Cadernos Lab. Xeolóxico de Laxe
Coruña. 2010. Vol. 35, pp. 127 - 146 ISSN: 0213-4497

Organic facies of Holocene carbonates in North Stromatolite Lake, Coorong region, South Australia

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Abstract
Numerous small, shallow, ephemeral lakes are scattered along the seaward margin of the extensive Pleistocene beach-dune ridge system that comprises the coastal plain of southeastern South Australia. Fed primarily by seasonal inflow of alkaline ground water, these lakes are sites of Holocene carbonate deposition. North Stromatolite Lake is part of a chain of such lakes located immediately south of Salt Creek, within the first interdunal corridor landward of the Coorong Lagoon. Here four different sedimentary facies (basal quartzose skeletal packstone; organic-rich mudstone with thin sapropel layers; laminated pelletal mudstone; and massive pelletal wackestone/mudstone) occur within a shoaling-upwards carbonate cycle (~3 metres thick) and define the following vertical succession of environments: estuarine, density-stratified lacustrine, perennial lacustrine and, finally, ephemeral lacustrine. Acquisition of X-ray diffraction, total organic carbon (TOC), Rock-Eval pyrolysis, visual kerogen and biomarker hydrocarbon data on sediment samples (n = 35) from a single core taken near the centre of the lake has allowed the recognition of five discrete organic facies, each

with a distinctive mineralogy. The organic-rich unit (6−12% TOC) may be subdivided into organic facies 1 (Type I/II kerogen) and 2 (Type II kerogen), whereas the organically leaner laminated and massive units are distinctly bimodal hosting both organic facies 3 (Type II/III kerogen) and 4 (Type III kerogen). The latter two facies together define an inverse relationship between hydrogen index and TOC content, a geochemical signature that may be attributed to differences in the extent of pelletisation of carbonate muds by a diverse salt-tolerant fauna including brine shrimp, gastropods and ostracods during the shallowing perennial and ephemeral phases of the Lake's history. The basal unit hosts organic facies 5 (Type IV kerogen). The aliphatic hydrocarbon distributions of these lacustrine sediments are dominated by C_{20} and C_{25} highly branched isoprenoids; and C_{12}−C_{33} n-alkanes displaying marked odd/even predominance above, and even/odd predominance below, C_{20}. This biomarker assemblage reflects the respective major contributions of bacillariophyceae (diatoms), chlorophyceae (green algae) and eubacteria (including cyanobacteria) to their preserved organic matter. Its passage through the guts of the aforementioned grazers and excretion as faecal pellets has dramatically enhanced the relative abundance of cholest-2-ene, thereby imparting to the pelletised upper sapropel, laminated and massive units a hitherto unrecognised molecular signature. This signature of ingestion may remain in such micritic limestones, even where their original pelleted texture has been obliterated by the physical compaction that accompanies early burial and diagenesis. Of wider significance is our finding that lacustrine sediments containing high levels of hydrogen-rich protokerogen may have accumulated beneath relatively shallow bottom waters (<5 m deep) that were not perennially anoxic.

Key words: Coorong, Holocene, lacustrine carbonates, organic facies, sapropel, pelletisation, biomarker hydrocarbons

INTRODUCTION

Located ~230 km southeast of Adelaide in the Coorong National Park, North Stromatolite Lake takes its name from the cyanobacterial mats along its muddy northeastern and southern shores (WALTER et al., 1973) and the domal stromatolites which grow in the northern reaches of the lake (WARREN, 1988). It is situated in the first interdunal corridor landward of the Coorong Lagoon, within the extensive Pleistocene beach-dune ridge system that comprises the coastal plain of southeastern South Australia (e.g. SPRIGG, 1952; COOK et al., 1977; SCHWEBEL, 1983), where it forms part of the Salt Creek lake chain (WARREN, 1988, 1990, 1994). These four shallow lakes (present maximum winter depth 20−30 cm) and their linking channel sands (figure 1) together delineate the site of marine siliciclastic and skeletal carbonate deposition that extended into a narrow embayment of the Coorong estuary during the early Holocene. Accreting beach ridges eventually severed the surface connection of the embayment to the marine lagoon, whereupon it evolved into four separate mineralogically distinct, carbonate-depositing lakes, fed by a combination of seaward-flowing groundwater (figure 2), direct winter rainfall, runoff and aerosols, and with initial maximum water depths of 3−5 m (WARREN, 1990). Radiocarbon dating of the oldest lacustrine unit in North Stromatolite Lake indicates that the lake chain became

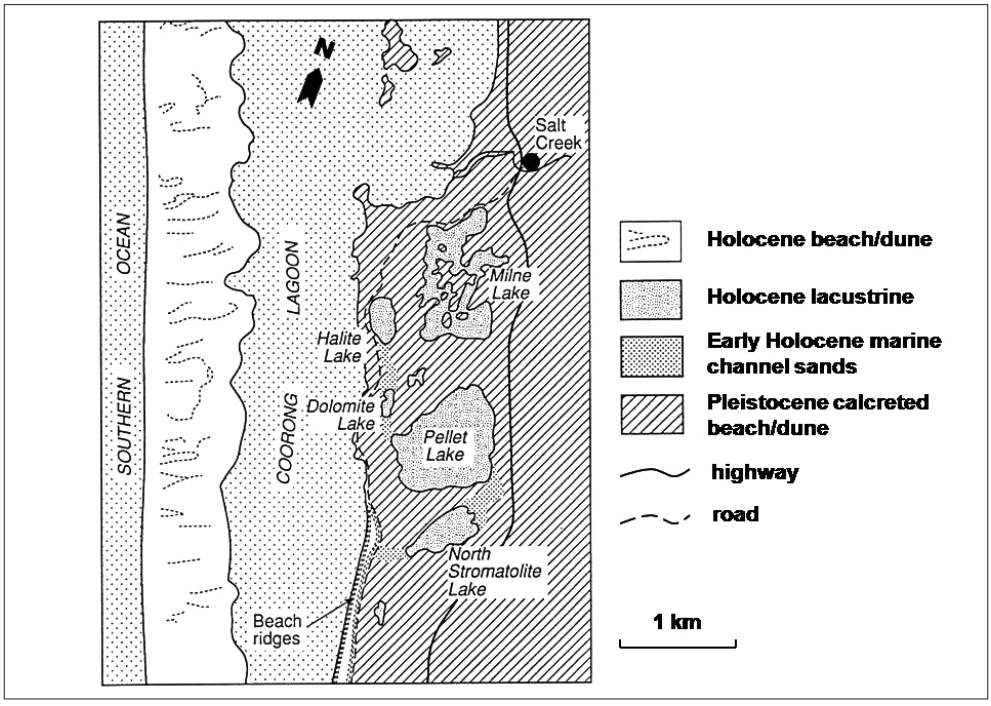


Fig. 1. Location of North Stromatolite Lake within the Salt Creek lake chain, Coorong National Park, South Australia (modified from WARREN, 1988).

isolated from the Coorong Lagoon at ca 6400 yr BP (MEE et al., 2007), shortly after sea level along Australia's southeastern margin reached its Holocene maximum. Nearby Milne Lake (figure 1), which hosts the thickest Holocene dolomite succession of all the Coorong Lakes, differs in never having been connected to the lagoon.

Various aspects of the stratigraphy, sedimentology and mineralogy of the Salt Creek lakes have been studied (e.g. BOTZ and VON DER BORCH, 1984; ROSEN et al., 1988, 1989; WARREN, 1988, 1990). Their Holocene shoaling-upward carbonate successions (figure 2) are remarkable, not only for their diverse mineral assemblages that include primary dolomite, but also for their enrichment in algal and cyanobacterial (i.e. sapropelic) organic matter. Total organic carbon (TOC) contents as high as 12% in the organic-rich unit, and the oil-prone character of its kerogen, make them useful as potential analogues of ancient lacustrine petroleum source beds (WARREN, 1986; McKIRDY et al., 1992). As an ideal carbon source for heterotrophic sulphate-reducing bacteria, such labile organic matter was arguably an essential link in the chain of microbially-mediated processes that led to the early diagenetic precipitation of dolomite in these lakes (WRIGHT, 1999; WRIGHT and WACEY, 2005). Recent studies of the micropalaeontology (diatoms, ostracods) of the organic-rich and laminated units in North Stromatolite Lake (EDWARDS et al., 2006), together with the bulk elemental (C, N) and isotopic (C, O, N) geochemistry and the radiocarbon dating of its entire lacustrine succession (MEE et al., 2004, 2005, 2006, 2007), have confirmed an earlier suggestion by McKIRDY et al. (2002) that the sapropels of the Coorong region may be proxies for Holocene climate change.

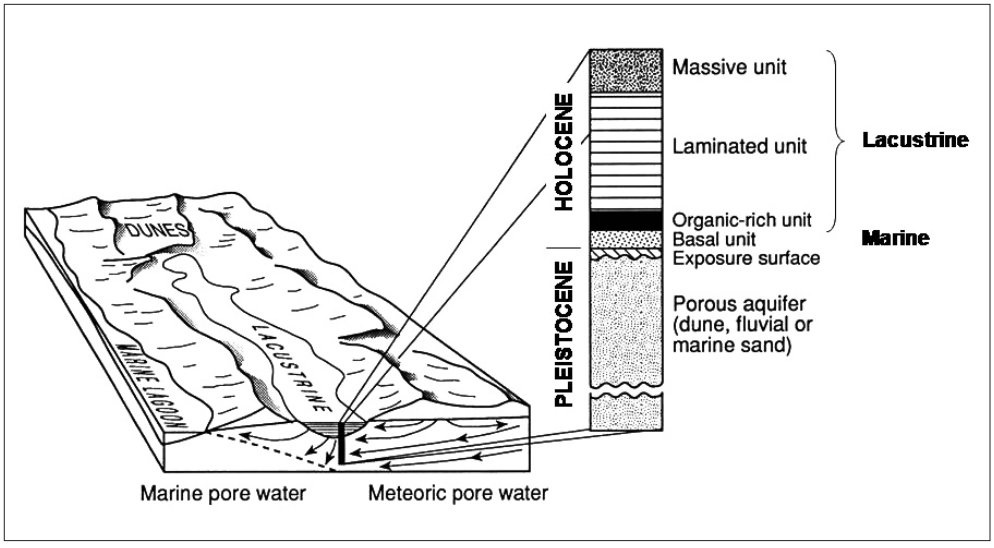


Fig. 2. Schematic physiography and generalised stratigraphy of a Coorong lake (modified from WARREN, 1988, 1990). Arrows highlight the seaward flow of brackish to saline meteoric groundwater.

The aims of the present study of a single core of unlithified Holocene carbonates recovered from the centre of North Stromatolite Lake (HAYBALL, 1990) were threefold:

- to ascertain whether the same strong correlation between sedimentary facies and organic carbon content exists here as in the adjacent Pellet Lake (WARREN, 1986);
- to determine the type(s) of kerogen preserved in its four sedimentary units and, if possible, the relative contributions of algal, bacterial and higher plant biomass to each; and
- to elucidate the organic geochemical signatures of metazoan grazing on organic-rich carbonate muds.

MATERIALS AND METHODS

Coring and sampling

A piston corer fitted with a slip hammer was used to drive 80 mm diameter PVC tubing into the Holocene sediment flooring the centre of North Stromatolite Lake. The total length of recoverable core was 2.71 m before the tubing encountered indurated Pleistocene calcrete. The use of large diameter tubing, in conjunction with a piston to apply a vacuum during penetration, helped minimise distortion and compaction (<20%) of the soft sediment. After retrieval with a winch mounted on a wooden palette the core tube was cut to size, sealed and transported back to Adelaide where it was stored at 0ºC until sampled. The tubing was split with an electric circular saw and the sediment core halved with a wire to reduce smearing along its length. Upon inspection of the exposed sediment, one half of the core was sampled every 10 cm along its upper 2 m; and then at 5 cm intervals through the remainder which comprised mostly dark, organic-rich mudstone. A total of 35 slices of half core (each 1 cm thick) were taken, placed in airtight containers and stored in a refrigerator. In preparation for analysis, these wet core samples were freeze-dried for 48 hr and then gently ground in a mortar and pestle. The other half of the core was logged and photographed before being sealed in a plastic sheath and archived in the School of Earth Sciences at Flinders University.

X-ray diffraction analysis

The mineralogy of each sample was determined with a Philips PW1050 diffractometer utilising cobalt Kα radiation of wavelength 1.7902 angstroms, scanning over a 2θ range of 3−75º at a step interval of 0.05º. Peaks were identified using the CSIRO XPLOT program and its JCPDS option.

TOC analysis and Rock-Eval pyrolysis

In order to retain the acid-soluble portion of their organic matter, the freeze-dried samples were prepared for organic carbon analysis using the procedure of ROBERTS et al. (1973). TOC was determined using a LECO carbon analyser. After reviewing their mineralogy and TOC contents, sixteen representative whole-sediment samples were submitted to Australian Mineral Development Laboratories, Adelaide, for Rock-Eval pyrolysis (ESPITALIÉ et al., 1985). In order to obtain a reliable oxygen index, the analysis was repeated on a decarbonated aliquot of each sample.

Kerogen isolation and petrography

Kerogen was isolated from a gently crushed portion (ca 1 g) of each sample analysed by Rock-Eval pyrolysis, using the procedure of PHIPPS and PLAYFORD (1984). The resulting strewn mounts were examined and photographed in reflected white light and UV-fluorescence mode using a Leitz Ortholux II polarising microscope fitted with a Wild Photoautomat MPS camera.

Solvent extraction and liquid chromatography

Powdered freeze-dried sediment from eight representative core samples was extracted in a Soxhlet apparatus with an azeotropic mixture of dichloromethane and methanol (87:13) for 24 hr. Activated copper turnings were added to the solvent flask to remove any co-extracted elemental sulphur. Upon subsequent removal of solvent in a rotary evaporator, the recovered extractable organic matter (EOM) was separated into its aliphatic hydrocarbon, aromatic hydrocarbon and polar fractions by conventional open-column liquid chromatography on activated alumina and silica, eluting respectively with petroleum ether; petroleum ether and dichloromethane (40:60); and dichloromethane and methanol (35:65). All solvents were AR grade and distilled prior to use.

Gas chromatography (GC)

The aliphatic hydrocarbon fractions of the sediment extracts were analysed using a Carlo Erba Mega 5160 gas chromatograph fitted with a 25 m x 0.22 mm internal diameter (i.d.) fused silica column (OV-101 stationary phase) and a flame ionisation detector (FID) and interfaced to a Perkin Elmer LC100 integrator. The oven was temperature-programmed from 40 to 300ºC at 8ºC min^{-1} and then held at 300ºC until all the peaks had eluted.

Gas chromatography-mass spectrometry (GC-MS)

GC-MS analysis of the aliphatic hydrocarbons was undertaken using a Varian 3400 gas chromatograph linked to a Finnigan TQS-70 quadrupole mass spectrometer at the Australian Wine Research Institute, Urrbrae. The gas chromatograph was fitted with a 60 m x 0.25 mm i.d. fused silica column (DB-1, 0.25 μm film thickness; J&W Scientific) interfaced directly with the source of the mass spectrometer. Hydrogen was used as the carrier gas at an inlet pressure of 103 kPa. Samples in *n*-hexane were injected using a split/splitless injector operated in the split mode (ratio 20:1) at 300ºC. The temperature programme of the oven was 50−300ºC at 4ºC min^{-1} followed by 20 min at 300ºC. The triterpenoid and steroid biomarker data reported herein were measured from the *m*/*z* 191 and *m*/*z* 215 fragmentograms of each sample. The identity of selected highly branched isoprenoid (HBI) hydrocarbons was determined from their mass spectra.

RESULTS AND DISCUSSION

The analytical data discussed herein are summarised in tables 1-3 and illustrated in figures 3-7.

Table 1: Rock-Eval pyrolysis data

Unit	Depth m	Tmax	S1	S2	S3	TOC wt %	HI	OI
Massive	0.10	407	0.32	4.80	4.24	1.70	282	249
	0.20	426	0.52	6.60	0.61	2.16	305	28
	0.40	420	0.66	6.75	3.70	3.73	180	99
	0.60	422	0.32	4.19	3.24	5.40	77	60
Laminated	0.80	432	0.24	4.44	3.74	4.35	102	86
	1.00	428	0.25	4.11	1.95	1.06	387	184
	1.20	415	0.21	3.57	2.20	1.34	266	164
	1.40	418	0.36	4.12	2.77	3.74	110	74
Sapropel	1.60	434	4.99	33.6	10.9	6.40	524	170
	1.70	435	3.81	29.1	5.94	8.99	323	66
	2.00	436	7.45	44.6	11.8	9.56	466	123
	2.15	432	24.3	75.5	12.8	11.7	647	110
	2.30	430	28.8	84.4	23.9	9.12	925	262
	2.40	432	23.2	74.9	28.9	10.1	740	285
	2.55	433	14.3	55.7	17.4	8.05	692	216
Basal	2.65	428	0.12	1.56	2.54	1.96	79	130

KEY

Tmax = position of S2 peak in temperature program (ºC)

S1 = free hydrocarbons (mg hydrocabons g^{-1} sediment)

S2 = kerogen-bound hydrocarbons (mg hydrocarbons g^{-1} sediment)

S3 = organic oxygen (mg CO_2 g^{-1} sediment)

HI = hydrogen index (mg S2 g^{-1} TOC)

OI = oxygen index (mg S3 g^{-1} TOC)

Table 2: Organic petrography of kerogen

Component	Basal	Lower sapropel	Upper sapropel	Laminated	Massive
Colonial algae	+	+++	+	+ / –	+
Filamentous cyanobacteria	+	+++ / ++	+++	+	+
Coccoid cyanobacteria	–	–	–	+++ / ++	++
Cuticle	–	–	++ / –	–	+++
Inertinite	+++	+	++ / –	+++	+++
Amorphous groundmass	+++	+++	+++	+++	+++

KEY

+++ abundant ++ common + rare – absent

Table 3: Extract yield and bulk composition

Depth	TOC	EOM yield		Aliphatic	Aromatic	Polar
m	wt %	ppm	mg g^{-1} TOC		% EOM	
0.20	2.16	9532	441	0.4	0.1	99.5
0.80	4.35	1244	29	2.5	0.7	96.8
1.20	1.34	2080	155	1.2	2.3	96.6
1.70	8.99	13012	145	0.1	1.7	98.2
2.00	9.56	10072	105	0.7	1.5	97.8
2.30	9.12	14594	160	0.7	4.8	94.5
2.55	8.05	12393	154	1.3	7.6	91.1
2.65	1.96	461	24	3.4	1.5	95.1

KEY
Aliphatic = aliphatic hydrocarbons
Aromatic = aromatic hydrocarbons
Polar = N,S,O-bearing compounds

Stratigraphy, sedimentary facies and mineralogy

Logging of the core revealed the same four-fold stratigraphic succession of unlithified Holocene calcareous sediments previously described by WARREN (1988, 1990) as characteristic of his type 2a lakes (figure 2). The ***basal unit***, here at least 8 cm thick (figure 3), comprises mottled, dark to light grey, quartzose shelly limestone. The skeletal remains are principally those of gastropods and small pelecypods, indicative of an estuarine to shallow marine environment. The quartz is very fine grained, sub-rounded to sub-angular, and most likely relict Pleistocene sediment washed or blown in from the enclosing dunes. Accordingly, the major mineral components are calcite and quartz. Minor dolomicritic cement in the basal unit would be classified as type B dolomite by ROSEN et al. (1988). During deposition the unit was constantly reworked by its fauna and hence lacks sedimentary structure. It is best described as a massive, mollusc-quartz wackestone to packstone.

The ***organic-rich unit*** (figure 2) is represented by 110 cm of cored sediment, herein described as ***sapropel*** (figure 3). On the basis of its TOC profile and organic facies (figure 4), it has been subdivided into lower and upper sapropels, respectively 76 and 34 cm thick. Dark grey to green in colour and rich in the small gastropod *Coxiella* sp. at its base, the ***lower sapropel*** grades upward into indistinctly laminated, dark green to black, rubbery mudstone with alternating dark and light bands 1−2 cm thick and sporadic lenses of the aforementioned gastropod, before reverting to thin intervals reminiscent of the basal facies. The lower and upper margins of the lower sapropel are paler in colour and lack the lamination of its middle portion, reflecting their greater bioturbation and pelletisation and consequent oxidation of their dispersed aquatic organic matter (table 2). Even today, *Coxiella* sp. becomes an active grazer around the shallow margins of the lake following its freshening by winter rainfall (WARREN, 1988).

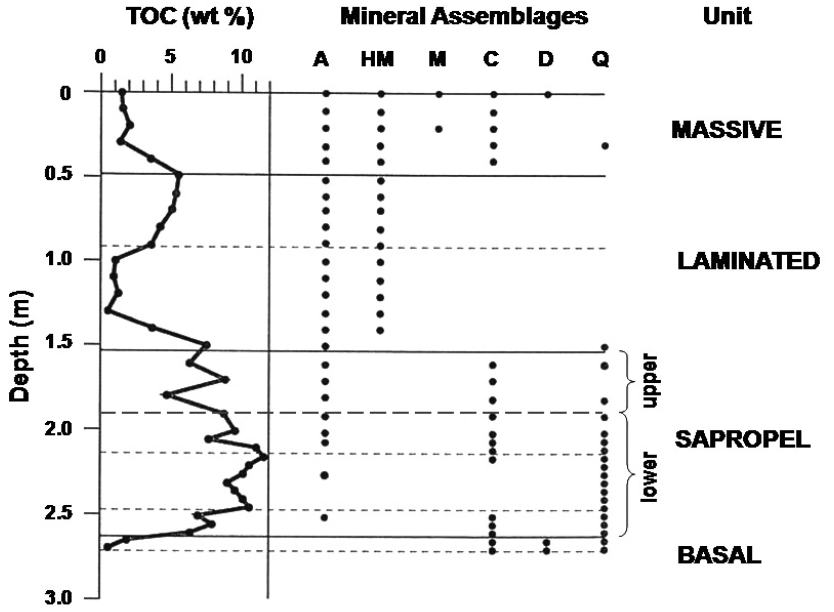


Fig. 3. TOC profile and mineral assemblages of central North Stromatolite Lake. Key: A = aragonite; HM = hydromagnesite; M = magnesite; C = calcite or low-Mg calcite; D = dolomite; Q = quartz; dashed lines mark changes in sediment character within units.

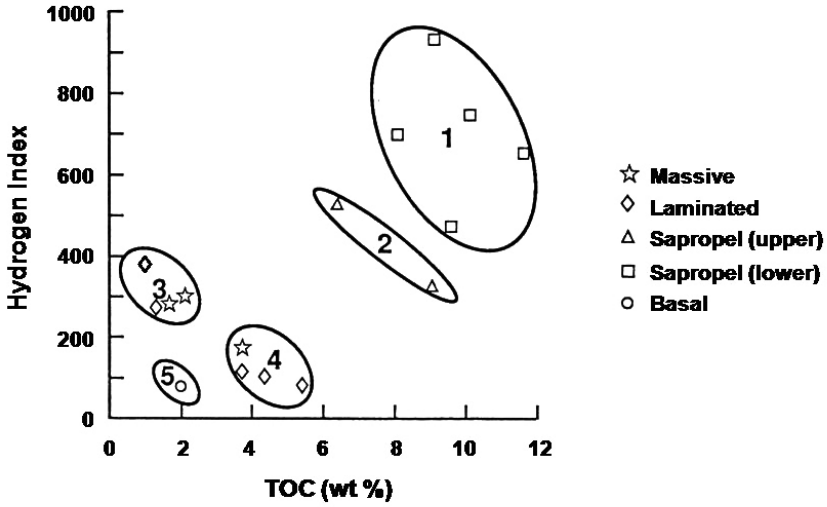


Fig. 4. Crossplot of hydrogen index versus TOC revealing five distinct organic facies in the Holocene carbonate succession of North Stromatolite Lake.

The mineralogy of the lower sapropel varies with its colour. The paler intervals are rich in aragonite, low-Mg calcite and quartz (figure 3). While the quartz is allochthonous (and, for the most part, probably aeolian: MEE et al., 2006, 2007), the carbonate mineralogy is biogenic and dictated by the *in situ* faunal assemblage of dwarf molluscs and ostracods (WARREN, 1990; EDWARDS et al., 2006). Interestingly, the darkest, most uniformly organic-rich interval lacks both aragonite and calcite in all but one of the samples analysed. Thus, the lower sapropel oscillates between two distinct organic-rich sub-facies: pelleted mudstone to wackestone; and laminated carbonate-poor mudstone.

The base of the ***upper sapropel*** is marked by a 7 cm zone of reworked lower sapropel, in the form of flake-like clasts up to 2−3 cm in size, accompanied by a concentration of intact *Coxiella* sp. Such disturbance of the underlying unit is most likely the consequence of wave action during a period of pronounced shallowing of the lake. This feature is significant because it also implies the waning of density stratification. The remainder of the unit is a light green to grey, massive pelletal wackestone. Mineralogically, it is indistinguishable from much of the lower sapropel (figure 3). The fine grain size of its carbonate fraction can be attributed to comminution of the delicate tests of the same biota that produced the pellets. At the very top of the upper sapropel is an oxidised, red to brown band (2 cm thick) which forms a gradational contact with the overlying unit. Such a feature is further evidence of shallowing of the lake as a result of its progressive infilling by sediment.

The pelleted ***laminated unit*** was deposited in a shallower, largely perennial water body and proportionally represents the largest volume of lacustrine sediment in North Stromatolite Lake (see the "fill and spill" model of WARREN, 1988, 1990). Its thickness in the present core is 104 cm, of which the lower 61 cm is considerably darker than the upper portion. Colours grade upward from light brown at the base, through dark greys, to light grey near the top. The unit is very susceptible to oxidation, its fresh sediment turning rapidly off-white upon exposure to air. This behaviour has been attributed to the presence of labile iron sulphides in the sediment (VON DER BORCH, 1965), which in turn implicates the activity of heterotrophic sulphate-reducing bacteria and associated anoxia in the pore fluids during early diagenesis. Aragonite and hydromagnesite comprise its unique mineral assemblage, which is independent of the colour variation throughout the unit (figure 3). The notable deficiency of detrital quartz is possibly a result of its dilution by the rapid precipitation and accumulation of carbonate mud. Another distinctive feature of this unit is its prominent lamination, at scales ranging from macro (centimetre) to micro (millimetre). Each macrolamina comprises several microlaminae. The latter are possibly varves formed by the annual variation in water depth and temperature between summer and winter. Macrolaminae have sharp bases, are dark and enriched in organic matter. Their gradational change to a light grey colour is accompanied by an increase in grain size. The development of such thick laminae is unlikely to have been due to annual cyclicity. Rather, it probably is a manifestation of some other periodic environmental forcing at this stage of the lake's history. Pellets are ubiquitous throughout this unit. Their distribution varies, resulting

in pellet-rich and pellet-poor microlaminae (WARREN, 1990). The pellets are products of the grazing of lake-floor sediment that has been colonised and bound by benthic algae and/or cyanobacteria. By analogy with this and other modern Coorong lakes, potential grazers and excreters of faecal pellets are ostracods, gastropods (e.g. *Coxiella* sp.), the Australian brine shrimp (*Parartemia zietziana*) and small burrowing beetles (DE DECKKER and GEDDES, 1980). The lamination is well preserved with no apparent disturbance by larger-scale bioturbation. The unit displays no evidence of subaerial exposure, apart from an indurated horizon at 110 cm depth in the core. This represents a single episode of prolonged exposure when the lake bed dried out completely and is probably correlative to a regional aridity event (AHMAD, 1996). Thus, the laminated unit in the central part of the lake can be classified as a pelletal mudstone.

The uppermost 49 cm of the core is designated the ***massive unit*** (figure 3). Its basal ~15 cm is indistinctly laminated carbonate mud and marks the transition from a mostly perennial water body to that of an ephemeral lake. The mud accumulated by lateral accretion from the marginal flats whenever the lake bed, by now approaching the regional water table, became inundated by winter rainfall and the seasonal inflow of groundwater (WARREN, 1990). The colour of the unit grades from alternating light and dark grey through its lower part to uniformly light grey near the top (the present-day lake depositional setting). While its contact with the underlying laminated unit is difficult to discern visually, the contrast in their respective mineral assemblages is conspicuous (figure 3). Calcite and aragonite again reflect the skeletal mineralogy of the contemporary lake fauna (notably prolific gastropods and ostracods), whereas hydromagnesite, magnesite and dolomite are micritic primary precipitates. Today, around the margins of the lake, dolomite (type A: ROSEN et al., 1988; WARREN, 1990) forms as a white precipitate with the texture of yoghurt. There it becomes mobile during winter, being spread by wind and wave action to form a thin veneer of sediment across the lake floor (VON DER BORCH and LOCK, 1979). Quartz is rare and, as in the other units, almost certainly allochthonous. While evident near its base, lamination is difficult to discern in the upper parts of the massive unit, reflecting an upward increase in the intensity of bioturbation and widespread pelletisation. According to WARREN (1990), bioturbation is here evidenced by the presence of crosscutting burrows, rhizomes and rootlets (presumably of the aquatic plant *Ruppia* sp.). When subjected to periodic subaerial exposure following high rates of summer evaporation, the massive unit develops mud cracks and becomes indurated, especially toward the lake edges. Subsequent accretion of mud to the rims of cracks in indurated crusts can lead to the development of tepee structures (KENDALL and WARREN, 1987). Here, in the uppermost part of the lake succession, the massive unit is essentially a pelleted mudstone that grades locally into pelletal packstones and wackestones.

Thus, the Holocene lacustrine succession atop the sapropel in North Stromatolite and other Coorong lakes is a mud-dominant sequence that has been variably but pervasively pelletised by ongoing faunal activity and variably reworked by wave-driven ripple migration (WARREN, 1988; 1990). Most of the pellets in the laminated and massive units

are soft and fine-sand sized. They are identical in terms of mineralogy to their muddy precursor sediment. In any ancient counterpart of this lacustrine depositional setting, the sediment upon burial would have been subjected to mechanical compression, which is very likely to have destroyed the original pelleted texture (LUCIA, 2007). It begs the question, is there any chemical signature that indicates variability in the intensity of pelletisation and bioturbation?

Organic facies

Rock-Eval pyrolysis of representative samples (table 1) revealed the existence of five different organic facies in the central part of North Stromatolite Lake (figure 4). The predominantly algal source affinity of their dispersed organic matter was subsequently confirmed by elemental and isotopic analysis of another core from the lake (C_{org}/N_{tot} = 12−15; $\delta^{13}C_{org}$ = -22 to -16‰: MEE et al., 2004).

Organic facies 1 is confined to the lower sapropel. Its kerogen is of Type I-II composition and petrographically comprises moderately fluorescing amorphous groundmass with lesser amounts of strongly fluorescent alginite in the form of colonial chlorophyte algae (*Botryococcus* sp.) and filamentous cyanobacteria; no recognisable higher plant remains are present (table 2). ***Organic facies 2*** is characteristic of the upper sapropel where the Type II kerogen is likewise predominantly amorphous; although here chlorophyte algae are rare and higher plant detritus is commonly present (notably cuticle, possibly from the aquatic metaphyte *Ruppia* sp., and finely particulate inertinite). ***Organic facies 3*** (Type II-III kerogen) is developed within the middle of the laminated unit and the upper 20 cm of the massive unit. Its principal components are coccoid cyanobacteria, weakly fluorescent groundmass and inertinite. ***Organic facies 4*** (Type III kerogen) occurs in the lower and upper parts of the laminated unit and in the lower massive unit. Petrographically, it differs from organic facies 3 in lacking coccoid cyanobacteria while also including a higher proportion of inertinite. ***Organic facies 5*** (Type IV kerogen) is represented by a single sample from the basal unit. The kerogen here comprises mostly inertinite and poorly fluorescent groundmass (probably degraded cyanobacteria), along with isolated small colonies of *Botryococcus* sp. Regardless of its host facies, the inertinite is almost without exception very finely divided (phytoclast size typically <7μm) and may represent wind-blown ash from occasional forest fires lit by lightning strikes (or, perhaps, the local indigenous inhabitants) in the Coorong hinterland.

While clearly discriminated on the basis of their organic richness and kerogen types (figure 4), facies 1 and 2 are even more sharply distinguished from each other and the other three facies by their respective hydrocarbon genetic potentials (S1 + S2, table 1):

Organic Facies	Genetic Potential (mg hydrocarbons g^{-1} sediment)
1	52−113
2	33−39
3, 4	4−7
5	<2

The higher genetic potentials of facies 1 and 2 are a direct reflection of the lipid-rich character of their precursor algal and eubacterial biomass, and the degree to which it has escaped degradation by aerobic and anaerobic heterotrophs during sedimenta-

tion and early diagenesis (KILLOPS and KILLOPS, 2005). Notwithstanding earlier assertions to the contrary (e.g. WARREN, 1988, 1990), when the sapropel was accumulating, perennial anoxic bottom waters were not an ongoing feature of the density-stratified bottom waters of North Stromatolite Lake during what was probably its deepest, meromictic phase. This contrasts with the suboxic to anoxic pore fluids in the massive unit that characterise the current ephemeral depositional system, as seen in measured O2 profiles of near-surface sediments in North Stromatolite and other Coorong lakes (WRIGHT AND WACEY, 2005; their Figure 2a). EDWARDS et al. (2006) demonstrated the existence of a flourishing benthic ostracod community in North Stromatolite Lake while its sapropel unit was being deposited. This, together with the diagnostic valve ornamentation of *Osticythere baragwanathi*, indicates that the hypolimnion was well oxygenated, at least seasonally, during this period of the Lake's history. Thus, high rates of primary production, in combination with minimal grazing and burrowing (and hence also internal aeration) of the organic-rich sediment on the lake floor by ostracods and dwarf molluscs, were the key factors responsible for the accumulation and preservation of ~1 m of sapropel beneath the centre of North Stromatolite Lake. Recent radiocarbon dating of this 'sapropel event' shows that these conditions persisted for 1400 years (between ca 6400 and 5000 yr BP: MEE et al., 2007).

The present-day subaqueous floors of Lake Lenore and Soap Lake in Washington State, USA (CASTENHOLZ, 1960) offer partial analogues for the bottom conditions in North Stromatolite Lake at the time its sapropel was deposited. In the littoral parts of Lake Lenore, diatoms seasonally form widespread epilithic layers atop cyanobacterially-bound microbial mats. Littoral lake-edge mats are not present in the more saline meromictic Soap Lake. Across the perennially water-covered deeper portions of both these saline lakes, diatoms constitute part of a crumbly gelatinous benthic aggregate, along with the cyanobacteria *Anacystis marina* and *Plectonema nostocorum*.

The micropalaeontological study of EDWARDS et al. (2006) also proved crucial in highlighting another important contributor to the organic matter preserved in the sapropel and laminated units of North Stromatolite Lake. While intact diatom microfossils (siliceous frustules) were not recognised in our initial studies of the sapropel, unusual T-shaped, C_{20} and C_{25} highly-branched isoprenoids (HBI) are prominent among the aliphatic hydrocarbons in its EOM (HAYBALL et al., 1991; see also figure 5) and were later recognised as bacillariophycean algal biomarkers (or molecular fossils: McKIRDY et al., 1995). Diatoms are not organic-walled, and the silica of their frustules is highly susceptible to dissolution in the present-day alkaline pore waters of this and other Coorong lakes. Hence, soon after burial, their cellular organic matter is destined to become part of the amorphous component of the kerogen (BARKER, 1992). As in the preservation of pelleted textures in ancient lacustrine counterparts, it is likely that the direct physical evidence for diatoms (viz. their siliceous frustules) is largely destroyed during early diagenesis, especially in the laminated unit where alkaline saline conditions were more pronounced (WARREN, 1990).

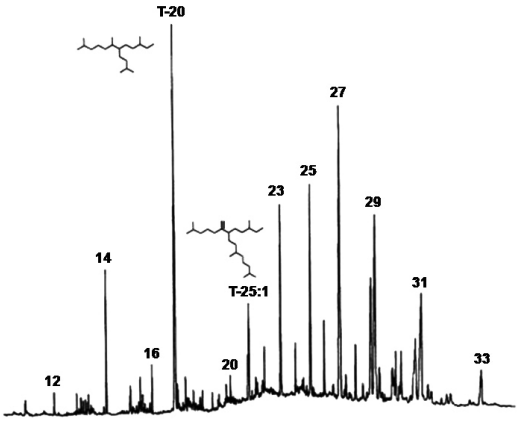


Fig. 5. FID-gas chromatogram of free aliphatic hydrocarbons preserved in the lower sapropel. Key: numbers indicate carbon number of *n*-alkanes; T-20 = 2,6,10-trimethyl-7-(3-methylbutane)-dodecane, a C_{20} highly branched isoprenoid (HBI) alkane; and T-25:1 = a C_{25} HBI alkane. See text for the likely sources of these biomarker hydrocarbons. Depth in core = 2 m.

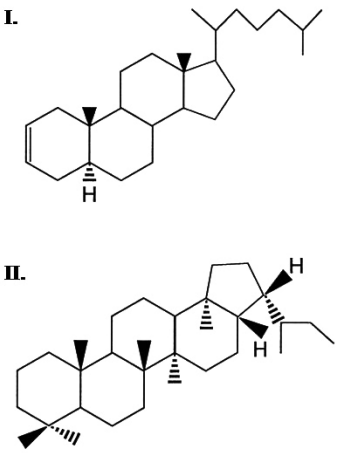
Geochemical signatures of pelletisation

The organically leaner carbonates of the laminated and massive units were deposited during the perennial and ephemeral phases of the Lake's history. Here represented by organic facies 3 and 4, they exhibit an inverse relationship between hydrogen index and organic carbon content (figure 4). As previously suggested by McKIRDY et al. (1992, 1995), this geochemical feature may be attributed to differences in the extent to which ostracods, gastropods, brine shrimp and other metazoans were actively grazing and burrowing the lake floor. This, in turn, is likely to have been driven by the progressive shallowing of the Lake as it filled with sediment, modulated by seasonal fluctuation of water depth and salinity. Another reason for the minimal pelletisation of the sapropel unit (particularly its rubbery lower part) is the significant contribution of diatoms to its biomass. The robust physical structure of its precursor diatomaceous ooze will have inhibited grazing and burrowing, and in the process limited access of oxygenated water to the sediment column, thus further enhancing the preservation of laminated organic-rich mudstone (cf. KEMP and BALDAUF, 1993).

Solvent-extractable bitumen comprises 1200−15000 ppm (dry weight) of the lacustrine carbonates in North Stromatolite Lake (table 3), of which <3% is aliphatic hydrocarbons. The biomarker geochemistry of these hydrocarbons will be reported in detail elsewhere. For the purposes of the present discussion, the aliphatic hydrocarbon distribution of one sample is shown here. Figure 5 illustrates some of its more prominent features, notably C_{20} and $C_{25:1}$ HBI hydrocarbons; and C_{12}−C_{33} *n*-alkanes displaying marked odd/even predominance above, and even/odd predominance below, C_{20}. This assemblage of biomarkers reflects the respective contributions of bacillariophyceae (diatoms), chlorophyceae (green algae) and eubacteria (including cyanobacteria) to the organic matter preserved in the lower sapropel unit.

In passing through the guts of ostracods, dwarf gastropods and other metazoan grazers, mud containing such organic

matter acquires a secondary molecular signature (or overprint) in the form of additional cholesterol. Soon after its excretion as faecal pellets, this animal cholesterol is converted to cholest-2-ene (structure I: figure 6) augmenting that formed via the early diagenesis of algal cholesterol (KILLOPS and KILLOPS, 2005, p. 187). Benthic cyanobacterial mats, together with diatomaceous ooze, were important food sources for the grazers. Homohopane (structure II: figure 6) is one of several triterpenoid biomarkers produced by cyanobacteria. Thus, the ratio of homohopane to cholest-2-ene may be used to monitor the degree of pelletisation of the lake-floor sediment. When plotted against depth in the core (figure 7), it reveals a steady upward increase in the extent to which the host sediment has been pelletised. As would be expected, this trend is paralleled by an increase in the proportion of cholest-2-ene in the total complement of C_{27}–C_{29} Δ^2-sterenes contributed to these lacustrine sediments by eukaryotic biota (algae, higher plants and animals).



CONCLUSIONS

The sedimentary succession of North Stromatolite Lake comprises a variety of unlithified, organic-rich, Holocene carbonates. These sediments were deposited in a progressively shallowing water body (initial maximum palaeo-depth = 3–5 m), beneath a halocline that first developed when the embayment, which is now the Salt Creek lake chain, was cut off from the marine influence of the Coorong Lagoon some 6500 y BP. Its previously described stratigraphy, comprising four units that each records a particular stage in the lake's evolution (viz. estuarine, density-stratified, perennial and ephemeral), has now been shown to host five discrete organic facies.

The organic-rich unit (sapropel) may be subdivided into organic facies 1 (Type I/II kerogen) and 2 (Type II kerogen), whereas the leaner laminated and massive units are distinctly bimodal hosting both organic facies 3 (Type II/III kerogen) and 4 (Type III kerogen). The basal unit is representative of organic facies 5 (Type IV kerogen).

The inverse relationship between Rock-Eval hydrogen index and TOC content manifest in organic facies 3 and 4 is here attributed to differences in the extent of grazing and pelletisation of carbonate muds by a diverse benthic fauna (including ostracods, gastropods and brine shrimp) during the shallowing perennial and ephemeral phases of the lake's history (figure 7).

Fig. 6. Carbon skeletons of two biomarker hydrocarbons which together provide a molecular record of the pelletisation of organic-rich carbonate muds in North Stromatolite Lake: I, cholest-2-ene (C_{27}); II, homohopane (C_{31}).

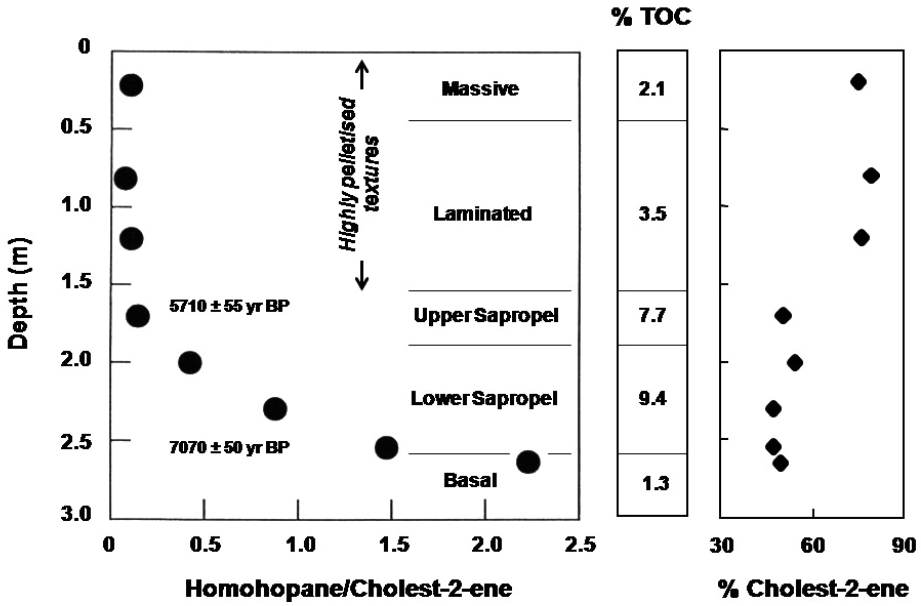


Fig. 7. Crossplot of homohopane/cholest-2-ene ratio *versus* depth recording the up-section addition of faecal cholesterol to the mud by benthic microfauna that grazed on algae and cyanobacteria. The right-hand panel highlights a parallel increase in cholest-2-ene as a proportion of the total eukaryotic input of C_{27}–C_{29} Δ^2-sterenes. The TOC values displayed in the central panel are unit averages. The ages are calibrated radiocarbon dates after MEE et al. (2007).

The aliphatic hydrocarbon distributions of these organic facies identify bacillariophyceae (diatoms), chlorophyceae (green algae) and eubacteria (including cyanobacteria) as major sources of their preserved organic matter. Its passage through the guts of the aforementioned grazers and excretion as faecal pellets has dramatically enhanced the relative abundance of cholest-2-ene, thereby imparting to the pelletised upper sapropel, laminated and massive units an animal biomarker signature.

The ability of grazing invertebrates to modify the texture and mineralogy of fine-grained sediments is well known. This study highlights their potential importance in also influencing the organic carbon content, kerogen type and biomarker geochemistry of modern carbonate sediments. In so doing it underlines some significant distinctions not recognised in many sedimentological studies. Absence or presence of lamination in a fine-grained lacustrine succession does not mean that the sediment has or has not been ingested; absence or presence of pellets at the time of deposition does. Where pellets are deposited as soft aggregations of micrite, the pelleted texture is quickly lost during the physical compaction associated with early burial and diagenesis, yet the molecular signature of ingestion may remain. Finally, lacustrine sediments containing high

levels of hydrogen-rich protokerogen may have accumulated beneath relatively shallow bottom waters (<5 m deep) that, although meromictic, were not perennially anoxic.

ACKNOWLEDGEMENTS

The South Australian Department of Parks and Wildlife kindly granted us permission to undertake coring in the Coorong National Park. This study is based largely on the B.Sc. (Honours) project of AJH. Preliminary accounts of its findings were presented at the 15th International Meeting on Organic Geochemistry at Manchester, U.K. in 1991 and the AAPG International Conference and Exhibition, Sydney, in 1992. Subsequent studies of this and other Coorong lakes by later students, notably Fiona Macdonald, Chris Hepplewhite, Tony Mazzoleni, Sally Edwards and Aija Mee, were invaluable in shedding additional light on the origin and significance of its organic facies. John Volkman rendered generous assistance with the interpretation of biomarker mass spectra. Alan Brenchley and Victor Gostin freely shared their knowledge of Coorong sedimentology in numerous discussions over many years; and Sherry Proferes drafted some of the figures. The contribution of DMMcK to this paper forms TRaX Record 61. Lastly, we thank reviewers Detlev Leythaeuser and Jennie Bourne for their comments on the manuscript. DE publishes with the permission of the Director, Geoscience Australia.

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