## ORIGINAL PAPER

# Pollen, biomarker and stable isotope evidence of late Quaternary environmental change at Lake McKenzie, southeast Queensland

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**Abstract** Unravelling links between climate change and vegetation response during the Quaternary is important if the climate–environment interactions of modern systems are to be fully understood. Using a sediment core from Lake McKenzie, Fraser Island, we reconstruct changes in the lake ecosystem and surrounding vegetation over the last ca. 36.9 cal kyr. Evidence is drawn from multiple sources, including pollen, micro-charcoal, biomarker and stable isotope (C and N) analyses, and is used to gain a better understanding of the nature and timing of past ecological changes that have occurred at the site. The glacial period of the record, from ca. 36.9 to

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Southern Cross Geoscience and School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia 18.3 cal kyr BP, is characterised by an increased abundance of plants of the aquatic and littoral zone, indicating lower lake water levels. High abundance of biomarkers and microfossils of the colonial green alga *Botryococcus* occurred at this time and included large variation in individual botryococcene  $\delta^{13}$ C values. A slowing or ceasing of sediment accumulation occurred during the time period from ca. 18.3 to 14.0 cal kyr BP. By around 14.0 cal kyr BP fire activity in the area was reduced, as was abundance of littoral plants and terrestrial herbs, suggesting wetter conditions from that time. The Lake McKenzie pollen record conforms to existing records from Fraser Island by containing evidence of a period of reduced effective precipitation that commenced in the mid-Holocene.

**Keywords** Quaternary · *Botryococcus* · Pollen · Palaeoecology · Fraser Island · Southeast Queensland

# Introduction

Lake sediment is an important source of information about late Quaternary climate and environmental change in southeast Queensland, Australia. The region has produced long and high-quality records focused on microfossils (pollen, diatoms and charcoal) and geochemistry, and these have been used to reconstruct past changes in vegetation, human activity and aeolian sedimentation (Longmore 1997; Longmore and Heijnis 1999; Donders et al. 2006; McGowan et al. 2008; Barr et al. 2013; Moss et al. 2013). Much of what is known about Quaternary environments in the subtropical region of Australia has come from lake records on North Stradbroke Island and Fraser Island, and records from these islands have recently been included in continent-scale climate syntheses produced by the OZ-INTIMATE project (Petherick et al. 2013; Reeves et al. 2013). Despite this region's importance in understanding factors driving climate in subtropical Australia, in comparison to temperate regions it has a low density of sediment-based proxy records extending into the last glacial.

This study focuses on reconstructing past environmental change at a lake site on Fraser Island, using microfossil, biomarker and stable isotope analysis techniques. This study builds on previous work at the site, using diatom and branched glycerol dialkyl glycerol tetraether (GDGT) distributions (Hembrow and Taffs 2012; Hembrow et al. 2014; Woltering et al. 2014), and aims to broaden understanding of past environmental conditions at the site. Some key benefits of including biomarker and compound specific isotope techniques in studies of Quaternary-aged sediment have, for example, been discussed by Bianchi and Canuel (2011), Eglinton and Eglinton (2008) and Sachs et al. (2007), and importantly include the attainment of otherwise unavailable information about past isotope reservoirs and presence of organisms not associated with hard fossil remains.

#### Site description

Lake McKenzie is a clear-water oligotrophic lake located in an elevated inland area of Fraser Island, about 7 km from the western coastline  $(25^{\circ}26'51''S)$ , 153°03'12"E; Fig. 1). The lake has an area of about 94 ha, an elevation of 85 m above sea level and lies amongst dunes that reach 150 m in elevation. The lake is positioned above the regional groundwater table, and its relatively impermeable base-layer (a B-horizon) restricts downwards percolation of water (Timms 1986; Longmore 1998). The lake has no inflow or outflow creeks and thus is highly responsive to changes in precipitation and evaporation. Concentrations of total phosphorus are low  $(2-5 \ \mu g \ l^{-1})$ , as is pH (4.8–5.8), and dominant types of phytoplankton are Sphaerocystis, Oocystis and Peridinium (Bowling 1988; Hadwen et al. 2003). Living Botryococcus has not been reported in this lake, although it is reported in other perched lakes on Fraser Island (Bowling 1988). The lake lies within a national park that has been largely protected from industrial and residential development.

The Fraser Island landmass is composed of Quaternary-aged sand dunes that were formed progressively during periods of lower sea level (Lees 2006). The climate is subtropical. Rainfall derives mostly from south-easterly trade winds and tropical cyclones from the north. Mean monthly rainfall for January and July is respectively around 160 and 90 mm, and mean monthly temperatures are between 20 and 32 °C in January and 12 and 23 °C in July (Australian Bureau of Meteorology 2013). Precipitation patterns on Fraser Island are strongly influenced by topography, and rainfall is substantially higher in elevated areas on dune slopes (Longmore 1998).

The sandy soils of Fraser Island support a diverse range of vegetation communities, including heathlands, woodlands, tall eucalypt forest, and closed rainforest. Local water table depth, nutrient availability, soil salinity and local burning regimes are important influences on the structure and composition of vegetation communities on the island. Common vegetation communities are Eucalyptus signata F. Muell.-Banksia wallum heathland; coastal woodland, sedgeland and swamp; tall eucalypt forest with Syncarpia hillii F. M. Bailey and Lophostemon confertus (R. Br.) Peter G. Wilson and Waterhouse; and tall closed forest with rainforest and Eucalyptus pilularis Smith (Ryan 2012). Vegetation on slopes surrounding Lake McKenzie is composed of tall forest with Eucalyptus racemosa Cav., E. pilularis, Eucalyptus microcorys F. Muell., Eucalyptus resinifera Sm. and S. hillii. Dominant plants of the littoral zone are Baumea spp., Juncus spp. and Lepironia articulata (Retz.) Domin (Ryan 2012).

## Methods

### Sampling and dating

The methods by which the Lake McKenzie cores were sampled and dated has been previously described by Hembrow et al. (2014) and Woltering et al. (2014). Two adjacent sediment cores were extracted from the centre of the deepest basin of Lake McKenzie in 2010, in 8.3 m water depth. The 5-cm-diameter cores (LM1 and LM2) were extracted using a gravity corer, extruded on the



**Fig. 1** a Location of the South Eastern Bioregion on the east coast of the Australian continent (*red coloured area*). b Vegetation map of Fraser Island (Queensland Herbarium 2013). The

lake edge, and sliced into either 0.25-cm-thick (LM1) or 1-cm-thick (LM2) samples. Total unextruded core length was measured at 5–10-cm intervals during sampling to monitor any loss of core recovery. Samples

*white triangles* mark locations of *1* Lake McKenzie; *2* Hidden Lake; *3* Old Lake Coomboo Depression (OLCD); and *4* Allom Lake. (Color figure online)

were placed in individual plastic zip-lock bags before being transported and stored in laboratory freezers.

The cores were composed of uniformly dark organic-rich mud, with no visible alterations in colour

or texture. With the exception of one large wood fragment recovered from core LM1, terrestrial plant macrofossils, such as leaves or seeds, were not encountered in the cores. For this reason, and in order to target terrestrially derived carbon, pollen residues were prepared for AMS <sup>14</sup>C dating. Preparation of pollen residues for AMS <sup>14</sup>C dating involved sieving to collect a 10-150-µm size fraction, separation by heavy liquid flotation (LST; SG = 1.8) and treatment with NaOH (10 %), HCl (10 %) and H<sub>2</sub>SO<sub>4</sub> (98 %). Pre-treatment of the wood fragment involved acidalkali-acid treatment and all samples were graphitised according to standard procedure at the Australian Nuclear Science and Technology Organisation (AN-STO) (Hua et al. 2001). Radiocarbon dates were calibrated using the IntCal09 calibration curve (Reimer et al. 2009). Calibrated ages in the text are followed with a 'cal kyr BP' post-fix, single calibrated dates mentioned in the text refer to the median age in the  $2\sigma$  calibrated age-range.

<sup>210</sup>Ph Abundance atmosphere-derived of  $(^{210}\text{Pb}_{unsupported})$  in the upper sediment was used to estimate recent sediment accumulation rates at Lake McKenzie. The method, which has been described in detail by Appleby and Oldfield (1978, 1992), and Appleby (2001), uses down-core change in <sup>210</sup>Pb<sub>unsupported</sub> activity to calculate an accumulation rate based on the <sup>210</sup>Pb half-life of 22.26  $\pm$  0.22 years. <sup>210</sup>Pb<sub>unsupported</sub> was estimated by subtracting activity of supported <sup>210</sup>Pb (<sup>210</sup>Pb<sub>supported</sub>), which was measured indirectly from its grandparent radioisotope Radium-226 (<sup>226</sup>Ra), from total <sup>210</sup>Pb (<sup>210</sup>Pb<sub>total</sub>) activity, which was measured indirectly from its progeny polonium-210 (<sup>210</sup>Po). Both the constant initial concentration (CIC) and the constant rate of supply (CRS) models (Appleby and Oldfield 1978; Appleby 2001) were applied and calendar ages estimated.

<sup>210</sup>Pb<sub>supported</sub> and <sup>210</sup>Pb<sub>total</sub> were measured in the upper 8.5 cm of core LM1. Between 0.18 and 1.23 g of sediment was prepared by heating the samples in HNO<sub>3</sub> at 60 °C. Once evaporated, small amounts of H<sub>2</sub>O<sub>2</sub> (10 %) were added with heating until the reaction subsided. The samples were evaporated again before refluxing in a mixture of HNO<sub>3</sub> and HCl (1:3; 50–60 °C) for at least 4 h. Samples were subsequently redissolved in HCl (6 M) and centrifuged to separate the supernatant from the residue. The supernatant was collected and processed to remove excess iron by diethyl ether solvent extraction. <sup>210</sup>Po and <sup>209</sup>Po were isolated by auto-deposition onto silver discs using NH<sub>2</sub>OH·HCl. <sup>226</sup>Ra and <sup>133</sup>Ba were isolated by coprecipitation and collected as colloidal micro-precipitates on 0.1 µm Millipore VV membrane filters. The recovery of the preparation method was assessed using radioactive tracers <sup>133</sup>Ba (~85 Bq) for <sup>226</sup>Ra recovery and <sup>209</sup>Po (~0.2 Bq) for <sup>210</sup>Po recovery, which were added at the start of the sample processing procedure. The auto-plated polonium on the silver discs and the radium micro-precipitates on membrane filters were analysed using ORTEC alpha spectrometers to determine <sup>210</sup>Po and <sup>226</sup>Ra activities. <sup>133</sup>Ba was analysed using a HPGE gamma spectrometer.

#### Microfossil analysis

Thirty-two samples from core LM2 were prepared for microfossil analysis. This preparation involved sieving using a 125- $\mu$ m mesh, treatment with HCl (10 %), KOH (10 %), HF (40 %), acetolysis and mounting in glycerol. A known quantity of Lycopodium marker grains was added to each sample to allow for quantification of microfossils. Microfossils were counted under an Olympus BX50 microscope at 600× magnification and pollen was counted until 300 grains of terrestrial plant types were observed. Pollen identification was assisted by online resources (Newcastle Pollen Collection 2002; Australasian Pollen and Spore Atlas 2013) and published literature (Pike 1956). Results are presented as percentages of the total terrestrial pollen sum. Pollen zones were assigned on the basis of a stratigraphically constrained cluster analysis (CONISS) (Grimm 1987) performed using Tilia software (v. 1.7.16) (Grimm 1992).

Micro-charcoal particle and *Botryococcus* colony concentrations were estimated using the point count method (Clark 1982). Micro-charcoal particles were identified based on their black or transparent grey colour and jagged outline and only particles with an axis longer than 10 µm were counted.

Total organic carbon (TOC), total nitrogen (TN) and bulk organic  $\delta^{13}C$  and  $\delta^{15}N$  analysis

All samples from core LM2 were analysed on a Delta V Advantage Continuous Flow Isotope Ratio Mass Spectrometer-Flash 2000 HT Elemental Analyser for C %, N %,  $\delta^{13}$ C and  $\delta^{15}$ N. Nitrogen measurements

were conducted on oven dried (40 °C), homogenised sediment. Carbon measurements were conducted on the same aliquots after they had been treated with HCl (10 %) to remove any carbonate material present in the sample. CO<sub>2</sub> was calibrated against IAEA CH6 with a consensus value of 10.449 ‰ Vienna Peedee Belemnite (VPDB) (Coplen et al. 2006). N<sub>2</sub> calibration used IAEA N-1 with a consensus value of  $\delta^{15}$ NAIR = + 0.4 ‰ (Bohlke and Coplen 1995), a working soil standard AILS SSA (ANSTO Isotope Laboratory Standard—Simulated Soil Aliquot), and acetanilide. The results are reported relative to VPDB for C and air for N.

#### Lipid analysis

Twelve samples from core LM2 were extracted using a Soxhlet apparatus and pre-extracted cellulose thimbles. Extractions were performed on 3–5 g of dried and ground sediment for 24 h, with a solvent mixture of dichloromethane and methanol (9:1). Activated copper turnings were added to the collection flask to remove elemental sulphur. Extracts were separated into two aliquots, evaporated to dryness and weighed. Aliquots of each sample were initially prepared for GC–MS analysis using the separation procedure described below. A modified separation procedure was then performed on remaining aliquots of 6 samples, prior to analysis by isotope ratio monitoring (irm)-GC–MS.

Aliquots of extracts were initially separated using a small column (50 mm  $\times$  5 mm) filled with activated silica gel pre-eluted with n-Hexane. Extracts were progressively eluted with 2 ml of n-Hexane (the saturated hydrocarbon fraction), 3:7 DCM: n-Hexane (the aromatic hydrocarbon fraction) and 1:1 DCM: n-Hexane (the polar fraction). Known volumes of squalane (Fluka 85629) were added to the saturated hydrocarbon fractions to allow for estimation of compound concentrations. A modified separation procedure was performed on samples prior to irm-GC-MS analysis in order to improve compound separation. Extracts were added to the top of a large column (20 cm  $\times$  1 cm) filled with activated silica gel and eluted progressively with *n*-Pentane (2 bed-loads; 'F1' fraction), 3:7 DCM: n-Pentane (2 bed-loads; 'F2' fraction), and 1:1 DCM: n-Pentane (2 bed-loads; 'F3' fraction). Fractions 'F1' and 'F2' were combined and reseparating using a small column (50 mm  $\times$  5 mm) and eluted with *n*-Hexane (1 bed-load; 'F1a' fraction), *n*-Hexane (2 bed-loads; 'F1b' fraction), *n*-Hexane (2 bed-loads; 'F1c' fraction), and 1:1 DCM: Methanol (2 bed-loads; 'F2' fraction). Aliphatic and aromatic fractions were analysed by GC–MS. In some cases individual fractions were combined prior to measurement by irm-GC–MS, in order to completely capture compounds that eluted across fractions.

GC–MS analysis used a Hewlett Packard (HP) 5973 mass selective detector interfaced to HP 6890 gas chromatograph, fitted with a DB-5MS column (60 m × 0.25 µm i.d.; J and W Scientific). The GC oven was programmed to increase from 40 to 300 °C at 3 °C min<sup>-1</sup> with an initial hold time of 1 min and a final hold time of 30 min. Samples were dissolved in *n*-Hexane and injected on-column using a HP 6890 auto-sampler. Helium was used as the carrier gas, at a linear velocity of 28 cm s<sup>-1</sup> and the injector operating at constant flow. Typically the MS was operating at an ionisation energy of 70 eV, a source temperature of 180 °C, with an electron multiplier voltage of 1,800 V and a mass range of 50–550 amu.

Compound specific carbon isotope ratios were measured on an HP 6890 GC equipped with a HP6890 autosampler and interfaced to an Isoprime Micromass isotope ratio monitoring mass spectrometer. GC conditions were identical to those for GC–MS analysis described above. Each sample was analysed at least twice and  $\delta^{13}$ C values are reported relative to VPDB. Maximum deviation between separate analyses was less than or equal to 0.5 ‰ for all but 7 of the biomarker  $\delta^{13}$ C values reported here. Standard mixes with compounds of known isotope values were run at least between every two samples in order to monitor the stability of the system.

#### Results

#### Age model

The age model for Lake McKenzie has been previously described by Woltering et al. (2014) and was based on a deposition model that was constructed using OxCal (version 4.1) (Bronk Ramsey 2008, 2009) (Fig. 2). The deposition model excluded three dates that appeared to be outlying (OZN680, OZN681 and OZO411). Two of those dates (OZN680 and OZN681) were obtained at the same depth on core LM1, and appear to mark a

Fig. 2 Age-depth diagram for Lake McKenzie incorporating AMS <sup>14</sup>C and <sup>210</sup>Pb ages. The IntCal09 calibration curve (Reimer et al. 2009) and the OxCal P\_Sequence program (k = 4) (Bronk Ramsey 2008, 2009) were used to construct the deposition model



sedimentary disturbance, which may be related to the presence of the wood fragment. The third date relates to an age reversal of 1970<sup>14</sup>C years, which occurs between dates at 20–21- and 23–24-cm depths. In the absence of an obvious reason to exclude either date from the deposition model, Oxcal overall Agreement Indexes and Oxcal Outlier Analyses were compared to determine which had a higher likelihood of being erroneous.

OZN685 was excluded in a P Sequence deposition model (58.2 %), compared to that produced when OZO411 was excluded (65.3 %), and Outlier Analyses indicated a higher posterior probability of OZO411 being an outlier compared with OZN685. Thus OZO411 was deemed to be a more likely outlier, and was excluded from the deposition model.

ANSTO ID	Depth interval measured on core LM1 (cm)	Corresponding depth interval on core LM2 (cm)	Total $^{210}$ Pb (Bq kg <sup>-1</sup> )	Supported <sup>210</sup> Pb (Bq kg <sup>-1</sup> )	Unsupported <sup>210</sup> Pb <sup>a</sup> (Bq kg <sup>-1</sup> )	Particle size ≤62.5 µm (%)	Calculated CIC age (years)	Calculated CRS age (years)
M897	0.00-0.25	0.0–0.7	614 ± 12	$14 \pm 2$	$601 \pm 12$	74.0	$5\pm 5$	$5\pm 2$
M898	0.25-0.50	0.7-1.4	$491 \pm 24$	$18 \pm 2$	$484\pm24$	74.0	$15\pm5$	$13 \pm 4$
M899	1.50-1.75	4.1-4.8	$168\pm 6$	$19 \pm 2$	$150 \pm 6$	90.0	$65 \pm 7$	$64 \pm 8$
M900	1.75-2.00	4.8–5.5	$98 \pm 4$	$15 \pm 2$	$85 \pm 5$	77.6	$75\pm 8$	$76 \pm 9$
M901	3.00-3.50	7.0–7.8	$31 \pm 1$	$20 \pm 2$	$12 \pm 2$	83.9	$131\pm14$	$130 \pm 11$
M902	4.50-4.75	9.4–9.8	$38\pm1$	$27 \pm 3$	$11 \pm 3$	78.9	-	-
M903	4.75-5.00	9.8-10.2	$76\pm4$	$63\pm 6$	$13 \pm 7$	79.9	-	-
N369	6.00-6.25	11.7–12.2	$86\pm4$	$22 \pm 3$	$67 \pm 5$	69.9	-	-
N370	6.25-6.50	12.2-12.6	$102\pm5$	$42 \pm 4$	$62 \pm 6$	72.5	-	-
N371	7.00-7.25	13.4–13.8	$34\pm2$	$33\pm3$	$1 \pm 4$	73.3	-	-
N372	7.25-7.50	13.8-14.2	$31 \pm 2$	$33\pm3$	Not detected	83.5	-	-
N373	8.00-8.25	15.0-15.2	$63 \pm 3$	$28\pm3$	$36 \pm 4$	81.5	-	-
N374	8.25-8.50	15.2-15.5	$63 \pm 3$	$32 \pm 3$	$32 \pm 5$	68.7	_	_

Table 1 Total <sup>210</sup>Pb, supported <sup>210</sup>Pb, unsupported <sup>210</sup>Pb, and particle size results for samples taken from core LM1

Calendar age estimates using the CIC and CRS models are shown (Appleby and Oldfield 1978; Appleby 2001). Both the original depths measured on core LM1 and the corresponding depths on core LM2, as estimated using tie-points on total organic carbon (%) curves, are shown

<sup>a</sup> Decay corrected to a fixed date

Table 2 AMS <sup>14</sup>C dates and calibrated age ranges for pollen residues and wood samples with depths measured on core LM2

Lab code	Depth (cm)	Core	Composition	<sup>14</sup> C age (years BP)	Error (1σ)	Calibrated age-range (cal year BP; 2σ)
OZN683	10–11	LM2	Pollen	2,395	±35	2,183–2,654
OZN684	15-16	LM2	Pollen	3,785	±35	3,931-4,230
OZN685	20-21	LM2	Pollen	6,485	$\pm 50$	7,260-7,431
OZO411	23-24	LM2	Pollen	4,515	$\pm 40$	5,044-5,309
OZN686	25-26	LM2	Pollen	12,110	$\pm 70$	13,786–14,148
OZO412	26-27	LM2	Pollen	15,100	$\pm 70$	18,026-18,589
OZN687	30-31	LM2	Pollen	18,670	$\pm 100$	21,872-22,545
OZN688	35-36	LM2	Pollen	23,270	$\pm 120$	27,785-28,499
OZN689	40-41	LM2	Pollen	30,940	±190	34,924–36,280
OZN690	45-46	LM2	Pollen	31,870	$\pm 180$	35,575-36,783
OZN680	21.3-21.5	LM1	Pollen	19,150	$\pm 210$	22,330-23,428
OZN681	21.3-21.5	LM1	Wood	11,470	$\pm 60$	13,188–13,457

The sediment cores lacked visible lithological changes, however a large age difference of about 4.3 kyr was observed between contiguous samples obtained from 25-26- to 26-27-cm depths (OZN686 and OZ0412). Despite any visible indication of a break in sediment accumulation, the radiocarbon dates suggest a slowing or ceasing of sediment accumulation in the time interval of ca. 18.3-14.0 cal kyr BP (Tables 1, 2).

## Geochemical analyses

Marked changes in TOC %, TOC/TN and bulk organic matter  $\delta^{13}$ C and  $\delta^{15}$ N occur with depth (Fig. 3) and are



**Fig. 3** *Diagram showing* elemental composition and stable isotope carbon and nitrogen isotope ratios measured for the Lake McKenzie core LM2. Concentrations of biomarker compounds are also shown as a sum of the 9 botryococcene compounds

observed in the samples, individual concentrations of two botryococcenes (A2 and C0) and concentrations of the  $C_{20}$  HBI. The *shaded area* indicates the location of the hiatus suggested by radiocarbon ages on contiguous samples

characterised by a down-core increase in TOC/TN and decrease in  $\delta^{15}N$  values. Nine compounds were observed that have been identified as botryococcenes (Fig. 4; Supplementary Material). Their identification was based on comparisons with published mass spectra of botryococcene compounds and Kováts indexes (Huang et al. 1999; Gao et al. 2007; de Mesmay et al. 2008). Botryococcenes from Lake McKenzie were also compared with a sample containing a compound previously identified as 1, 6, 17, 21-octahydrobotryococcene by Huang et al. (1999). A good match in elution time and mass spectra was found between this sample and the compound described here as the A2 botryococcene. With the exception of the C0 botryococcene, all botryococcenes display higher concentrations in the lower samples, below 26 cm depth (Fig. 3). The CO botryococcene however, shows a distinct down-core trend: concentrations of this compound peak at 17 cm and are low below 26 cm. Botryococcene compounds were observed to have  $\delta^{13}$ C values in the range of -31.7 to -22.5 % (Table 3).

Long chain *n*-alkanes observed in the Lake McKenzie samples had a strong odd-over-even predominance (Fig. 4) and had average chain lengths (C25–C33) between 27.6 and 29.1. Chain length was observed to increase with depth.  $\delta^{13}$ C values of odd C23–C33 *n*alkanes ranged from -38.6 to -30.3 ‰ (Table 3). A C<sub>20</sub> HBI was also observed in the samples and showed higher concentrations in the upper samples and had a maximum concentration at 10 cm depth (Fig. 3).

## Microfossil analyses

The pollen diagram for Lake McKenzie is presented in Fig. 5. A depth-constrained cluster analysis (CONISS) was performed using all pollen types in order to identify pollen zones (Grimm 1987), and characteristics of each pollen zone are described below.

Fig. 4 Total ion chromatogram of saturate fraction of Lake McKenzie core LM3, from a 1 cm depth and b 31 cm depth. *Filled squares* refer to *n*alkanes and the number above the square refers to their carbon number. Compounds A2, C1, C2, B3, B4, C3, C4 and C5 are observed botryococcene compounds



*Pollen zone LM2-1: 46-34 cm depth, ca. 36.9–26.9 cal kyr BP* 

Pollen zone LM2-1 is characterised by high proportions of terrestrial herb pollen (mean = 15.3 %), of which Poaceae pollen is of highest abundance (11.1 %), and is followed by *Amperea* (1.6 %) and Asteraceae (Tubuliflorae) (1.3 %). Percentages of aquatic/littoral pollen are moderately high through most of this zone (9.6 %), and are dominated by Cyperaceae and Restionaceae. Casuarinaceae pollen dominates the arboreal taxa (42.5 %) and of the Myrtaceae pollen identified to genus level, *Eucalyptus* and *Melaleuca* dominate. Moderate concentrations of micro-charcoal occur (195.9 cm<sup>2</sup> g<sup>-1</sup>). Concentrations of *Botryococcus* colonies are high (323.6 cm<sup>2</sup> g<sup>-1</sup>) compared to the overlying zones.

*Pollen zone LM2-2: 34-26 cm depth, ca.* 26.9–18.3 *cal kyr BP* 

Pollen zone LM2-2 is characterised by high percentages of pollen from aquatic/littoral plants (17.3 %) and relatively high percentages of terrestrial herb pollen (14.5 %). Highest percentages of *Typha* pollen occur in this zone (5.3 %) and a sharp peak in *Typha* occurs at 33 cm depth. Cyperaceae also occurs in high abundance (8.5 %). A gradual replacement of Casuarinaceae with Myrtaceae pollen occurs up-core through this zone. Terrestrial herb pollen is dominated by Poaceae (9.9 %) and to a lesser degree Asteraceae (Tubuliflorae) (1.6 %), Chenopodiaceae (1.3 %) and *Amperea* (0.8 %). Concentrations of micro-charcoal are high in this zone (519.9 cm<sup>2</sup> g<sup>-1</sup>), peaking at 27 cm depth. *Botryococcus* colonies remain abundant (291.9 cm<sup>2</sup> g<sup>-1</sup>).

#### Hiatus: 26-25 cm depth, ca. 18.3-14.0 cal kyr BP

An age difference of about 4.3 kyr is observed between contiguous samples taken from 25–26 to 26–27 cm depth. Although no lithological change occurs at this depth, the AMS  $^{14}$ C dates suggest a hiatus is present spanning the time period from ca. 18.3–14.0 cal kyr BP.

		10 mm 11 10 mm	finon nim co		m enmodure		Non m amd							
Depth	<i>n</i> -alkane	δ <sup>13</sup> C (‰)					Botryococ	cenes $\delta^{13}$ C ( <sup>6</sup>	%00)					Zone
(cm)	C23	C25	C27	C29	C31	C33	A2	CI	C2	B3	B4	C3	C4	
1–2	-38.6 (0.0)	-36.6 (0.0)	-34.4 (0.4)	-33.0 (0.0)	-33.2 (0.2)	-33.0 (0.0)	I	I	I	I	I	I	I	LM2-5
10-11	, , 1	, I	, I	-34.1 (0.1)	-33.5 (0.1)	-33.0 (0.0)	I	I	I	Ι	I	I	I	LM2-4
21–22	-35.4 (0.3)	-34.6 (0.1)	-32.7 (0.4)	-32.2 (0.0)	-32.7 (0.3)	-34.5 (0.0)	I	I	-25.7 (0.4)	I	I	I	I	LM2-3
24–25	I	-35.9 (0.0)	-32.4 (0.4)	-31.3 (1.5)	-31.9 (0.5)	-32.2 (0.3)	I	-24.6 (0.2)	-22.6 (0.2)	I	I	-24.1 (1.2)	I	
27–28	I	-35.7 (0.0)	-34.0 (1.5)	-31.5 (1.0)	I	-31.8 (0.2)	-32.0 (1.3)	-23.9 (0.2)	-22.5 (0.7)	-23.1 (0.5)	-24.0 (0.4)	-23.1 (0.2)	-24.5 (0.5)	LM2-2
31-32	I	-35.2 (0.2)	-34.3 (0.1)	-30.3 (0.0)	-31.9 (0.0)	-31.2 (0.2)	-29.8 (0.0)	-23.6 (0.2)	-24.3 (0.2)	I	-23.7 (0.1)	-22.8 (0.2)	-24.6 (0.1)	
38–39	I	I	-32.0 (0.7)	-32.7 (0.2)	-32.4 (0.0)	-31.9 (0.1)	I	-26.9 (0.1)	-23.6 (0.0)	-25.1 (0.2)	-26.2 (0.1)	-25.3 (0.2)	-27.2 (0.1)	LM2-1
The maxii	mum per mil	deviation of	the measurem	tents is shown	1 in brackets l	below each $\delta^1$	<sup>13</sup> C value. Th	e dash symbo	I indicates wh	here no data is	s available			

5

Pollen zone LM2-3: 25-18 cm depth, ca. 14.0-6.1 cal kyr BP

A large change in the microfossil assemblage marks the lower boundary of this pollen zone. At the commencement of this zone, pollen of aquatic/littoral taxa are markedly reduced compared with the underlying zone (3.1 %), as is Poaceae pollen (2.1 %) and concentrations of both micro-charcoal (90.7 cm<sup>2</sup> g<sup>-1</sup>) and *Botryococcus* colonies (39.2 cm<sup>2</sup> g<sup>-1</sup>). Casuarinaceae pollen dominates the arboreal pollen (45.7 %), and of the myrtaceous pollen types, Lophostemon and Callistemon are increased compared with the underlying zone (respectively 2.3 and 4.7 %), while Acmena is decreased (0.2 %). Percentages of Monotoca are higher (7.8 %), while percentages of Asteraceae (Tubuliflorae) and Chenopodiaceae pollen are lower (respectively 0.2 and 0.4 %) than the underlying zone.

# Pollen zone LM2-4: 18–10 cm depth, ca. 6.1–2.5 cal kyr BP

Pollen zone LM2-4 is characterised by having the highest percentages of Myrtaceous pollen (59.6 %). Percentages of Moraceae (0.5 %) and Dodonaea (1.2 %) are slightly increased compared with the underlying zones. Percentages of Casuarinaceae pollen are low (19.2 %) while Myrtaceae pollen is high (59.1 %). Pollen from aquatic/littoral taxa is slightly more abundant in this zone (3.7 %) and two peaks in their abundance occur at 15 and 10 cm depth. Microcharcoal and Botryococcus concentrations also show slight increases around 15 and 10 cm depth, but on the whole are low in this zone. Percentages of Poaceae pollen are increased slightly (2.9 %), compared with the underlying zone.

## Pollen zone LM2-5: 10–0 cm depth, ca. 2.5–0 cal kyr BP

The uppermost pollen zone is characterised by reduced percentages of aquatic/littoral pollen (1.8 %) and high percentages of *Monotoca* (12.6 %). Casuarinaceae pollen is more abundant compared with the underlying zone (29.0 %), as is *Dodonaea* (2.8 %) and Eucalyptus (15.3 %). Concentrations of microcharcoal and Botryococcus colonies are slightly increased compared with the underlying zone (respectively 92.1 and 59.0 cm<sup>2</sup> g<sup>-1</sup>), and show a small





increase around 4 cm depth. Pollen from *Pinus* increases markedly at 4 cm depth.

## Discussion

Chronological assessment of the Lake McKenzie record

Obtaining reliable radiocarbon age estimates on organic remains from lake sediments can be problematic, as lake sediments are susceptible to producing dates that appear greater than the date of sediment deposition. Processes leading to erroneously old radiocarbon ages commonly arise when organic matter that is depleted in <sup>14</sup>C in relation to the contemporaneous atmosphere is incorporated into the sediments via dissolved forms of carbon, or via organic remains transported to the lake after a period of storage in the catchment (Bjorck and Wohlfarth 2001; Walker et al. 2007).

Terrestrial plant remains are preferentially selected for radiocarbon dating as those remains are unaffected by lake water reservoir effects, and when those remains are relatively fragile they are unlikely to withstand sediment reworking and long term storage processes in the catchment. They thus have a <sup>14</sup>C composition that is consistent with the atmosphere contemporaneous to sediment deposition (Bjorck and Wohlfarth 2001; Walker et al. 2007). A lack of suitable terrestrial macrofossils in the Lake McKenzie cores led to pollen residues being targeted for radiocarbon dating. Pollen is an advantageous material as it is primarily of terrestrial origin, it often has a short transport time from site of production, and is commonly abundant in lake sediments (Vandergoes and Prior 2003). However, prepared pollen fractions typically contain some organic detritus of unknown sources, and this potentially influences radiocarbon age estimates (Bjorck and Wohlfarth 2001). And as pollen exines are robust, pollen can be stored for lengthy periods of time on catchment slopes prior to being deposited in lake sediments and thus potentially incorporate a time lag into radiocarbon age estimates. At Lake McKenzie, the proportion of pollen transported to the lake via surface runoff is minimised by the lack of inflowing water channels. Additionally, the lake catchment has been predominantly vegetated with forest or woodland, and thus major events of sediment input would be largely restricted to periods following vegetation disturbance, after severe fire or storm, for example. Therefore time lags associated with sediment storage prior to deposition are unlikely to be a major influence on age estimates at Lake McKenzie.

The exact reason for the observed slow rate of sediment accumulation at Lake McKenzie is difficult to determine. Physical and chemical characteristics of Lake McKenzie are distinctly different to Lake Allom and Hidden Lake, where faster rates of sediment accumulation have been reported (Longmore 1998; Donders et al. 2006). Comparable rates of sediment accumulation are reported at Old Lake Coomboo Depression (Longmore and Heijnis 1999) and both Lake McKenzie and Old Lake Coomboo Depression are similar in the sense that they have relatively flat lake-bed topographies, as opposed to Hidden Lake, which has steeper slopes. While Lake McKenzie, Lake Allom and Hidden Lake are all oligotrophic and acidic (pH 4.0-5.8), Lake McKenzie has markedly clearer water, and lower total phosphorus ( $\leq 5 \ \mu g \ l^{-1}$ ), total nitrogen ( $\leq 70 \ \mu g \ l^{-1}$ ) and chlorophyll-a ( $\leq 0.2 \ \mu g \ l^{-1}$ ) content (Bowling 1988; Longmore 1998; Hadwen et al. 2003). These parameters may be related to a low rate of lake productivity or high rate of sediment diagenesis, and thus a slower sediment accumulation rate at Lake McKenzie. Bioturbation does not appear to have played a major role at the Lake McKenzie coring site over the last 130 years as a clear monotonic decrease in <sup>210</sup>Pb<sub>unsupported</sub> is observed in the upper part of the record. High water content, and low bulk density (Hembrow et al. 2014) in the upper layers of the sediment may account in part for the observed increase in sediment accumulation rate above 7 cm depth.

Environmental conditions at Lake McKenzie from ca. 36.9 to 18.3 cal kyr BP

The combined evidence presented here indicates that during the glacial period Lake McKenzie was shallow or ephemeral, and had an expanded littoral zone compared to present. Plants of the littoral or shallow water zone were abundant between ca. 36.9 and 18.3 cal kyr BP, as indicated by the high proportions of Cyperaceae and Restionaceae pollen in the record. Poaceae abundance is high at this time, which reflects either expanded grassy openings in surrounding vegetation, or an expanded littoral zone. The presence of long-chain *n*-alkanes with an odd-over-even predominance and  $\delta^{13}$ C values within the range of -35.7 to -31.5 % indicates a major source from terrestrial C3 plants (Eglinton and Hamilton 1967; Rieley et al. 1991). As do the  $\delta^{13}$ C values of bulk organic matter which range from -28.5 to -27.7 % (Smith and Epstein 1971; Tieszen 1991). High TOC/TN values suggest emergent and terrestrial plants are a dominant source of organic matter to the lake sediment (Bianchi and Canuel 2011), however caution in the interpretation of TOC/TN ratios is required at Lake McKenzie as *Botryococcus braunii* Kützing is known to produce bulk organic matter with high values. TOC/TN ratios greater than 20 have previously been observed for the algal colonies (Grice et al. 1998, 2001; Huang et al. 1999).

The green colonial alga Botryococcus braunii is the likely source of the botryococcene compounds observed in the Lake McKenzie sediments (Maxwell et al. 1968; Metzger et al. 1991). Down-core changes in abundance of botryococcenes and microfossils of Botryococcus show similar variation (Figs. 3, 5), with highest abundance of both proxies occurring in two separate periods, at around 36.0-30.8 and 23.5–20.3 cal kyr BP. The reason for the high abundance of Botryococcus during the glacial period is not known, but could be linked to factors such as the nutrient status of the lake water, or the presence of other phytoplankton with faster growth rates at the site. These factors influence the modern distribution of the algae (Cook et al. 2011). The lower atmospheric CO<sub>2</sub> partial pressure of the glacial period would presumably have been favourable to this green alga, as it has a CO<sub>2</sub> concentrating mechanism (Street-Perrott et al. 1997; Huang et al. 1999). The modern distribution of Botryococcus is broad and the alga appears to have a wide ranging environmental tolerance, however the alga is most commonly observed in freshwater oligotrophic lakes and ponds (Cook et al. 2011) and its presence has previously been used to understand past changes in eutrophication resulting from human activity (Smittenberg et al. 2005).

Botryococcene  $\delta^{13}$ C values for the glacial period of the record range from -31.7 to -22.5 ‰ and this is within the range of botryococcenes observed in Quaternary lake sediments at other sites (Grice et al. 1998; Huang et al. 1999; Smittenberg et al. 2005; Gao et al. 2007; Grossi et al. 2012). This large range in  $\delta^{13}$ C values is seen in a single sample from 27 cm depth (Table 3). Wide and contemporaneous variation in  $\delta^{13}$ C values of botryococcenes has previously been observed, and suggested to derive from their synthesis during successional periods of an algal bloom, when lake water characteristics such as dissolved nutrients, pH and dissolved CO<sub>2</sub> were undergoing alteration (Huang et al. 1999). This is a potential cause for the wide range in  $\delta^{13}$ C values observed within the one centimetre thick samples from the Lake McKenzie core.

Although the number of  $\delta^{13}$ C values obtained on individual botryococcene compounds from Lake McKenzie is small, a  $\delta^{13}$ C maximum occurs in zone LM2-2 (ca. 26.9-18.3 cal kyr BP) (Table 3), and this <sup>13</sup>C enrichment is also observed in the C29, C31 and C33 *n*-alkanes from this zone. The timing of this apparent carbon isotope excursion corresponds with the terminal period of the last glacial and a similarly timed positive shift in botryococcene  $\delta^{13}$ C values has previously been observed in a lake record from Mt Kenya (Huang et al. 1999). While the magnitude of the shift is greater in the Mt Kenya record, the proposed cause for the isotopic shift at that site, from the depletion of  $CO_2(aq)$  under the lower atmospheric  $pCO_2$  of the LGM, may also explain the observed shift to more positive botryococcene  $\delta^{13}C$  values at Lake McKenzie.

Cooler conditions at Lake McKenzie during the glacial are suggested by the slightly higher abundance of Asteraceae (Tubuliflorae). Previous work on GDGT distributions at Lake McKenzie, using a global soil calibration, estimated mean annual air temperature to have been 4.1 °C cooler at the site around 18.8 cal kyr BP compared to present (Woltering et al. 2014).

Micro-charcoal particles are abundant during the glacial period of the record and reflect a higher frequency and/or intensity of burning, probably as a result of dryer conditions. The influence of humans on fire activity at Lake McKenzie during the glacial period is difficult to discern however. The record does not extend far enough into the past to capture the initial occupation of the Australian continent, and the record does not contain information about short-term alterations in fire activity, as the time resolution for each sample is low. The presence of humans in SEQ during the glacial period is confirmed by the occupation of Wallen Wallen Creek site on North Stradbroke Island around 21,800<sup>14</sup>C year BP (Neal and Stock 1986; Ulm 2011). However, very little is known about pre-Holocene human occupation of this area, as an extremely low number of archaeological sites have been discovered (Bowdler 2010). In a continent that was dryer, windier and cooler than present (Harrison and Dodson 1993; Hesse et al. 2004; Williams et al. 2009), resources available on Fraser Island—from perched lakes, swamps and rainforest refugia for example—would seemingly have been attractive to people. However further archaeological work is required to understand the extent of human-induced fire activity on Fraser Island and on the nearby mainland.

## Deglaciation

The observed ceasing or slowing of sediment accumulation at Lake McKenzie during deglaciation (ca. 18.3-14.0 cal kyr BP) is likely to have been caused by the lake becoming perennially or intermittently dry. Perched lake sediments are prone to hiatuses, due to their sensitivity to change in precipitation and evaporation (Verschuren 2003). A hiatus is reported in the Lake Allom record, persisting to around 12.0 cal kyr BP (Donders et al. 2006), and while detection of hiatuses in the Old Lake Coomboo Depression (OLCD) record is restricted by the low frequency of radiocarbon dates, a sandy layer bounded by radiocarbon dates of ca. 26.0 and 14.5 cal kyr BP has been suggested to indicate dry conditions (Longmore and Heijnis 1999). Although the presence of hiatuses limits the amount of information that can be gained, all three of the lake sediment records that extend into the glacial that are now available from Fraser Island contain evidence of dry conditions occurring between the time period of ca. 18.3-14.5 cal kyr BP.

The timing of dry periods observed in Fraser Island records during deglaciation does not conform to climate shifts observed on North Stradbroke Island. There, vegetation reconstructions show arid periods occurring later than those on Fraser Island. The Native Companion Lagoon record shows evidence of dryer conditions at ca. 13.7 and 10.5 cal kyr BP, at Welsby Lagoon drying appears at ca. 14.0–12.0 cal yr BP and 11.5 cal kyr BP, and at Tortoise Lagoon drying appears at 14.0–12.0, 11.8 and 11.0 cal kyr BP (Moss et al. 2013). Higher resolution work in both regions, but particularly on or near Fraser Island, is required to more precisely understand the timing and synchroneity of deglaciation climate changes in southeast Queensland. However, as the islands are separated by more than 1.5° of latitude, a time lag in climate shifts occurring in the two areas is feasible given current understanding about changes that were occurring in offshore marine currents at that time. According to evidence from marine cores, the zone of separation of the East Australian Current (EAC) from the Australian continent gradually migrated southwards after the last glacial maximum, passing Fraser Island and then North Stradbroke Island (Bostock et al. 2006). This current is part of a major circulation system transporting warm tropical waters southwards, and has the effect of warming ocean water east of Fraser and North Stradbroke Islands. Thus deglaciation change in the position of this current might have had a non-synchronous influence on precipitation regimes in southeast Queensland. However other factors, such as differences in the islands' topography or the effects of sea level rise, may also have affected local moisture regimes of the two regions.

Environmental conditions at Lake McKenzie since ca. 14.0 cal kyr BP

Deeper water conditions at the sampling site from around 14.0 cal kyr BP are suggested by the reduction in abundance of plants of the littoral and shallow water zones, and the reduced contribution of terrestrial or emergent plant organic matter in the lake sediments. Wetter conditions are also suggested by the denser vegetation at the site, indicated by the reduced abundance of Poaceae and Asteraceae, and reduced fire activity. *Monotoca* and *Lophostemon* are more abundant during the Holocene and may track the establishment of modern types of eucalypt forest at the site. Those taxa are abundant in the eucalypt forests that currently occur on the high dunes and sand plains of Fraser Island, including those surrounding Lake McKenzie (Ryan 2012).

Superimposed on the underlying trend of higher effective precipitation during the Holocene is evidence of a subtle reduction in moisture at the site, commencing around ca. 6.1 cal kyr BP and persisting to around 2.5 cal kyr BP, suggested by the small increase in littoral plants. This evidence for dryer conditions commencing around the mid-Holocene is consistent with previous findings from diatom remains at the site (Hembrow et al. 2013). However unlike the pollen record presented here, the diatom record showed shallower water conditions persisting to present. Other lake records on Fraser Island show evidence of dry conditions during the mid-Holocene. At Hidden Lake, a dry period is reported from ca. 9.5-2.6 cal kyr BP, and is further described as progressing from a period of falling groundwater levels from ca. 9.5 to 6.3 cal kyr BP, to stable and low groundwater levels from ca. 6.3 to 5.1 cal kyr BP, and to rising groundwater levels from ca. 5.1 to 2.6 cal kyr BP (dates are recalibrated using the original <sup>14</sup>C dates reported by Longmore (1998)). At Lake Allom, dry conditions are the proposed cause for a sedimentary hiatus spanning from ca. 6.5 to 5.4 cal kyr BP (Donders et al. 2006), after which a period of moist conditions and rising lake levels is reported, persisting to ca. 3.0 cal kyr BP. Large-scale synthesis studies of palaeoclimate records conclude conditions across eastern Australia to have been more variable or dryer from around 6–5 cal kyr BP, and suggest this to have been due to an increasing intensity of the El Niño Southern Oscillation (ENSO) (Donders et al. 2007; Petherick et al. 2013; Reeves et al. 2013). As the area of influence of ENSO is wide, its influence on climates of eastern Australia is expected to have been synchronous (Donders et al. 2007). The return to wetter conditions in the late Holocene at some Fraser Island sites contrasts with the general trend for eastern Australia, and suggests that local factors may have been an important influence on the island's hydrological regimes during the late Holocene.

Unlike other botryococcenes detected in the Lake McKenzie record, the **C0** botryococcene has a maximum concentration at ca. 5.5 cal kyr BP (Fig. 3). This unique down-core trend of the **C0** botryococcene could be explained by: (1) more than one race of *Botryococcus braunii* occurring in the lake over time; or (2) the same organism synthesising different compounds at different times during the lake's history. Further work on the alga and its biomarkers is required to determine whether environmental factors were driving the observed down-core changes in botryococcene distributions at Lake McKenzie.

Despite the apparent increase in human occupation of southeast Queensland during the mid-Holocene (Ulm and Hall 1996; Ulm 2011), evidence of human activity in the form of large shifts in fire activity or vegetation composition are absent in the Lake McKenzie record. This contrasts with lake records from parts of North Stradbroke Island where increased burning is detected from the mid- to late-Holocene and is linked with intensified human activity (Moss et al. 2013). Despite the absence of human impact evidence in Fraser Island sediment records, archaeological investigations find occupation of the mainland adjacent to Fraser Island to date to at least ca. 5.5 cal kyr BP (McNiven 1992) and occupation of Fraser Island itself to date to ca. 3 cal kyr BP (Ulm 2011). This mismatch highlights the need for further palaeoecological and archaeological work to better understand past human activity in the region.

## Conclusions

The Lake McKenzie record provides a reconstruction of changes to ecosystem composition occurring over the last approximately 36.9 cal kyr, inferred from sedimentary microfossils, biomarkers and stable isotope ratios (C and N). Elevated abundance of littoral plants at the site and increased contribution of allochthonous organic matter to the lake sediment, along with increased abundance of terrestrial herbs, is interpreted as reflecting sustained dry conditions to at least ca. 18.3 cal kyr BP. The underlying trend for increasing effective precipitation after ca. 14.0 cal kyr BP is interrupted ca. 6.1 cal kyr BP, when a subtle shift towards dryer conditions is detected in the pollen record. This conforms to other evidence of mid-Holocene aridity on the island, and in the broader eastern Australian region. Abundance of both fossil Botryococcus colonies and Botryococcus-derived biomarkers indicate that maximum growth of this colonial green alga occurred during the glacial period, when conditions were drier and cooler, and surrounding vegetation was sparser and more prone to burning. The evidence presented here for the Lake McKenzie sediment record contributes to the understanding of spatial and temporal variability of ecological changes occurring on Fraser Island and in subtropical eastern Australia, and permits a better assessment of the significance of those ecological shifts in a regional context.

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