overlap one of the six Holocene periods of rapid climate change recognised by Mayewski *et al.* (2004). The global rapid climate change episode in question (6000 – 5000 cal y BP) is one of several characterised by 'cool poles, dry tropics.' According to Mayewski *et al.* (2004 p. 250), at lower latitudes this rapid climate change interval 'marks the end of the early to mid Holocene humid period in tropical Africa, beginning a long-term trend of increasing rainfall variability and aridification.'

Old Man Lake

The Old Man Lake core in this study did not reach the basal Pleistocene aeolianite or intersect the transgressive humic unit that overlies it in places. Radiocarbon dates from the lagoonal unit indicate its rapid deposition between around 4500 and 4000 cal y BP. However, the relatively large error (±185 y) associated with the lower sample (OZH207) means that the sedimentation rate is difficult to calculate accurately. The charcoal sample (OZH208) from this unit has a radiocarbon age of 7660 cal y BP, making it some 3200 years older than the bulk sedimentary organic matter from the same depth. This indicates that the charcoal (≤ 1 cm^3) is derived from terrestrial vegetation which was burnt earlier and later carried into the lagoonal system of the Robe – Woakwine corridor by runoff, high onshore coastal winds or, possibly, by human activity (Cann *et al.* 1991).

Charcoal from an aboriginal midden at nearby Little Dip is somewhat older (^{14}C age = 9160 ± 130 cal y BP) but has the same stable carbon isotopic signature ($\delta^{13}C = -24.0‰$: Cann *et al.* 1999).

The transition from lagoonal to lacustrine conditions in Old Man Lake (Figure 3), represented by samples OZH366 and OZH206, occurred at *ca* 4100 cal y BP. Thereafter, the sapropel-rich interval of the laminated lacustrine unit records 50 cm of sediment accumulation in ~1500 years. Thus, the rate of sapropel deposition here is three times slower than in North Stromatolite Lake. It is also evident from the position of the sapropel interval in the Old Man Lake core (Figure 3) that the sediment accommodation space was appreciably less here than in North Stromatolite Lake and, hence, that its sapropel accumulated beneath a much shallower water column. Seasonal fluctuation of the lake level and its water chemistry is likely to have been greater, resulting in episodes of accelerated carbonate precipitation. This would perhaps explain the otherwise atypical presence of numerous calcitic nodules and several hardpans throughout the sapropel of Old Man Lake. The uppermost 50 cm of the core (not sampled for this study) comprises the mottled (less organic-rich) zone of the laminated unit plus the massive unit and was deposited in ~2600 years, which is two-thirds of the rate of sapropel accumulation.

The apparent halt in deposition of organic-rich sediments in Old Man Lake occurs some 2400 years later than the equivalent paleolimnological event in North Stromatolite Lake (Figure 2) but broadly coincides with a shift toward shallower water depths in nearby Lake Leake at *ca* 3 ka. Deposition of the organic-rich sediments of Old Man Lake took place between 4100 and 2600 cal y BP. Although this sapropel event post-dates the end of the aforementioned early to mid-Holocene humid period at 5000 y BP, it overlaps two subsequent rapid climate change periods of 'cool poles, dry tropics', namely 4200–3800 and 3500–2500 cal y BP (Mayewski *et al.* 2004). Its conclusion is coincident with the subsequent phase of drying that is evident in numerous palynological records from southeastern Australia (Bowler & Teller 1986; McKenzie & Kershaw 1997). Therefore, this lake provides further evidence for the association of sapropel deposits with periods of rapid climate change.

Lake Amy

This core represents approximately 4100 years of lacustrine sedimentation. The nine radiocarbon dates taken over the lower 185 cm of the core indicate a relatively uniform rate of accumulation of organic-rich mudstone for some 2200 years. Within this succession, two notably sapropelic intervals (dated at *ca* 4100–3400 and 2700–1900 cal y BP) are separated by an interval of variably laminated and pelletal mudstone (109–196 cm depth in core: Figure 3) that is likewise organic-rich (10–12% TOC) but lacks the characteristic gelatinous texture of a typical Coorong lacustrine sapropel.

The sapropelic sediments of Lake Amy are almost contemporaneous with those in Old Man Lake, and associated with the same two rapid climate change periods of Mayewski *et al.* (2004). Deposition of the intervening organic-rich but non-sapropelic mudstones (dated at *ca* 3400–2700 cal y BP) occurred under fluctuating arid conditions recorded in Lake Keilambete (Figure 2). The transition into the organically leaner massive unit at 66 cm depth in the core marks a halving of lacustrine sedimentation rate and is dated at *ca* 1900 cal y BP (sample OZH360). This transition is some 3100 years later than the equivalent event in North Stromatolite Lake but only 700 years later than a similar reduction in sedimentary organic-matter content in nearby Old Man Lake. This suggests the possibility of a latitudinal influence on the late Holocene microclimate of the study area (Figure 1) and its modulation of the cessation of sapropel deposition in these shallow coastal lakes.

Finally, it is significant that the times of sapropel formation in all three lakes should coincide with periods of rapid change towards more arid conditions. The accompanying influx of dust containing nutrients such as silica, phosphate and iron may well be the process that triggered the diatom blooms that were the precursors to sapropel. Stanley and De Deckker (2002) documented three such discrete intervals of enhanced aeolianite input to Blue Lake in the Snowy Mountains of southeastern Australia. Dated at 5500–4900, 3500–3000 and 2500–2300 cal y BP, these intervals correspond remarkably closely to the Coorong lacustrine sapropel events of the present study. The likely source of the dust was the continental dunefield of the Mallee region, located due north of the Coorong coastal plain (Pell & Chivas 1995).

CONCLUSIONS

The new radiocarbon dates reported herein constrain the timing of sapropel deposition in three shallow lakes of the Coorong region, thereby helping to refine our understanding of climatically induced environmental change along the coastal plain of southeastern South Australia during the mid to late Holocene. At the north of the ephemeral Coorong lagoon, sapropel in the sedimentary succession of North Stromatolite Lake indicates that the Salt Creek lake chain was cut off from surface connection with the open Coorong lagoon at *ca* 6400 cal y BP shortly after Holocene sea-level reached its maximum in southern Australia. Here, sapropel deposition under restricted lacustrine conditions continued for some 1400 years and halted abruptly at *ca* 5000 cal y BP. Since that time, the lake basin has progressively filled with carbonate mud, and the lake has evolved from perennial to ephemeral, increasingly saline conditions in line with the mid-Holocene transition toward more arid conditions across southern Australia.

Approximately 100 km further south in the Robe Range, the upward shoaling sedimentary sequences of Old Man Lake and Lake Amy record similar mid-Holocene environmental change. In Old Man Lake, the onset of lacustrine conditions and sapropel deposition is dated at *ca* 4100 cal y BP. Hence, isolation of Old Man Lake from the marine system of the Robe–Woakwine corridor occurred more than 2000 years later than that of North Stromatolite Lake from the Coorong lagoon. Sapropel formation in Old Man Lake and Lake Amy coincides with recognised periods of rapid global climate change previously unrecorded in southern Australia. The cessation of sapropel formation occurred at *ca* 2600 cal y BP in Old Man Lake and at *ca* 1900 cal y BP in Lake Amy, both markedly later than in North Stromatolite Lake. This latitudinal difference is further evidence of local environmental variability across southeastern Australia during the Holocene. Even so, the sapropel events recorded in these coastal lakes can be temporally linked to three recently recognised episodes of rapid global climate change, each characterised by cool poles and dry tropics. Their coincidence with periods of aridification points toward aeolianite dust as the likely trigger of sapropel formation.

ACKNOWLEDGEMENTS

ACM acknowledges financial support from an Australian Postgraduate Award and a scholarship from the Cooperative Research Centre for Landscape Environments and Mineral Exploration. AINSE grant 04/172 to MAJW funded the radiocarbon dating. We thank Environment and Heritage South Australia for permission to take samples in North Stromatolite Lake and Old Man Lake (Permit Y24660); Angus MacGregor and Karen Hulme for invaluable assistance with coring; and John Enright of The Hermitage near Robe for kindly allowing us access to Lake Amy. DMMcK and ACM are indebted to Alan Brenchley for numerous discussions on the sedimentology of Old Man Lake and Lake Amy. Finally, we are grateful to Patrick De Deckker and John Cann for their forensic reviews of the submitted manuscript. Their queries and helpful suggestions greatly assisted our revision of the paper.

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Received 27 April 2006; accepted 28 February 2007

Holocene environmental change recorded in shallow coastal lakes of the Coorong region, southeastern Australia

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SUMMARY

Elemental (TOC, C/N), isotopic ($\delta^{13}C_{org}$) and molecular (^{13}C-NMR) analysis of sapropels within the Holocene carbonate mudstone successions of three coastal lakes of the Coorong region, South Australia, indicates that they are composed primarily of aquatic organic matter derived from algae and other photoautotrophs that utilised HCO_3^- as their dissolved inorganic carbon source. Isotopic analysis of sedimentary carbonate ($\delta^{13}C_{inorg}$, $\delta^{18}O$) suggests that this lacustrine organic matter was subject to post-depositional methanogenesis, that lake water salinity has increased during the late Holocene and that sapropel deposition in the southernmost two of these lakes was not restricted to times of wetter environmental conditions.

Key words: Holocene environment, coastal lakes, sapropel, stable isotopes.

INTRODUCTION

Many groundwater-fed lakes along the Coorong coastal plain of southeastern South Australia contain sapropels (total organic carbon >2%; hydrogen index >300 mg hydrocarbons/g TOC) within their Holocene calcareous mudstone successions (e.g. Warren, 1990; Hayball et al., 1991; McKirdy et al., 1999, 2002; Mee et al., 2004, 2005). Sapropels have been studied extensively in the Mediterranean Sea and their deposition is known to coincide with precessional minima of the Earth's orbital cycle (e.g. Rossignol-Strick, 1985; Hilgen, 1991). During these times of increased humidity high levels of precipitation boost surface runoff and tributary flow, which increases the input of both terrestrial organic matter and nutrients to offshore marine basins and promotes stratification of their water column. The increased nutrient supply enhances aquatic primary productivity, leading to oxygen-depletion of the bottom waters and enhanced preservation of autochthonous algal organic matter. Such aquatic organic matter is the predominant contributor to sapropels in both marine (e.g. Bouloubassi et al., 1999; Tolun et al., 2002) and deep lake (e.g. Hassan et al., 1997; Meyers and Lallier-Verges, 1999) settings.

The three coastal lakes of the present investigation (North Stomatolite Lake, Old Man Lake and Lake Amy) represent a distinctly different aquatic environment in that they are shallow and have become increasingly ephemeral over time. Therefore, this study adds a new perspective to the dynamics of sapropel genesis. Sedimentation in these lakes spanned the Mid-Holocene transition from generally warmer and wetter to cooler and drier (or more seasonal) conditions documented in many Australian palynological and palaeolimnological studies (e.g. Dodson and Ono, 1997). The current geochemical investigation aims to establish the extent to which this climatic variability is recorded by secular variations in the elemental, molecular and isotopic composition of their sedimentary organic matter and the isotopic composition of the co-existing carbonate.

Environmental Setting

North Stromatolite Lake (NSL) is part of the Salt Creek lake chain situated at the northern end of the ephemeral Coorong Lagoon. Its present water depth (<1 m) fluctuates seasonally. At the peak of the post-glacial marine transgression this group of four lakes existed as a narrow extension of the Coorong Lagoon, connected to it via the southern end of NSL. Isolation of the embayment restricted water movement within the system and resulted in the build up of sandy estuarine sediments in the interlake corridors. This effectively converted the water body from an estuarine/marine environment into the chain of isolated lakes that exists today. These are designated Type 2 lakes by Warren (1990) to distinguish them from Type 1 lakes that were not initially connected to the Coorong Lagoon. The upward-shoaling calcareous mudstone succession of the Salt Creek lake chain is well documented by Rosen et al. (1988) and Warren (1990) and typically contains three distinct Holocene lacustrine carbonate units (sapropelic mudstone; laminated pelletal mudstone; massive pelletal mudstone/packstone) that overlie Pleistocene siliciclastic-carbonate grainstone to wackestone and beach-dune sands. This textural transition from laminated to massive sedimentary units is typical of a change from perennial to ephemeral aquatic conditions in a setting of relatively low energy (Warren, 1990).

Old Man Lake (OML) is a shallow (<4 m) perennial lake situated just south of Robe, approximately 100 km south of NSL. Like NSL, it was a restricted embayment of a local back-barrier lagoon during the early Holocene and has since become isolated from the marine system. The upward-shoaling transition from marine to lacustrine conditions is apparent in the three distinct carbonate units: lagoonal silts and muds with abundant remains of shallow marine fauna; laminated lacustrine mudstone with sapropel intervals; massive pelletal mud with abundant remains of the gastropod *Coxiella striata* (McKirdy et al., 1999).

Lake Amy (LA) is another shallow (<4 m) perennial lake that nestles within a topographic low of the Robe Range and is located only a few kilometres from OML. Unlike NSL and

OML, it has never had a surface connection with the marine system. Instead LA is an expression of local groundwater changes associated with sea-level fluctuations. Here a massive bioturbated pelletal carbonate mudstone overlies a laminated mudstone with sapropel intervals, hardgrounds and variable amounts of ostracod and gastropod remains. This sequence represents an upward shoaling lacustrine succession analogous to those deposited in the Type 1 lakes near Salt Creek.

METHOD

A D-section corer was used to collect uncompacted sediment cores to depths of 2.0 m, 2.5 m and 3.0 m in Old Man Lake, Lake Amy and North Stromatolite Lake, respectively. Radiocarbon (^{14}C) dating of bulk organic matter was undertaken at the ANSTO AMS facility (Fink et al., 2004) and used to establish a depositional chronology for each core. All radiocarbon dates were converted to calendar years by calibration against the known atmospheric ^{14}C curve using the program Fairbanks0605 (Fairbanks et al., 2005). Bulk sediment samples were treated with 5% w/w H_2SO_4 prior to incineration at 1300°C in a LECO C 144 carbon analyser to determine total organic carbon (TOC). Wet sediment samples were treated with 1.0 M HCl and then with 2% HF to remove carbonates and paramagnetics before 50.309 MHz cross polarisation with magic angle spinning (CP/MAS) ^{13}C-NMR spectra were obtained on a Varian Unity 200 spectrometer with a 4.7 T wide-bore Oxford super-conducting magnet. All spectra were obtained using a contact time of 1 ms, a recycle delay time of 500 ms, 50 Hz Lorentzian line broadening and 0.01 s Gaussian broadening. Chemical shift assignments were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. The proportional contribution of the functional groups ketonic/aldehyde (220-190 ppm), carbonyl (190-165 ppm), O-aryl (165-140 ppm), aryl (140-110 ppm), O-alkyl (110-45 ppm) and alkyl (45-0 ppm) was calculated by integration of peak areas. Analysis of 0.5 M HCl-treated samples on a 20-20 Europa Scientific Automated Nitrogen Carbon Analysis – Mass Spectrometer (ANCA-MS) yielded carbon isotope values of the lacustrine organic matter ($\delta^{13}C_{org}$), and also total nitrogen (TN) percentages which were used to calculate atomic C/N ratios for all samples with TOC >1%. Isotopic analysis of sedimentary carbonate ($\delta^{13}C_{inorg}$, $\delta^{18}O$) was completed at Waikato Stable Isotope Laboratory (New Zealand) on a GEO 20-20 Dual Inlet Mass Isotope Ratio Spectrometer with an attached Carbonate Automated Preparation System. All isotope results are reported in conventional δ notation, expressed in parts per mil (‰) relative to the standard Pee Dee Belemnite for both carbon and oxygen.

RESULTS

Depositional Chronology

The onset of sapropel deposition in NSL marks isolation of the Salt Creek Lake Chain from the Coorong Lagoon and the transition from an estuarine environment to a perennial lake system (Warren, 1990). ^{14}C dating places this event at c. 7000 cal yr BP and the transition to shallower and less productive conditions represented by the overlying laminated unit at c. 5800 cal yr BP. The transition from lagoonal to lacustrine conditions in OML occurred at c. 4800 cal yr BP. The halt in deposition of organic-rich sediments is dated at c. 3300 cal yr BP, some 2500 years later than the equivalent palaeolimnological event in NSL. Accumulation of organic-rich laminated lacustrine mudstone sediments in LA lasted until c. 2500 cal yr BP, some 800 years later than the similar change to deposition of organically leaner sediments that is evident in OML.

Source of Lacustrine Organic Matter

The ^{13}C-NMR spectra are remarkably similar for all 17 samples analysed, with the exception of that from the basal lagoonal unit of OML (OML6). The spectra are dominated by alkyl carbon (carbohydrates and proteins) with only minor signals in the aromatic carbon region (Figure 1). This finding confirms that there has been a significant contribution of algal and bacterial biomass to the organic matter pool of all three lakes throughout their history.

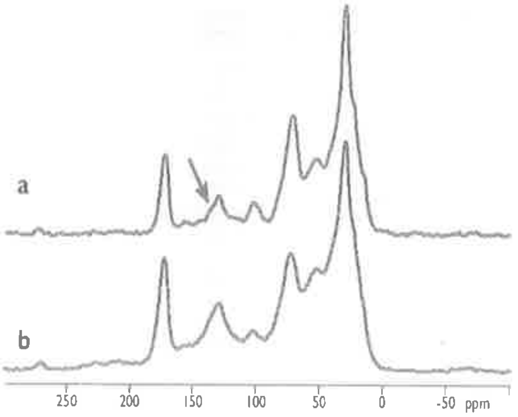

Figure 1. Comparison of ^{13}C-NMR spectra: a) representative of sapropel in most lacustrine samples, b) organic matter in lagoonal sample OML6. The weaker peak (arrowed) in the aromatic region (~130 ppm) of the lacustrine samples is interpreted as unsaturation associated with the alkyl carbon, whereas the strong peak in this region of the second spectrum is attributed to charcoal.

Elemental and isotopic data do not clearly point towards a predominantly aquatic origin for the lacustrine organic matter but instead appear to suggest a mixed aquatic and terrestrial source. Many researchers have used C/N ratios to characterise lacustrine sedimentary organic matter (e.g. Talbot and Lærdal, 2000; Tolun et al., 2002). Typically, organic matter of algal origin (high in N-rich proteins and nucleic acids) will have an atomic C/N ratio between 4 and 10, whereas vascular land plants (high in C-rich lignin and cellulose) produce organic matter with C/N ratios of 20 and greater (Meyers, 1994).

In NSL C/N ratios (n = 8) decrease from 19.8 at the base to 14.1 at the top of the sapropel, averaging 16.4 throughout the 1.3 m interval. At face value this suggests that initially the sapropel's organic matter was chiefly terrestrial in origin, but became increasingly influenced by an aquatic contribution. Previous studies of biomarker hydrocarbons and microfossils identified benthic diatoms as major contributors to Coorong sapropels, including that in NSL (e.g. McKirdy et al., 2002). The C/N-based classification of NSL sapropelic organic matter as mixed but predominantly terrestrial contradicts both the findings of these earlier workers and the aquatic character of the organic matter indicated by its ^{13}C-NMR spectra. This suggests that the C/N ratio ranges for terrestrial and aquatic organic matter as published in Meyers (1994) should be used only as a preliminary indication of possible contributors to a lacustrine system. Many environmental variables could lead to the production of either terrestrial or aquatic organic matter with C/N ratios that fall outside these broad and generalised ranges.

As in NSL, C/N ratios imply a mixed source affinity for the sedimentary organic matter in both OML and LA. Throughout OML's sedimentary succession C/N ratios (n = 12) fluctuate too dramatically to warrant calculating an average (maximum 21.5; minimum 2.7). The lower values are consistently associated with discrete sapropels, such as the 35 cm thick interval that dominates the laminated lacustrine mudstone unit. In LA C/N ratios (n = 20) also vary widely, although most are between 11-17. Notable exceptions are those from the lowermost sapropel (7.2) and two samples (19.8, 20.0) that immediately precede finely laminated zones of the lacustrine mudstone. There is no significant difference between the means calculated from the entire core (14.3), the massive unit (14.3), or the two major sapropel intervals (upper, 14.1: lower, 14.4). Attempts to identify the source(s) of sedimentary organic matter in these lakes using atomic C/N ratios alone are bound to be inconclusive.

Stable carbon isotope analysis of the sedimentary organic matter ($\delta^{13}C_{org}$) yielded a similar range of results for each lake: NSL −22.3 to −16.4‰; OML −22.6 to −17.5‰; AMY −23.2 to −15.9‰. These values fall between the $\delta^{13}C_{org}$ values typical of C4 (average −14‰) and C3 (average −27‰) terrestrial biomass. $\delta^{13}C_{org}$ values of aquatic biomass reflect the dissolved inorganic carbon (DIC) source utilised during photosynthesis. For freshwater plants this is dissolved CO_2, which is usually in isotopic equilibrium with atmospheric CO_2 and so produce organic matter with $\delta^{13}C_{org}$ values around −27‰ (Meyers and Lallier-Verges, 1999). Marine organic matter is produced from CO_2 in equilibrium with dissolved carbonate and bicarbonate ions and has $\delta^{13}C_{org}$ values between −20 and −22‰ (Meyers, 1997). Previous research and the ^{13}C-NMR spectra of the present study indicate that there is a significant aquatic component of the sedimentary organic matter from NSL, OML and LA. Therefore, the $\delta^{13}C_{org}$ results of this study are predominantly indicative of algae utilising $HCO_3^-{}_{(aq)}$ as their DIC source during photosynthesis. An additional terrestrial component is indicated but remains unquantified.

Environmental Significance

Since the Coorong lakes are wholly groundwater-fed, amplified surface water flow arising from increased rainfall in the local catchment cannot have triggered deposition of their sapropel units. In tributary-fed environments a wetter climate increases nutrient-rich freshwater inflow, which enhances aquatic primary productivity and leads to sapropel deposition (Meyers and Lallier-Vergès, 1999). It also results in a significant influx of terrigenous plant detritus (Tolun et al., 2002), whereas the terrestrial component of sediments within groundwater-fed lakes is likely to be entirely aeolian. Recognising this difference in environmental setting is crucial to appropriate interpretation of the geochemical results obtained in this study.

Isotopic analysis of sedimentary carbonate (Figure 2) was used to investigate the secular changes in each lake's environment that may have been linked to sapropel deposition. In NSL $\delta^{13}C_{inorg}$ and $\delta^{18}O$ values fall into two distinct groups. The massive, laminated and upper sapropel (B) units are enriched in both $\delta^{13}C_{inorg}$ and $\delta^{18}O$ above the lower sapropel (A) and the basal unit. The isotopic enrichment is interpreted as an evaporation signature resulting from the progressive removal of $^{12}C_{inorg}$ and ^{16}O from the lake waters and the subsequent deposition of isotopically heavier carbonates over time. Rosen et al. (1988) and Warren (1990) interpret a similar increase in $\delta^{13}C_{inorg}$ and $\delta^{18}O$ as evidence of evaporation in shallowing Coorong lakes. They argue that although positive $\delta^{13}C_{inorg}$ values can result from post-depositional methanogenesis of lacustrine organic matter, abiogenic processes are more likely the cause of the positive values observed in the Salt Creek Lake Chain sediments. Thus, the distinct isotopic enrichment of NSL's carbonate sediments at ca. 5800 cal yr BP is herein attributed to the increased influence of evaporation on the surface waters of this shallowing lacustrine system across the Mid-Holocene transition from warmer, wetter to cooler, drier conditions.

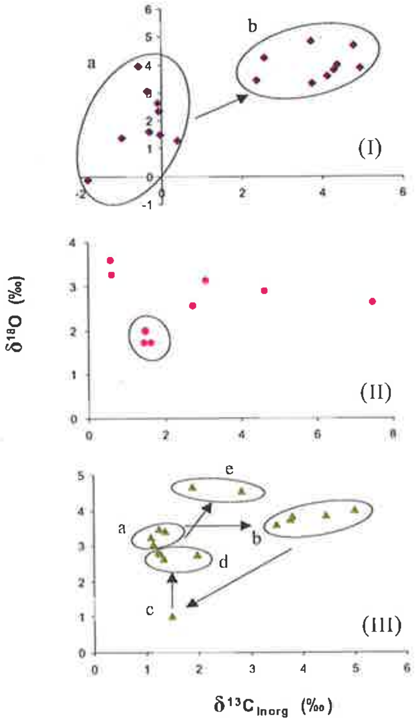

Figure 2: δ13C and δ18O values from the sedimentary carbonates of (I) NSL, (II) OML and (III) LA. Evaporative processes are responsible for the marked δ13C and δ18O enrichment from the lower sapropel and basal units (a) into the organically leaner upper units (b) of NSL. The lagoonal unit of OML (circled) is isotopically distinct from the overlying laminated lacustrine unit. Carbonates of this unit have been influenced by fluctuations in aquatic productivity within the lake. The increase in δ13C values from the lower sapropel (a) of LA into the overlying laminated unit (b) results from methanogenic breakdown of sedimentary organic matter. A freshening episode (c) triggers further sapropel deposition (d). The amplified

effect of evaporation in a shallowing lake is evident in the increased δ13C and δ18O values of the organically leaner surface sediments (e).

The transition from lagoonal to lacustrine conditions in OML also coincides with a significant increase in $\delta^{18}O$ values during the Mid-Holocene, herein dated at ca. 4800 cal yr BP. $\delta^{13}C_{inorg}$ values do not increase up-section as in NSL but instead fluctuate between 0.6 and 7.5‰. The lack of correlation between the changes in $\delta^{18}O$ and $\delta^{13}C_{inorg}$ throughout OML precludes an evaporative cause. The $\delta^{18}O$ enrichment from the lagoonal to the lacustrine sediments of OML is considered a reflection of the isolation of the lake from the marine system rather than the more subtle effects of evaporation in a closed lacustrine system. Within the laminated lacustrine sediments the more organic-rich sediments have more positive $\delta^{13}C_{inorg}$ values than the organically leaner sediments. Preferential incorporation of ^{12}C into aquatic organic matter increases the ^{13}C content of the DIC reservoir and can lead to deposition of carbonates with progressively heavier $\delta^{13}C_{inorg}$ values (Talbot, 1990). The association of more positive $\delta^{13}C_{inorg}$ values with organically richer intervals of the sedimentary succession accords with increased aquatic productivity leading to the deposition of ^{13}C-enriched carbonates.

LA is presently hypersaline and is effectively the surface expression of a perched water table. As it was never directly connected to the marine system, secular variations in the isotopic composition of its carbonates must reflect internal lake processes. The lowermost sapropel interval has average $\delta^{13}C_{inorg}$ and $\delta^{18}O$ values of 1.2 and 3.3‰, respectively. $\delta^{13}C_{inorg}$ values increase markedly to 4.1 ‰ in the overlying laminated unit. There is no parallel change in $\delta^{18}O$ and therefore the $^{13}C_{inorg}$ enrichment cannot be due to evaporation. In this instance, the observed $^{13}C_{inorg}$ enrichment represents a distinction between sedimentary units rather than a steady increase up-section. It also coincides with a slight drop in TOC and is therefore thought to reflect post-depositional production of isotopically heavy HCO_3^- by methanogenic bacteria (see also McKirdy et al., 1999), rather than preferential removal of ^{12}C from the water column as a result of increased aquatic productivity. A drop in both $\delta^{13}C_{inorg}$ and $\delta^{18}O$ toward the top of the laminated unit is interpreted as a freshening episode in LA at ca. 3500 cal yr BP. Beyond this time $\delta^{18}O$ values increase in two phases: from the minimum of 1.0‰ to 2.7‰ in the overlying sapropel and 4.6‰ in the organically lean massive unit. $\delta^{13}C_{inorg}$ values average 1.4‰ in the sapropel and increase slightly to 2.4‰ in the massive unit. The coincident increase in $\delta^{13}C_{inorg}$ and $\delta^{18}O$ from the sapropel into the massive unit is interpreted as the amplified influence of evaporation on carbonate deposition within the increasingly saline waters of this shallowing lake during the Late Holocene.

CONCLUSIONS

The respective compositions of sedimentary OM and co-deposited carbonate in these Coorong lakes extend our understanding of sapropel genesis. The salinity increase that accompanied an extended period of sapropel deposition in NSL is further testimony to the Mid-Holocene transition to a drier environment that is evident in the current regional palaeoclimatic record. Sapropel continued to be deposited in OML and LA beyond this time. In contrast to marine and deep lake sapropels, the deposition of these organic-rich Coorong lacustrine sediments is not restricted to times of wetter environmental conditions.

Marked ^{13}C-enrichment in the carbonate of OML is a reflection of high aquatic productivity, whereas similar isotopically-heavy carbonate in LA is more likely to be a product of post-depositional methanogenesis. This difference highlights the importance of comparing multiple geochemical parameters when attempting palaeoenvironmental reconstruction of any lacustrine system.

ACKNOWLEDGMENTS

This work was supported by an Australian Postgraduate Award and a scholarship from the Cooperative Research Centre for Landscape Environments and Mineral Exploration to A.Mee. AINSE grant 04/172 funded the radiocarbon dating. We thank the Department for Environment and Heritage for permission to take cores in North Stromatolite and Old Man Lakes (Permit Y24660); Mr J. Enright of The Hermitage for access to Lake Amy; and Angus MacGregor for assistance with coring.

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GEOCHEMICAL ANALYSIS OF ORGANIC-RICH LACUSTRINE SEDIMENTS AS A TOOL FOR RECONSTRUCTING HOLOCENE ENVIRONMENTAL CONDITIONS ALONG THE COORONG COASTAL PLAIN, SOUTHEASTERN AUSTRALIA

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INTRODUCTION

Lake sediments have consistently proven to be valuable sources of information on the extent and variability of palaeoenvironmental conditions throughout the Holocene. Lacustrine Organic Matter (OM) is a remnant of the biota that lived within the lake and its hinterland during sediment accumulation. Thus, elemental, isotopic and molecular analysis of the preserved OM is capable of revealing secular changes in the primary sources of the OM and the extent of its degradation—two fundamentals aspects of palaeoenvironmental reconstruction.

The Coorong coastal plain of southeastern Australia includes many small, ephemeral to semi-permanent lakes fed by alkaline groundwater. Combined organic and inorganic techniques have been used by previous researchers to aid in reconstructing the depositional history of some of these lakes, many of which are known to contain either one or multiple 'sapropelic' (organic-rich) mudstone layers within their sedimentary successions. North Stromatolite Lake (NSL) is a particularly striking example in that it contains a 1 m thick sapropel layer within an otherwise organic-poor carbonate mud sequence. NSL is a part of the Salt Creek lake chain (approx. 230 km SSE of Adelaide), which, during the Early Holocene, was an arm of the open Coorong Lagoon until dune migration and sediment deposition isolated it into separate waterbodies. This transition from estuarine to lacustrine conditions is evident within the sedimentary fill of NSL (Hayball 1990). Through Rock-Eval pyrolysis, gas chromatography (GC) and GC-mass spectrometry of aliphatic hydrocarbons, Hayball *et al.* (1991) determined that organic matter within NSL's carbonate sequence had a predominantly, though not wholly, aquatic source. More recent work by Edwards *et al.* (in prep), focussing on diatom assemblages and ostracod carbon and oxygen isotopic data, suggests that the sapropel interval was deposited under a stratified, increasingly saline water column. Approximately 100 km south of NSL, and just south of Robe, Old Man Lake (OML) and Lake Amy (AMY) lie nestled within the modern Robe Range. Like NSL, OML has evolved from a lagoonal to a lacustrine setting. McKirdy *et al.* (2002) determined a predominantly aquatic algal-bacterial source for its organic matter through combined use of hydrogen indices (HI = 300-900) and carbon isotopes ($\delta^{13}C_{org}$ = -22 to -17‰). Deposition beneath a stratified water column lacking an anoxic hypolimnion is suggested by the diverse ostracod assemblage preserved within the sediments. Although AMY has received much less attention than NSL and OML, like them its Holocene succession also includes highly organic-rich, sapropelic intervals.

SIGNIFICANCE

Numerous studies across the world have linked sapropel deposition in marine and deep-lake settings to abrupt changes in palaeoclimate and palaeoenvironment (e.g., Hassan *et al.* 1997, Tolun *et al.* 2002). The shallow coastal lakes of this study represent a distinctly different environmental setting and yet they too are able to preserve aquatic OM in high concentration (maximum wt. % TOC: NSL 12; OML 25; AMY 23). The rationale of this study is that it will not only add a new perspective to our understanding of sapropel formation, but may also help refine our knowledge of Holocene environmental variability (fluctuating wet-dry phases) in southeastern Australia.

RADIOCARBON DATES

Critical to the better understanding of Holocene climatic and environmental change that this study may provide is a solid framework and chronology of sapropel deposition. The peak of the Holocene marine transgression in southern Australia was reached at 6 ka BP (von der Borch 1979, Belperio 1995). Since this time there has been a change to generally cooler and drier conditions across the globe. Previous researchers suggest that in southeastern Australia the shift from generally wetter to drier conditions occurred at approximately 5 ka BP (Dodson & Ono 1997).

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New radiocarbon data (n=13, Table 1) confirm preliminary dating that suggested Coorong lacustrine sapropel deposition occurred between 8 and 2.5 ka BP (McKirdy *et al.* 2002) and thus coincided with a time of significant climatic variation across not only Australia but also the globe. This new data set raises some interesting questions regarding the conditions required for sapropel deposition during the Holocene. Sapropel deposition in NSL lasted for approximately 1,200 years and halted abruptly at approximately 5 ka BP. However, in OML and AMY the deposition of similar (albeit not as uniform) organic facies occurred from approximately 4 to 3 ka BP. Why did sapropel deposition in NSL not continue during this later time? Perhaps this is an indication of local fluctuations within the well-recognised peak of warm, wet conditions during the Mid-Holocene.

Table 1: New radiocarbon dates obtained on sedimentary organic matter from NSL, OML and AMY.

Lake	Sediment depth (cm)	Depositional setting	^{14}C age (yr BP)
NSL	152	Base of organic-poor laminated carbonate mud unit	5050 ± 50
	183	Transition 'Sapropel A' to 'Sapropel B' (Hayball 1990)	4930 ± 50
	237	Middle of 'Sapropel A'	5930 ± 50
	282	Base of 'Sapropel A'	6280 ± 50
OML	52	Upper surface of sapropelic sediment	3090 ± 50
	85	Lower surface of sapropelic sediment	4380 ± 50
	105	Transition between lagoonal and lacustrine environment	4150 ± 50
	182	Lagoonal environment (bulk OM)	4550 ± 160
	182	Lagoonal environment (charcoal fraction)	6890 ± 50
AMY	109	Middle of uppermost sapropelic level	3060 ± 50
	211	Upper surface of lower sapropelic level	4020 ± 50
	223	Lower surface of upper sapropelic level	4140 ± 50
	245	Basal sapropel bounded by hardgrounds	4140 ± 50

ORGANIC GEOCHEMISTRY

Elemental and isotopic analysis confirms previous findings (Hayball *et al.* 1991, McKirdy *et al.* 2002) that the OM within these lacustrine sediments is of predominantly aquatic origin. Many researchers have used C/N ratios to characterise marine and lacustrine sedimentary OM, in particular to distinguish between terrestrial and aquatic inputs (e.g., Tolun *et al.* 2002). Typically, OM of algal origin will have an atomic C/N ratio between 4 and 10, whereas vascular land plants produce OM with C/N ratios of 20 and greater (Meyers 1994). Although these differences between algal and terrestrial sources generally survive sinking through the water column and sedimentation, C/N ratios can potentially suggest a misleading OM origin if not used thoughtfully. For example, measurement of C and N contents after removal of sedimentary carbonate leads to the comparison of an organic carbon value with a nitrogen value that incorporates both organic and inorganic fractions. In sediments with C_{org} greater than 1%, N_{org} is much greater than N_{inorg} and thus, use of N_{tot} in C/N ratios produces a reliable indication of OM source (Meyers 1997). C_{org}/N_{tot} ratios for all three lakes in this study lie between those typical of aquatic and terrestrial OM, although skewed heavily toward the former (NSL average = 12.6, OML average = 11.6, AMY average = 11.2).

Although the C/N ratios of the Coorong lacustrine OM suggest a predominantly aquatic origin and thus strengthen the findings of earlier researchers in the area, determination of OM source is most reliably achieved through the use of multiple parameters. In a cross-plot of C/N against $\delta^{13}C_{org}$ (Figure 1) the Coorong lacustrine OM plots closest to the region typical of, and therefore suggests a significant contribution from, an algal source. The ranges for the major OM sources that are displayed in this plot are broad and generalised and should thus be used as a preliminary indication of the probable contributors to these lakes. Missing from the figure is a generalised range for soil organic matter (SOM), another possible contributor to the lacustrine system. C/N ratios for SOM are commonly around 10 and $\delta^{13}C_{org}$ values vary depending on the proportion of C3 and C4 plants in the landscape. Although it could be argued that the data in Figure 1 indicate a major contribution of SOM from a landscape with approximately 50% C3 and 50% C4 plants, consideration of the Coorong lacustrine setting suggests otherwise. Each of the three lakes in this study is groundwater fed. They receive no fluvial input and probably only minor surface runoff from the surrounding dunes. Therefore, any contribution from SOM would be primarily aeolian. The prevailing wind direction in the region is currently south-southwesterly resulting from the passage of mid-latitude anticyclonic high-pressure systems (summer) and cold fronts associated with cyclonic low-pressure systems originating at high-latitudes (winter). Low, crescent-shaped lunette ridges border the eastern shore of modern playa lakes across southeastern South Australia, which suggests that the current wind regime has been in place for some time. Although there is much evidence for aeolian dust being able to travel long distances (e.g., Simonson 1995) often it is related to extreme and isolated storm events. So, with the predominant winds of the Coorong coastal plain being maritime in origin, and with previous evidence pointing to a primarily aquatic OM source, there is little reason to suggest a consistent contribution of SOM to the lacustrine OM pool.

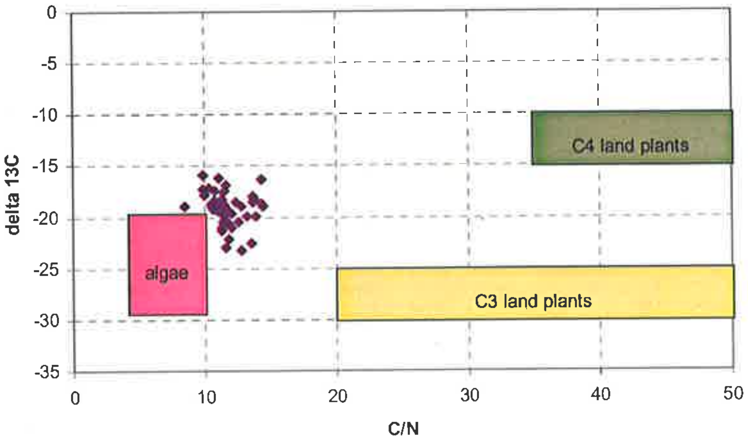

Figure 1: Generalized carbon isotopic values and C_{org}/N_{tot} ratios for the major organic matter sources to lacustrine sediments (modified from Meyers 2003). Data points are from the entire sequences of all three Coorong lakes.

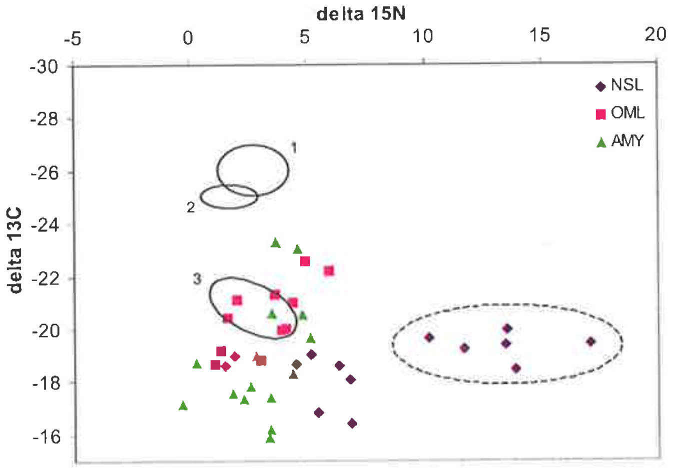

Figure 2: Carbon and nitrogen isotopic values of sedimentary OM from NSL, OML and AMY with encircled data points (dashed line) being from the organic-poor (< 2% TOC) laminated unit of NSL. Also indicated are isotopic ranges for sapropels from 1: Lake Bosumtwi, Ghana (Meyers & Lallier-Verges 1999), 2: Swan Lake, Nebraska (Hassan *et al.* 1997) and 3: Mediterranean Sea (Bouloubassi *et al.* 1999). Isotopic values from the organic-rich (> 2% TOC) lacustrine sediments plot closest to the realm commonly observed for marine sapropels thereby emphasising the geochemical similarity of organic matter from the two depositional settings.

The $\delta^{13}C_{org}$ values of aquatic OM are influenced by the dissolved inorganic carbon (DIC) source that is utilised during photosynthesis (Dean 1999). Freshwater algae utilising DIC in equilibrium with atmospheric CO_2 produce isotopically lighter OM ($\delta^{13}C_{org}$ ca. -27 ‰) than that synthesised by marine algae. The latter utilise dissolved HCO_3^-, and hence produce OM less depleted in the heavier isotope ($\delta^{13}C_{org}$ ca. -20 to -22 ‰). This isotopic distinction is evident in published literature and in Figure 2, where it can be seen that the Coorong lacustrine sedimentary OM shows a range of $\delta^{13}C_{org}$ and $\delta^{15}N$ values more similar to the isotopic signatures of Mediterranean (marine) sapropels than to OM produced in a freshwater system. Use of HCO_3^- as the DIC source for the aquatic OM in these Coorong lakes results from the ratio of HCO_3^- to CO_2 being kept high in the alkaline lake waters. Henderson (1997) reported a pH ca. 8 for both OML and AMY, being slightly higher in winter and slightly lower in summer (pH data not available for NSL). At pH = 8 HCO_3^- makes up nearly 100% of the DIC pool.

DISCUSSION

Each of the three lakes displays a slightly different geochemical signature (Figure 3) and thus records varying responses to local environmental changes. A considerable degree of overlap is evident in the geochemical signatures of OML and AMY. This may result from the contemporaneous sapropel deposition in these two lakes, or may be a reflection of a similar groundwater inflow to OML and AMY, which both lie within the modern Robe range and approximately 100 km south of NSL. The groundwater of the Upper Gambier Limestone aquifer, which feeds all of these lakes, is known to vary across the Coorong coastal plain. Salinity increases northwards and the dominant ions shift from Ca^+ and HCO_3^- to Na^+ and Cl^- (Henderson 1997). As salinity influences the survival and abundance of different species of aquatic biota, groundwater variability may contribute partially to the geochemical differences observed in the northern and southern lacustrine sediments.

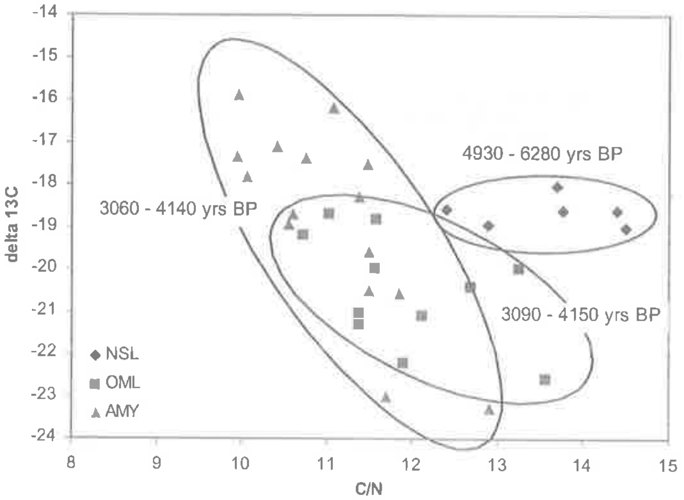

Figure 3: Carbon isotope values of OM and C_{org}/N_{tot} ratios for the 'sapropelic' (> 2% TOC) sediments of NSL (n = 5), OML (n = 11) and AMY (n = 15). The distinct grouping of the NSL samples suggests that the set of environmental conditions that influenced organic matter production and preservation was more similar in OML and AMY than in NSL.

Both OML and AMY began sapropel deposition at approximately 4 ka BP, yet have experienced very different sediment accumulation rates. Over the course of 1,000 years OML deposited only 50 cm to AMY's 135 cm, which makes the sedimentary fill of AMY much more sensitive to environmental changes. The two lakes are also significantly different in that OML evolved from an initial marine flooding with subsequent groundwater inflow whilst AMY has evolved from groundwater seepage and inflow only. This distinction between effectively one and two lake water inputs may contribute to the differences in $\delta^{13}C_{org}$ seen within the lacustrine sedimentary sequences. Whilst $\delta^{13}C_{org}$ values for OML fluctuate between –18.7 ‰ and –22.6 ‰, the $\delta^{13}C_{org}$ values from AMY show a reasonably steady increase from –23.3 ‰ to –15.9 ‰ over time. Surely the steady isotopic trend that is observed in the sedimentary OM of AMY is related to the evolution of a single water mass. Photosynthesis preferentially utilises ^{12}C and thus leads to an isotopically enriched DIC pool. As this continues the OM produced and stored within the lacustrine sediment is progressively enriched in the heavier isotope. The gradual (although substantial) increase in the $\delta^{13}C_{org}$ values of AMY may be due to this carbon cycle process, and will be further investigated through isotopic analysis of sedimentary carbonate that is presumed to have deposited in isotopic equilibrium with the DIC pool.

The $\delta^{13}C_{org}$ values of sapropelic sediment from OML and AMY span a significantly broader range than those from NSL. The most depleted $\delta^{13}C_{org}$ values of OML and AMY are associated with the highest C/N ratios, and may therefore be a product of some C3 terrestrial contribution to the OM pool. The NSL sapropel is striking in that its $\delta^{13}C_{org}$ values vary by no more than 1‰ over the 1 m interval, thus implying relatively steady state conditions within NSL that lasted for approximately 1,200 years. Marginally elevated C/N values for the NSL sapropel (relative to those for most of OML and AMY) may be indicative of a larger terrestrial contribution to the NSL OM pool, or may reflect more extended preferential microbial degradation of N-rich proteins within the NSL water column and below the sediment-water interface. ^{13}C-NMR analysis of the lacustrine OM (pending) will provide molecular structural information, thus allowing further evaluation of the relative aquatic (short-chain) and terrestrial (long-chain) contibutors. Distinction between those geochemical trends related to changes in OM source and those due to variations in environmental conditions (e.g., lake salinity) is essential to a thorough interpretation of these elemental and isotopic data.

CONCLUSION

The OM preserved within the sedimentary sequences of these alkaline groundwater-fed lakes is largely a remnant of aquatic algae that used HCO_3^- as their DIC source. A terrestrial component of this OM is known to exist (Hayball *et al.* 1991, McKirdy *et al.* 2002) and is suggested in the elemental and isotopic data reported herein. Further quantification and characterisation of this input will aid in separating the geochemical signatures related to OM sources and to environmental changes. This, plus more detailed analysis of these sapropels and co-deposited sedimentary carbonate, is likely to throw further light on the temporal and/or spatial variation in the Holocene environment of southeastern South Australia.

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