

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 fundamental 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 ($\delta^{13}\text{C}_{\text{org}} = -22$ 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).

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 \pm 50
	183	Transition 'Sapropel A' to 'Sapropel B' (Hayball 1990)	4930 \pm 50
	237	Middle of 'Sapropel A'	5930 \pm 50
	282	Base of 'Sapropel A'	6280 \pm 50
OML	52	Upper surface of sapropelic sediment	3090 \pm 50
	85	Lower surface of sapropelic sediment	4380 \pm 50
	105	Transition between lagoonal and lacustrine environment	4150 \pm 50
	182	Lagoonal environment (bulk OM)	4550 \pm 160
	182	Lagoonal environment (charcoal fraction)	6890 \pm 50
AMY	109	Middle of uppermost sapropelic level	3060 \pm 50
	211	Upper surface of lower sapropelic level	4020 \pm 50
	223	Lower surface of upper sapropelic level	4140 \pm 50
	245	Basal sapropel bounded by hardgrounds	4140 \pm 50

ORGANIC GEOCHEMISTRY

Elemental and isotopic analysis confirms previous findings (Hayball *et al.* 1991, McKirby *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). $C_{\text{org}}/N_{\text{tot}}$ 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 $\delta^{13}\text{C}_{\text{org}}$ (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 $\delta^{13}\text{C}_{\text{org}}$ 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.

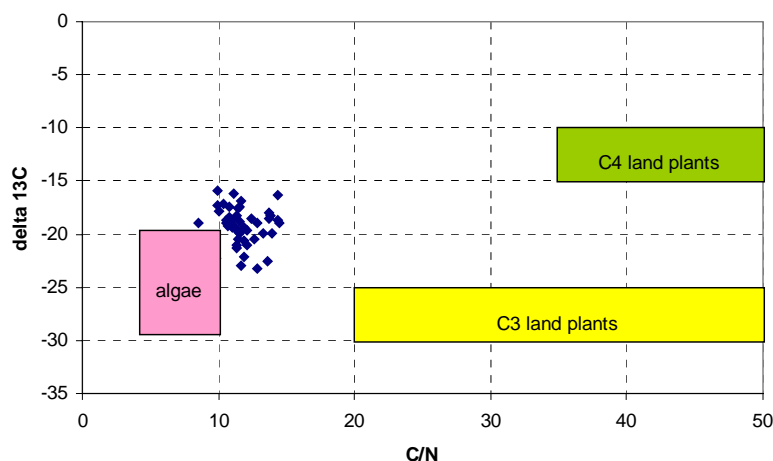


Figure 1: Generalized carbon isotopic values and C_{org}/N_{tot} ratios for the major organic matter sources to lacustrine sediments (modified from Meyers 2003). Data points are from the entire sequences of all three Coorong lakes.

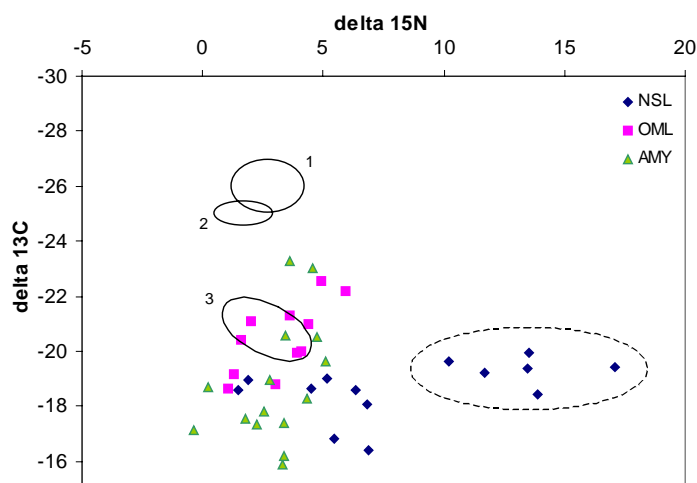


Figure 2: Carbon and nitrogen isotopic values of sedimentary OM from NSL, OML and AMY with encircled data points (dashed line) being from the organic-poor (< 2% TOC) laminated unit of NSL. Also indicated are isotopic ranges for sapropels from 1: Lake Bosumtwi, Ghana (Meyers & Lallier-Verges 1999), 2: 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.

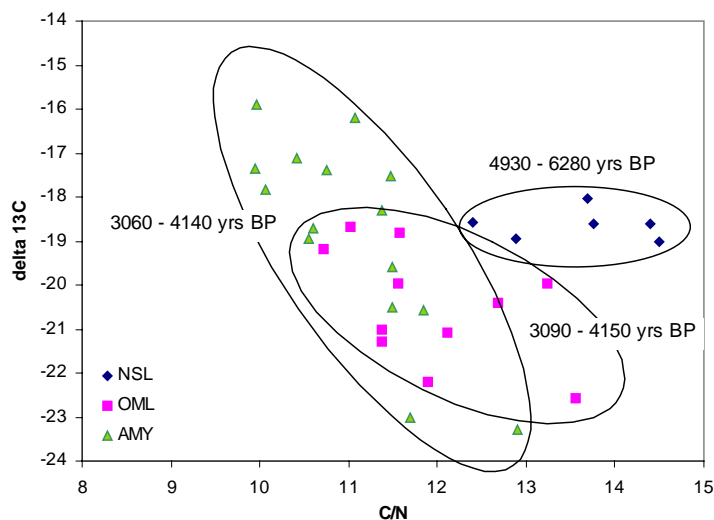


Figure 3: Carbon isotope values of OM and C_{org}/N_{tot} ratios for the 'sapropelic' (> 2% TOC) sediments of NSL (n = 5), OML (n = 11) and AMY (n = 15). The distinct grouping of the NSL samples suggests that the set of environmental conditions that influenced organic matter production and preservation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