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Radiocarbon analysis of halophilic microbial lipids from an Australian salt lake

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ABSTRACT

Assigning accurate dates to hypersaline sediments opens important terrestrial records of local and regional paleoecologies and paleoclimatology. However, as of yet no conventional method of dating hypersaline systems has been widely adopted. Biomarker, mineralogical, and radiocarbon analyses of sediments and organic extracts from a shallow (13 cm) core from a hypersaline playa, Lake Tyrrell, southeastern Australia, produce a coherent age-depth curve beginning with modern microbial mats and extending to ~7500 cal yr BP. These analyses are furthermore used to identify and constrain the timing of the most recent change in hydrological regime at Lake Tyrrell, a shift from a clay deposit to the precipitation of evaporitic sands occurring at some time between ~4500 and 7000 yr. These analyses show the potential for widespread dating of hypersaline systems integrating the biomarker approach, reinforce the value of the radiocarbon content of biomarkers in understanding the flow of carbon in modern ecologies, and validate the temporal dimension of data provided by biomarkers when dating late Quaternary sediments.

Introduction

Accurate dating of intracontinental hypersaline playa sediments provides access to important paleoecological records. However, hypersaline playa lakes are difficult to date for three reasons. First, sedimentation rates in hypersaline basins are highly variable and sedimentation frequently stops altogether, allowing basin deflation and creating substantial disconformities within sedimentary sequences. Second, the organic content in hypersaline lakes is typically very low, making the size of samples required for conventional (liquid scintillation counting) radiocarbon analyses impractical. Third and perhaps most importantly, allochthonous ancient carbon washed in from dunes or blown in by wind can cause serious over-estimations of sediment ages using conventional bulk radiocarbon analyses. Utilization of accelerator mass spectrometric (AMS) radiocarbon analysis of indigenous microbial biomarkers (source-specific biologically derived organic molecules) extracted from lake sediments could potentially be a method for dating hypersaline sediments. The theory of using AMS for radiocarbon dating was outlined by Muller (1977) and the first AMS radiocarbon dates were reported the same year (Bennet et al., 1977; Nelson and Korteling, 1977). AMS can detect very small samples (<100 μg carbon), thus enabling analysis of biomarkers from sediments.

Utilizing biomarkers rather than non-extractable or bulk carbon allows for the critical assessment of carbon sources. The use of source specific organic molecules was initially developed as a tool for exploring petroleum systems, but has since expanded to paleoenvironmental reconstruction and ecological characterization. Biomarkers can characterize the organisms in sediments and rocks, and, in turn, characterize the geochemistry of the environment itself. Biomarker studies of this type have yielded enormous information about the evolution of the earth and its varied systems. Fortunately, hypersaline ecologies are relatively simple and well understood; as salinity increases metabolic diversity decreases, and in extreme hypersaline conditions, such as those at Lake Tyrrell, only a few metabolic strategies are capable of coping with the ionic stresses (Sorenson et al., 2004). The relative simplicity of hypersaline ecologies reduces some of the complexities of assigning biomarker provenance.

The microbial community at Lake Tyrrell appears consistent with that observed in hypersaline lakes and salterns globally (e.g., Sorenson et al., 2004; Oren et al., 2009). Primary producers, cyanobacteria and species of *Dunaliella*, a halophilic micro-algae—typically the sole algae present in hypersaline lakes (Madigan et al., 2009)—fix carbon, which is later taken up by a limited diversity of heterotrophic bacteria and archaea. The algae inhabit the lake waters, while microbial mats containing cyanobacteria exist below salt crusts and on the surface of the lake. Underlying the phototrophic bacterial mats is a shallow (2–4 cm) zone of sulfate reducing bacteria (SRB) (Fig. 1). DNA analyses limited to the shores of Lake Tyrrell affected by acidic groundwater springs show the presence of halotolerant/halophilic bacteria (Roden et al., 2009), and visual inspection of the lake sediments clearly shows the microbial community present (Fig. 1).

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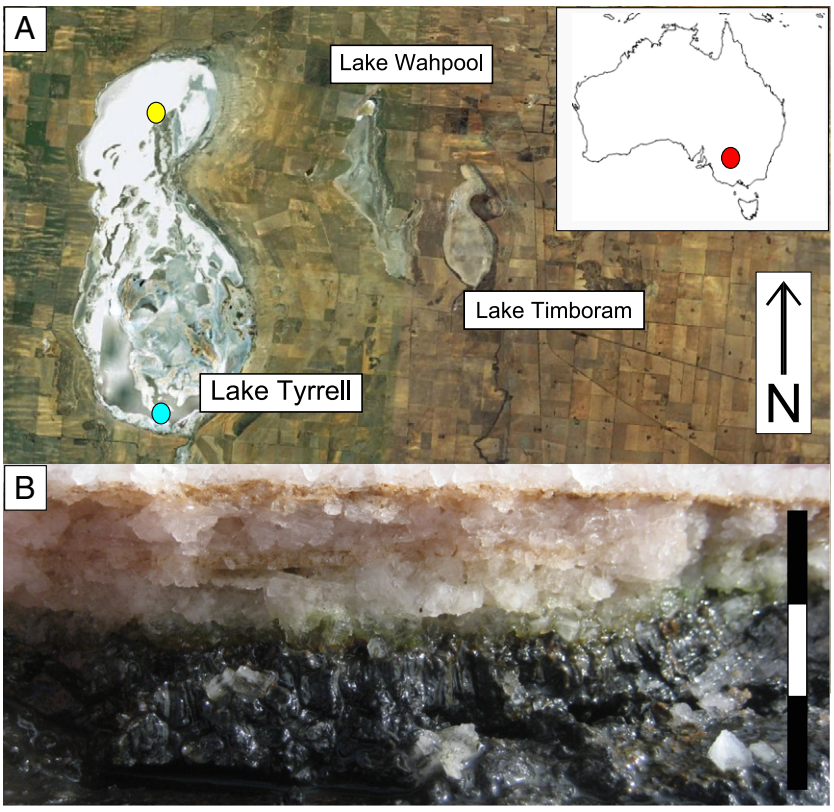

Figure 1. A) The location of Lake Tyrrell in southeast Australia. Note the two smaller lakes, Wahpool and Timboram, to the east. Lake Tyrrell is approximately 21 km in length north to south. The red dot refers to the location of Lake Tyrrell in Australia; the yellow dot refers to the location of previous dating studies in Lake Tyrrell; the blue dot refers to the study area discussed in this paper. Image courtesy of Google Earth. B) Pink salt overlying fresh green microbial mats, underlain by a black sulfidic layer. Black scale bars = 1 cm.

Radiocarbon analysis of biomarkers adds a temporal dimension of data onto the source-specific information and, while the technique is relatively new, has already been applied to diverse paleo-oceanographic and terrestrial questions (Pearson and Eglinton, 2000; Pearson et al., 2000, 2001; Ohkouchi et al., 2002; Shah et al., 2008). An important outcome of early radiocarbon studies of organic extracts showed that biomarkers of different classes can be sourced from various reservoirs, and the different classes can therefore have variable radiocarbon ages (Eglinton et al., 1997; Ohkouchi et al., 2002). Compound specific radiocarbon analysis (CSRA) was subsequently developed, allowing individual biomarkers to be analyzed and thus reducing interference from bulk organic mixtures (Eglinton et al., 1996, 1997). However, extract concentrations in salt lakes can be so minute that here we first attempt to characterize bulk lipid extracts and assess radiocarbon data from total organic extracts from a hypersaline lake, Lake Tyrrell, southeastern Australia (Fig. 1).

Study site

Lake Tyrrell, approximately 21 km length north to south, is the remnant of a freshwater paleo-mega lake, Lake Bungunnia which began to drain approximately 1.8 Ma (Stephenson, 1986) (Fig. 1, red dot). The modern groundwater flow in the area is from east to west: groundwater surfaces in lakes Timboram and Wahpool to the east, undergo evapo-concentration, refluxes and continues toward Lake Tyrrell. Groundwater again surfaces at Lake Tyrrell, evapo-concentrates, and refluxes as a hypersaline brine. No drainage outlets exist at Lake Tyrrell, and the only other sources of recharge for Lake Tyrrell include precipitation (~325 mm/yr), relatively low direct run-off, and intermittent flow from Tyrrell Creek at the south end of the lake. Salinity in Lake Tyrrell ranges between 260,000 mg/L (Teller et al., 1982) to saturation (360,000 mg/L), and the lake is inhabited exclusively by micro-organisms. In recent years (2008–2010), Lake Tyrrell contained water unevenly distributed across its surface during winter and spring. During the summers it usually dried out completely, leaving a salt crust ~3 cm thick.

Methods

A small core (15 cm depth, 15 cm diameter) was collected from sediments in the southern part of Lake Tyrrell (Fig. 1, blue dot). The core was transported to the laboratory, and stratigraphic units were identified by color, X-ray diffraction (XRD), and comparison of the core to previous reports of hypersaline microbial mat stratigraphy (Fig. 2). The outer cm of the core, in contact with the coring device, was removed and discarded. The remaining core interior was sectioned into 1-cm-thick samples, freeze-dried and ground using a mortar and pestle.

Solvent extraction and gas chromatography–mass spectrometry

Homogenized freeze-dried samples (~125 g) were extracted using a Dionex 300 Accelerated Solvent Extractor with the following program: preheat = 5 min; heat = 5 min; static = 5 min; pressure = 1500 psi; flush = 70%, purge = 300 s.; cycles = 3; solvent = 9:1 dichloromethane:methanol (dichloromethane, Science Supply Australia; methanol, Lomb Scientific). Solvent extracts were reduced by rotary evaporation, followed by total drying under a gentle stream of nitrogen using a heating block. Extracts were redissolved in 2 mL dichloromethane and passed over columns of activated copper turnings to remove elemental sulfur. Aliquots of the total lipid extracts were derivatized using N,O-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane; derivatized aliquots were analyzed

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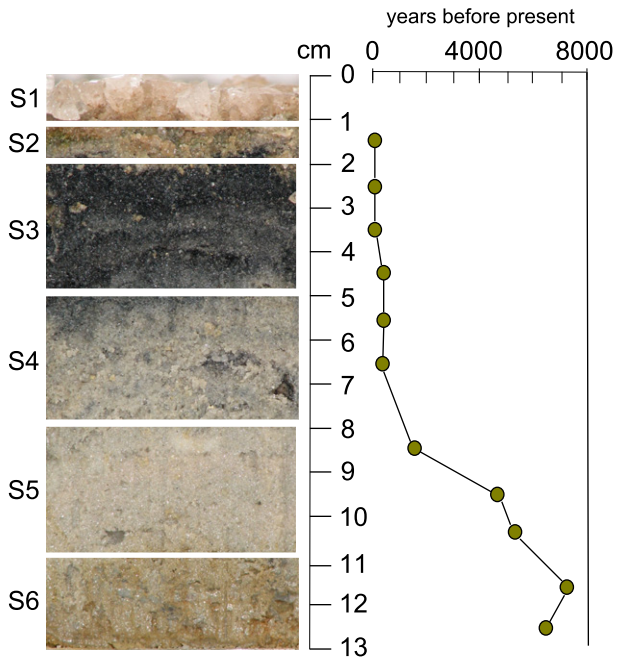

Figure 2. Age-depth curve showing radiocarbon data (years before present) schematically next to stratigraphy. See text for description of the six units (S1–S6). Black scale bars = 1 cm.

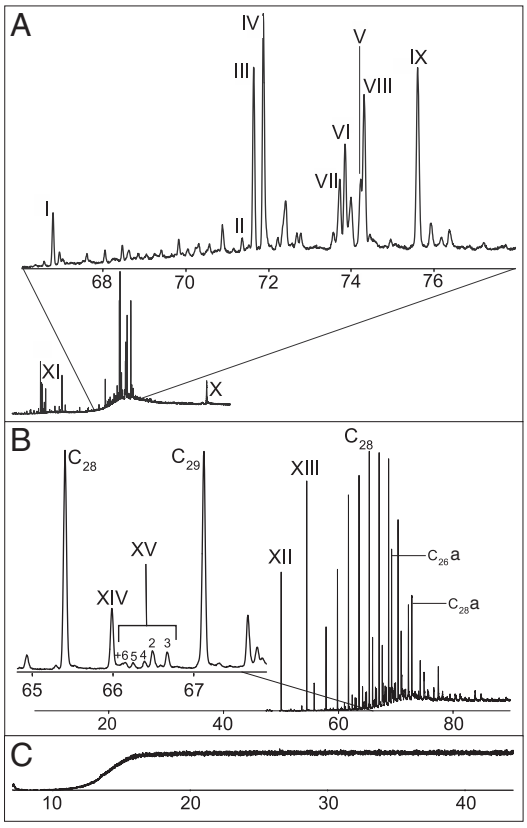

Figure 3. A) A typical total ion chromatogram of the Lake Tyrrell derivatized total extracts from sedimentary units S2–S5. The chromatogram shown is from core section 6–7 cm (S4). The lower chromatogram is the complete total ion chromatogram; the upper chromatogram is the total ion chromatogram is expanded to highlights steroids. Assignments reported underivatized. I — 5α-cholest-2-ene; II — octacosanol; III — cholesterol; IV — 3β,5α-cholestan-3-ol; V — stigmasterol; VI — 24-methyl-5b-cholestan-24(28)-en-3β-ol; VII — unassigned; VIII — unassigned; IX — β-sitosterol; X — archaeol; XI — aldehydes. B) A total ion chromatogram of derivatized total extract from sedimentary unit S6 with expanded inset to characterize minor components. Assignments reported underivatized. XII — hexadecanoic acid; XIII — octadecanoic acid; XIV — C_{28} alkanoic acid; XV — 1-, 2-, 3-, 4-, 5-, and +6- monomethylated C_{28} alkanes. C_{28} and C_{29} indicate *n*-alkane carbon number. C_{26}a and C_{28}a refer to C_{26} and C_{28} alkanoic acid, respectively. C) Laboratory blank.

using an Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer. The derivatized lipid extracts were injected through a programmable temperature vaporization injector operating at 310°C in splitless mode onto a DB5MS column (60 m × 0.25 mm i.d, 0.25-μm film thickness). The oven temperature was started at 40°C (held for 2 min), increased at a rate of 4°C/min to 310°C, and was then held for 40 min. Blanks of laboratory instruments and equipment were frequently analyzed to monitor potential contamination during sample processing (Fig. 3C).

AMS

Aliquots of the underivatized lipid extracts were loaded into precombusted quartz tubes using 200 μL dichloromethane (CH_2Cl_2) and the solvent was driven off by gently heating. CuO and Ag wires were added to the extracts, and the tubes were evacuated to $<10^{-3}$ Torr and sealed. The sealed tubes were combusted at 900°C and the subsequent CO_2 was then converted to graphite in the presence of Fe powder and H_2 gas (water being removed during reaction with Mg $(ClO_4)_2$). The amount of sample present was calculated using the pressure of the CO_2 produced by combustion in a known volume. Three samples containing 10× the sample amount of dichloromethane (3 mL) was prepared in the same manner as the samples, the pressure transducers recorded no CO_2 was present. Attempts to graphitize blanks were unsuccessful, implying that the contribution of contaminant carbon by the solvent is negligible. Radiocarbon analysis was performed using the single-stage AMS at Australia National University, Canberra (Fallon et al., 2010). Samples were normalized to oxalic acid-I and a coal blank was subtracted from the individual samples. Conversion of radiocarbon years to calendar years was performed using Calib 6.0 using the southern hemisphere calibration curve offered SH Atmosphere (Stuiver and Reimer, 1993) (http://calib.qub.ac.uk/calib/). The quoted uncertainty on the radiocarbon age (at 2-sigma) is reported in Table 1, using the convention of Stuiver and Polach (1977).

Results

Six stratigraphic units were identified in the small core on the basis of sedimentology and color (Fig. 2). The topmost unit (S1) is composed of pink precipitated halite and is underlain by green and pink stratified microbial mats (S2), which are commonly identified in hypersaline lakes (Oren et al., 2009). Below the mats is a black zone of sulfate reduction mediated by SRB (S3), which grades into a gray unit (S4), then to beige (S5), before the mineralogy changes creating the bottommost brown clay unit (S6). Units S2–S5 are composed of halite and gypsum sands, while S6 is primarily composed of illite and smectite clays (Table 1).

Typical total ion chromatograms from two representative sections are shown in Figure 3. The upper sediments (S2–S5) are dominated by sterols and archaeol, along with a small suite of aldehydes, such as hexadecanal (Fig. 3A). The aldehydes are here unassigned to any particular biogenic source as their origin is unclear. Phytanol and phytol, here interpreted as breakdown products of the lipid side chain of chlorophyll a, were also identified in the chromatogram. A series of nearly exclusively even-numbered long chain alcohols (C_{22}–C_{28}) were also identified in the upper sediments. The dominant sterols were 5α-cholest-2-ene (I), cholesterol (III), 3β,5α-cholestan-3-ol (IV), stigmasterol (V), 24-methyl-5b-cholestan-24(28)-en-3β-ol (VI), β-sitosterol (IX), and sterols that could not be identified

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Table 1
Radiocarbon ages of extracts with depth.

Stratigraphic unit	S-ANU#	Sample	Mineralogy	Size (mg)	^{14}C yr BP	95.4% (2 s) cal age ranges	Average cal yr BP ages
S2	11732	4B-2_1–2 cm	Halite, gypsum	0.602	>Modern	–	>1950
S3	11731	4B-2_2–3 cm	Halite, gypsum	0.651	>Modern	–	>1950
S3	11713	4B-2_3–4 cm	Halite, gypsum	0.73	>Modern	–	>1950
S3	11738	4B-2_4–5 cm	Halite, gypsum	0.557	340 +/− 20	358–447	403
S4	11736	4B-2_5–6 cm	Halite, gypsum	0.878	570 +/− 20	516–553	531
S4	11735	4B-2_6–7 cm	Halite, gypsum	0.557	540 +/− 25	504–545	525
S4	–	4B-2_7–8 cm	Halite, gypsum	lost	–	–	–
S5	11711	4B-2_8–9 cm	Halite, gypsum	0.218	1800 +/− 40	1560–1723	1642
S5	11710	4B-2_9–10 cm	Halite, gypsum	0.011	3540 +/− 480	2696–5053	3875
S5	11709	4B-2_10–11 cm	Halite, gypsum	0.169	4075 +/− 35	4412–4586	4499
S6	11712	4B-2_11–12 cm	Illite, smectite	0.514	6920 +/− 40	7606–7795	7701
S6	11720	4B-2_12–13 cm	Illite, smectite	0.186	6000 +/− 40	6668–6888	6778

Radiocarbon data of the organic matter from core sections. Sample 7–8 cm was lost during graphitization. Data was corrected using the small sample correction based on Santos et al. (2007).

(compounds VII and VIII). There is no significant difference in the distribution of these biomarkers between layers S2 and S5. The bottommost unit, S6, is dominated by homologous series of long chain *n*-alkanes and *n*-alkanoic acids, along with minor monomethylated alkanes (dominantly the 2- and 3-methyl isomers; Fig. 3B). The *n*-alkanes (C_{22}–C_{34}) have a unimodal, smooth distribution, with a maximum at C_{28}. There is no indication of any odd-over-even carbon-number predominance with a carbon preference index = 1.01 (Bray and Evans, 1961). The *n*-alkanoic acids are dominated by the C_{16} and C_{18} homologues, followed by a continuous distribution from C_{22}–C_{30} in which the even carbon numbers (C_{24}, C_{26}, C_{28} and C_{30}) predominate. Of these, C_{26} and C_{28} alkanoic acids are the major even-numbered acids observed.

The results of radiocarbon analyses are shown in Table 1 and Figure 2. The results show that the microbial mats and underlying 2 cm are modern, while extracts from 4–8 cm have slightly older ages (403–525 cal yr BP). From 8 cm downwards, ages are significantly older, with a generally increasing age trend with depth. The entire time period captured by these sediments covers less than 8000 cal yr BP. The age-depth curve was constructed using the average of the range of years before present.

Discussion

Two important biomarker classes dominate the organic extracts from the upper sediments; sterols and archaeol. Sterols are fundamentally derived from eukaryotic precursors as sterols are physiologically required in eukaryotic cell membranes (Madigan et al., 2009). Archaeol, on the other hand, is produced exclusively by members of the Archaea (Peters et al., 2007). Sterols are virtually unknown to occur in bacteria or archaea, and archaeol is unknown in eukaryotes or bacteria; hence, the provenance of these biomarkers is restricted. The sterols therefore likely originate from eukaryotic algae in the water column (indeed, sterols are often used as biomarkers for algae; e.g., Volkman, 1986), and archaeol from the halophilic archaea present in the waters and the mats. However, sterols that are best attributed to higher plants, such as β-sitosterol, are also present (e.g., Volkman, 1986). Plant sterols could derive from the numerous saltbushes surrounding the lake, as bulk plant material washed into the lake has been observed during fieldwork. While potentially older plant-derived carbon could have been introduced into the lake sediments, for instance by the erosion of soil, the modern ages of the top few centimeters suggest that plant input into the lake predominantly includes recent material. No evidence for plant waxes such as high molecular weight *n*-alkanes with strong odd-over-even high molecular weight predominance was observed in the upper sediments.

The biomarkers in the lower sediments contain virtually no sterols or archaeol. The even-dominated C_{24}–C_{28} *n*-alkanoic acid distribution is typical of higher plant waxes (Peters et al., 2007), but algal or bacterial sources may be responsible for the C_{16} and C_{18} *n*-alkanoic acids. The high molecular weight *n*-alkane distribution present in the lower sediments is not typical of that derived from higher plants, which is characterized by strong high molecular weight odd-over-even carbon number predominance (Bray and Evans, 1961). Rather, the alkanes present in the lower sediments have a carbon preference index (CPI) of ~1, indicating virtually no predominance of odd or even alkanes.

This signal is similar to that commonly seen in anthropogenic petroleum-derived products. However, two lines of evidence argue for the autochthonous nature of these molecules. First, lipids extracted from an additional core collected substantially later (two years) from the same location and depth are compositionally nearly identical to the presented data, but vary in concentration (data not shown). Some new extracts show the more expected odd-over-even predominance, suggesting that small-scale lateral variation in biomarker distribution exists in these sediments. The unusual lack of odd-number alkane predominance in these young sediments is not currently fully understood, but further isotopic and biomarker analyses on replicate samples will unravel the sources of these molecules. Second, petroleum-derived molecules would artificially age recent organic extracts (petroleum-derived products inherently being radiocarbon dead). The chromatogram presented contains nearly exclusively, by percentage, alkanes and alkanoic acids. Integration of the areas of the alkanes versus the alkanoic acids show the alkanes account for nearly 70% of the total GC resolvable compounds. Hence, if these molecules were petroleum derived the radiocarbon age of these extracts would be at least older than 20,000 yr. The resultant young ages provided by radiocarbon analysis and the repeatability of biomarker analysis argue that the observed distribution is derived not from anthropogenic petroleum sources but rather is a true signal from Lake Tyrrell sediments.

The age-depth curve presented in Figure 2 shows a good trend of increasing age with depth. Sample contamination during preparation and analysis is possible, and incorporation of modern carbon into AMS samples can influence results more drastically than the larger samples used for conventional radiocarbon analyses (Mollenhauer et al., 2005). Radiocarbon-free coal and wood are routinely analyzed in the ANU laboratory as procedural blanks to monitor sample contamination (Fallon et al., 2010). One age reversal is present in the data presented here, at 12–13 cm, but is considered a minor reversal that does not appear to compromise the overall trend in the data. A second very small age reversal appears at 5–7 cm, but this reversal is within the error of measurement and could reflect instrumental inaccuracy rather than contamination.

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The modern ages of the first ~4 cm of the core could be the result of (i) reworking of the top sediments during periodic disappearances of salt crust, (ii) a tightly coupled fixation of carbon by photosynthesizers and substrate uptake by SRB, or (iii) rapid sedimentation during the last decades. In the first option, the laminated nature of the surface sediments shows that reworking did not take place. As an argument in favor of the second model, carbon uptake by SRB in deeper layers, has been shown to be tightly coupled to carbon fixation in overlying mats (Buhring et al., 2009). However, the abundant sterols observed at 3–4 cm were clearly produced by photosynthetic organisms in the water column or at the sediment surface and are, thus, clearly not derived from late stage heterotrophs that incorporate recent carbon coming from above. Model (ii) would thus require diffusion of modern sterols centimeters into underlying sediments, a mechanism that is highly implausible given the hydrophobic nature of these lipids. It would also require fast and near-quantitative degradation of older sterols in deeper layers, a requirement that is probably impossible in anoxic sediments. Rather, the third and simplest scenario, rapid recent sedimentation, appears to satisfactorily explain the modern ages of the topmost sediments.

The modern ages of the top centimeters help address a potential problem when radiocarbon dating molecules derived from a groundwater-fed lake. Groundwater can have long residence times and could deliver ancient carbon to the lake waters that is taken up by microorganisms and subsequently incorporated into biomarkers. Four sources of carbon exist in groundwaters, the first being carbon brought into the aquifer during recharge, the second from carbonate dissolution, the third from volcanic or metamorphic outgassing, and the last from methanogenesis (Cartwright, 2010). In the Lake Tyrrell basin, volcanics and metamorphism may be excluded, as well as methanogenesis (oxygenated groundwater precludes methanogen activity), and as the aquifers feeding Lake Tyrrell are silica-dominated the input of carbonate dissolution should be low. Still, there is some ancient carbon; ^{14}C analysis of the groundwater derived from the primary aquifer feeding Lake Tyrrell shows a percent modern carbon of ~70% (Petrides et al., 2006). However, the modern ages of the top centimeters suggest that the groundwater quickly reaches equilibrium with the atmosphere, perhaps by thorough mixing of the atmosphere with lake waters by the consistent breezes at Lake Tyrrell. If the lake waters contained a substantial amount of dead carbon, then the ages of the lipids within the microbial mats would be older, not modern.

Radiocarbon ages increase when transitioning from S3 to S4, and then a noticeable break in slope of the radiocarbon ages at ~11 cm depth coincides with changes in mineralogy and biomarker content of the stratigraphic sections. The shift in mineralogy from S5 to S6 indicates a change in the paleohydrology regime, driven by an unknown mechanism that occurred between ~4500 and 7000 cal yr BP. The significant jump in ages across unit S5 (from ~4500 yr to ~500 yr) likely records a significant deflationary period during regime change. While the radiocarbon data does not elucidate the mechanism driving the changes in sedimentology, it does provide a powerful and convincing constraint on the timing of the mechanism. This timing is supported by studies of early- to mid-Holocene climate variability in southeastern Australia. At 3 to 4 ka a neighboring playa to the northwest, Lake Eyre, ceased being perennially semi-permanent and the modern playa regime was established (Magee et al., 1995). The drying of Lake Eyre was coincident with the onset of overall aridification of southeastern Australia during the mid-Holocene (Moros et al., 2009). The regional drying during the Holocene could therefore be the mechanism driving changing hydrological regimes at Lake Tyrrell. Finally, the radiocarbon data, in corroboration with unchanging biomarker and mineralogical data in the overlying sediments, demonstrates that the modern hydrological regime has persisted for approximately the last 4500 yr.

Other attempts have been made to date the sediments in Lake Tyrrell. In the northern basin of Lake Tyrrell, Bowler and Teller (1986) reported dolomitic carbonate derived ^{14}C dates of approximately 33,000 ^{14}C yr BP at 1 m depth (Fig. 1, yellow dot); also from the northern basin Luly et al. (1986) reported sedimentary organic matter dates of 2000 ^{14}C yr BP at 16.5 cm depths (Fig. 1, yellow dot). Gillespie et al. (1991) reported, from an unknown location within the Lake Tyrrell basin, pollen and charcoal derived AMS ^{14}C dates of 7300 cal yr BP at 90 cm depth—this study was likely based on samples from the northern basin of Lake Tyrrell as well. The apparent inconsistency with the data presented here and previous studies could ultimately be linked to sediment facies differences between sites separated by nearly 20 km. However, the carbonate dates of Bowler and Teller (1986) are near the analytical limit of radiocarbon analyses from two and a half decades ago and may reflect (nearly) radiocarbon-dead geological samples with some modern contamination. The younger dates of Luly et al. (1986) near the same depth in the lake sediments are most similar to the dates reported here. There may be differences in sedimentation rates at the locations, or there may have been some modern contamination of the organic samples previously collected. A third possibility could be the presence of recalcitrant and ancient (^{14}C-dead) molecules in the organic extracts analyzed here. Future compound specific radiocarbon analysis of Lake Tyrrell biomarkers will improve the assessment of provenance and identify allochthonous or recalcitrant carbon sources.

Conclusions

Radiocarbon analyses of organic extracts suggest the most recent episode of halite and gypsum precipitation at Lake Tyrrell has existed for approximately 4500 yr. The analysis of total extractable organics from this hypersaline lake results in a coherent age–depth curve, with a maximum age at 13 cm of ~7000 cal yr BP. Final interpretations of radiocarbon data from hypersaline extracts should include CSRA for the characterization of recalcitrant compound classes. As a preliminary study, the radiocarbon analysis of biomarkers from a hypersaline environment, paired with a critical assessment of biomarker provenance, reinforces the value of radiocarbon analyses of biomarkers in diverse environments.

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