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Evidence of late Quaternary environmental change in a continental east Antarctic lake from lacustrine sedimentary pigment distributions

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Abstract: A sediment core from Progress Lake, one of the oldest lacustrine sequences in East Antarctica, contains distinct zones dating from a previous interglacial (most likely Marine Isotope Stage 5e, *c*. 125–115 kyr BP) and the present interglacial (Marine Isotope Stage 1), separated by a transition zone representing when the lake became sub-glacial. Profiles of fossil pigments, determined using high performance liquid chromatography and liquid chromatography-tandem mass spectrometry, show distinct differences in the photoautotrophic community during these two interglacial periods. The first was dominated by algae and purple phototrophic bacteria, with periods of photic zone euxinia indicated by pigments from anoxygenic phototrophic bacteria. Specific chlorophyll *a* derivatives reveal periods when grazing pressure impacted significantly on the phytoplankton community. The virtual absence of pigments in the transition zone reflects severe restriction of photoautotrophic activity, consistent with the lake having become sub-glacial. Retreat of snow and ice in the late Holocene (3345 ^{14}C yr BP) allowed establishment of a less diverse primary producer community, restricted to algae and cyanobacteria. Grazers were severely restricted and oxidative transformation was more important than during the previous interglacial. The pigment data provide a unique and detailed insight in to the evolution of the lake ecology over an interglacial-glacial-interglacial transition and strong evidence that the Marine Isotope Stage 5e interglacial in this region of coastal East Antarctica was several degrees warmer than at present.

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Key words: bacteriochlorophyll *e*, chlorophyll transformation products, HPLC-mass spectrometry, Larsemann Hills, palaeoenvironmental reconstruction, Progress Lake

Introduction

Terrestrial records of environmental change in Antarctica, including those from lakes, are often limited to the last *c*. 10 000 years as a result of the denudation caused by glaciation during the Last Glacial Maximum (LGM). Recent studies have identified some areas of East Antarctica that remained ice free at the LGM (Hodgson *et al*. 2001). In such cases, lake sediments can provide unique records of environmental change spanning the last glacial interglacial cycle (Hodgson *et al*. 2005, in press). These records enable changes in lake ecology and species composition to be explored in the contexts of ice core records of climate change from the Antarctic continent and the marine geological record of oceanographic changes on the continental shelf.

Various inorganic, physicochemical, biological and biogeochemical markers determined from lake sediments can be used to reconstruct records of late Quaternary environmental change in Antarctica (Hodgson *et al*. 2004a). Thus, insights into past species composition and ecology can be obtained from visually identifiable cellular remains of photoautotrophic organisms, for example the siliceous frustules of diatoms (Moser *et al.* 1996). Notably, however, the cells of many photoautotrophs do not incorporate structures that are of sufficient resistance to survive diagenesis. Such inputs can be revealed by the presence of specific molecular fossils including the chlorophyll (Chl, Fig. 1), bacteriochlorophyll (BChl, Fig. 1) and carotenoid pigments that are ubiquitous components of photoautotrophic organisms. Together with their transformation products, these pigments become incorporated into marine and lacustrine sediments either directly, through deposition and/or burial of the remains of photoautotrophs, or indirectly *via* the grazing activities of heterotrophic organisms (Keely *et al*. 1990, Keely in press). Pigments are, therefore, particularly valuable markers of past photoautotrophic communities extending from the present into the geological timeframe (see, for example Hurley & Watras 1991, Keely & Maxwell 1993, Keely *et al*. 1995, Leavitt & Hodgson 2001, Squier *et al*. 2002, Walker *et al*. 2002, Airs & Keely 2003).

Pigment distributions in marine and lacustrine sediments can be exploited to identify the types of organisms and the environmental conditions that existed in the past (see e.g.

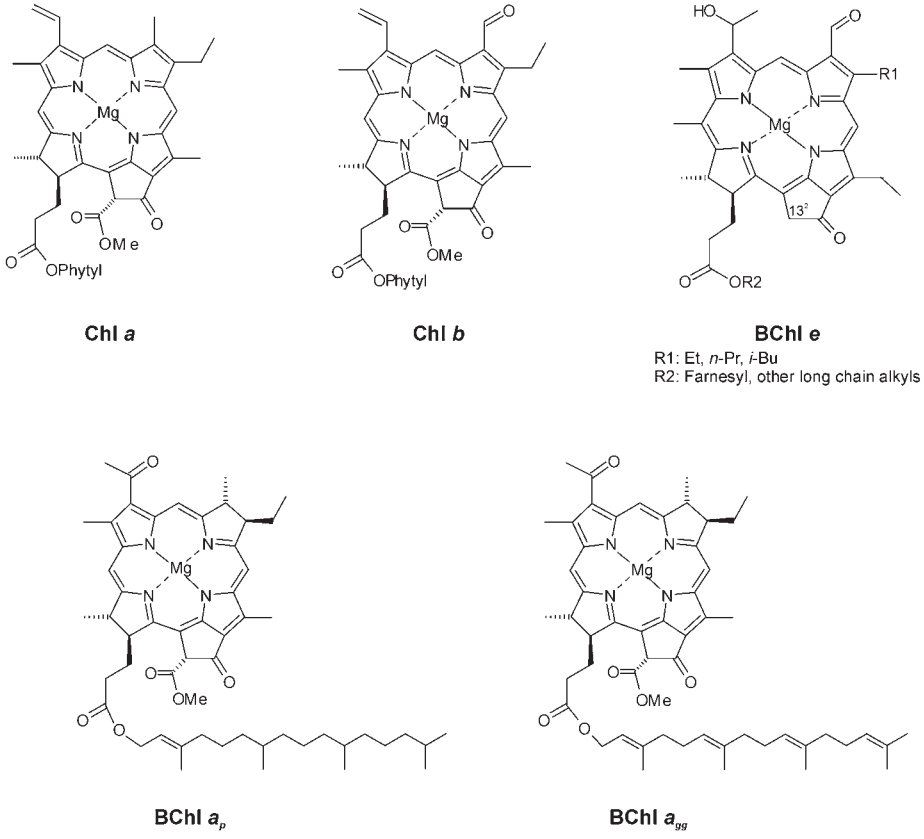

Fig. 1. Structures of the chlorophyll (Chl) and bacteriochlorophyll (BChl) pigments from which all of the tetrapyrrole transformation products identified in Progress Lake are derived.

Squier *et al*. 2002, Airs & Keely 2003). Some pigments are specific to particular groups of photoautotrophs (Jeffrey *et al*. 1997, Pfennig 1978) and can be used as chemotaxonomic markers, providing valuable insight into the historical composition of the photoautotrophic community that produced them. In certain situations, environmental conditions can be inferred directly from the presence of particular pigments. For example, sedimentary BChls (Repeta *et al*. 1989, Hodgson *et al*. 1998, Squier *et al*. 2002) and porphyrins derived from them (Keely & Maxwell 1993, Keely *et al*. 1995), and the bacterial carotenoid isorenieratene and its aromatic hydrocarbon counterpart isorenieratane (Repeta 1993, Sinninghe Damsté *et al*. 1993), have been used to identify periods of (at least partial) water column anoxia and to infer variations in chemocline depth in a number of palaeo-waterbodies. Because of their requirement of sulphide during photosynthesis, the presence of green bacteria also attests to euxinic conditions within the photic zone. Other pigments, for example Chl *a* (Fig. 1), occur more widely and their value lies in the record that they provide of photoautotroph abundance (Hurley & Watras 1991, Harris *et al*. 1996, Tani *et al*. 2002) and the dominant transformation processes operating at the time of deposition (Villanueva *et al*. 1994a, Louda *et al*. 2000).

Chlorophylls are susceptible to a variety of transformation reactions (Fig. 2) which follow two principal routes. Cleavage of the tetrapyrrole macrocycle results in compounds that lack a chromophore and hence are not detected as pigments (Carpenter *et al*. 1986, Grice *et al*. 1996). By contrast, progressive defunctionalization progresses through various phaeophytin (Phe) and phaeophorbide (Pheid) intermediates (Fig. 2), leading ultimately to sedimentary porphyrins (Keely *et al*. 1990). Numerous attempts have been made to identify the specific sources of particular Chl transformation products with a view to increasing their value as biomarkers and incorporating them into palaeoenvironmental proxies. For example, Pheids formed by demetallation and dephytylation at C-17[3] (see Fig. 2 for numbering), occur in the faecal pellets of copepods (Daley 1973, Shuman & Lorenzen 1975) and the digestive tracts of macrozooplankton (King & Wakeham 1996), mussels (Hawkins *et al.* 1986) and a short-necked clam (Watanabe *et al*. 1993) and are regarded as markers of heterotrophic grazing of photoautotrophs. They are, however, also formed during algal senescence (Head *et al*. 1994, Louda *et al*. 1998). Indeed, it has been shown that Pheid *a* and its metallated counterpart, chlorophyllide *a*, are formed in the senescent cells of algae, in particular diatoms, that possess high levels of the enzyme chlorophyllase (Jeffrey & Hallegraeff 1987). Similarly, the formation of pyro-derivatives, by decarbomethoxylation at C-13[2] (Fig. 2), has been reported to occur both as a consequence of ingestion by herbivores (Head & Harris

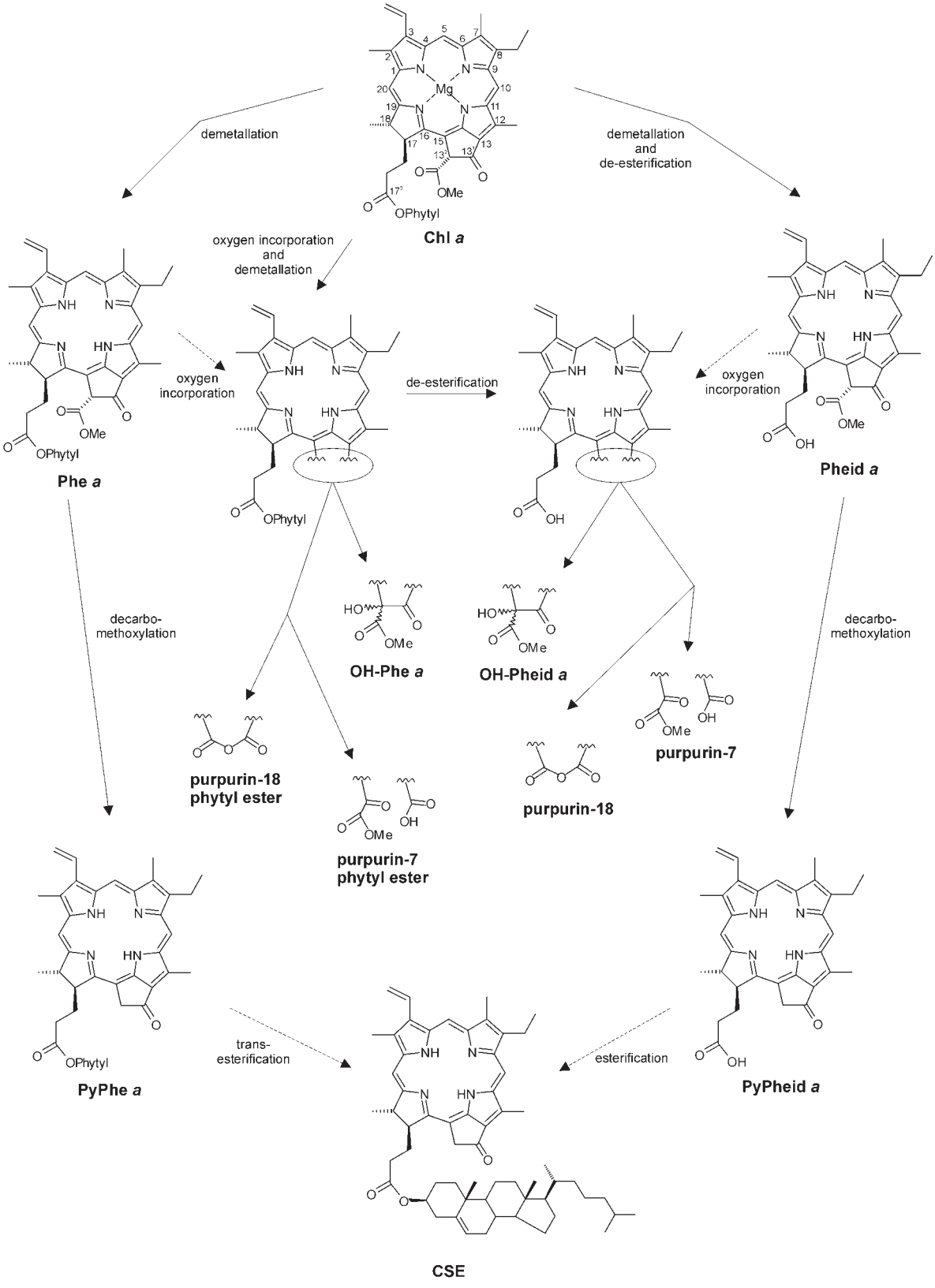

Fig. 2. Schematic representation relating the Phe, PyPhe, Pheid, PyPheid CSE and HO-Chl derivatives to Chl *a*. The diagram is illustrative rather than comprehensive and additional transformation routes to those shown are possible. Solid lines indicate transformations that are known to occur, broken lines indicate possible alternative routes to selected products. Detailed descriptions of chlorophyll transformation can be found in the specialist literature (e.g. Keely in press and references therein).

1992, Otsuki *et al*. 1993) and in algal cultures deprived of light (Schoch *et al*. 1981, Louda *et al*. 1998). Clearly, therefore, interpretations based on the presence of these compounds must consider all possible sources and, where possible, make reference to other palaeoecological proxies.

The Chl *a* oxidation products purpurin-7 phytyl ester and purpurin-18 phytyl ester and their dephytylated (i.e. Pheid) counterparts (Fig. 2) have been identified in a number of sedimentary environments (Naylor 1997, Naylor & Keely 1998, Ocampo & Repeta 1999, Airs *et al*. 2000) including Lake Baikal, Russia and Loch Ness, UK, both of which have deep, fully oxygenated water columns. The Chl *a*-derived allomer, 13^2-hydroxyphaeophytin *a* (OH-Phe *a*; Fig. 2) was found to co-occur with the purpurins described above. A study of the pigment distributions in Kirisjes Pond, Larsemann Hills, Antarctica, revealed an inverse correlation between the incidence of water column anoxia and the abundances of OH-Phe *a* and its dephytylated counterpart, 13^2-hydroxyphaeophorbide (OH-Pheid *a*; Fig. 2). From this observation, a relationship between the extent of Chl oxidation and pigment residence time in an oxygenated water column was inferred (Walker *et al*. 2002). The 13^2-hydroxy allomers of Chl *a* have also been observed during algal aging experiments (Louda *et al*. 1998) and in copepod faecal pellets produced during feeding experiments (Talbot *et al*. 2000) and during overturn of a marine algal bloom (Walker & Keely 2004), indicating the susceptibility of chlorophylls to oxidative transformation in the presence of molecular oxygen, an essential reactant in the oxidation mechanism. The occurrence of Chl *a* oxidation products provides evidence that, even when subjected to oxidising conditions, the tetrapyrrole macrocycle and hence the Chl signature can be preserved in the sediment record.

The presence of chlorin steryl esters (CSEs; Fig. 2), secondary transformation products of chlorophylls, in lake sediments can also be indicative of past environmental conditions (see, for example, Eckardt *et al*. 1992). Although the detail of their mechanism of formation is not known, it is clear that CSEs are products either of the esterification of Pheids or pyrophaeophorbides (PyPheids), or of transesterification of Phes or pyrophaeophytins (PyPhes) by stanols or sterols. To date, however, the only model studies in which CSEs have been observed are grazing experiments, where they were identified in faecal pellets (Harradine *et al*. 1996, Pearce *et al*. 1998, Talbot *et al*. 1999a, 1999b, 2000). Consequently, these compounds are widely regarded as specific markers of grazing activity. Grazing and aging studies aimed at characterizing the transformation of Chl are, for the sake of clarity, typically carried out using restricted systems involving single organisms. While this is attractive in order to minimize the number of experimental variables, it constrains the extent to which the results obtained can be extrapolated to natural settings where community structures are more complex. Clearly, the complexities of the processes that operate during Chl transformation present difficulties in the interpretation of natural pigment distributions. Despite these imposed limitations, a number of palaeoecological studies have demonstrated the great value of pigment analysis in revealing the nature of, and changes in, environmental conditions (e.g. Squier *et al*. 2002, Walker *et al*. 2002, Airs & Keely 2003), especially when interpreted using present-day reference data (e.g. Hodgson *et al*. 2004b). Such studies require rigorous identification and the ability to profile pigments and their transformation products in sediment sequences. The excellent preservation of pigments in sediments from Antarctic lakes makes them ideal environments to recover records for the Holocene and for glacial interglacial timescales up to at least 120 000 yr BP (Hodgson *et al*. 2005, in press).

Lakes in the Larsemann Hills region of East Antarctica are of particular interest for palaeoenvironmental reconstruction because the sediments in several of them

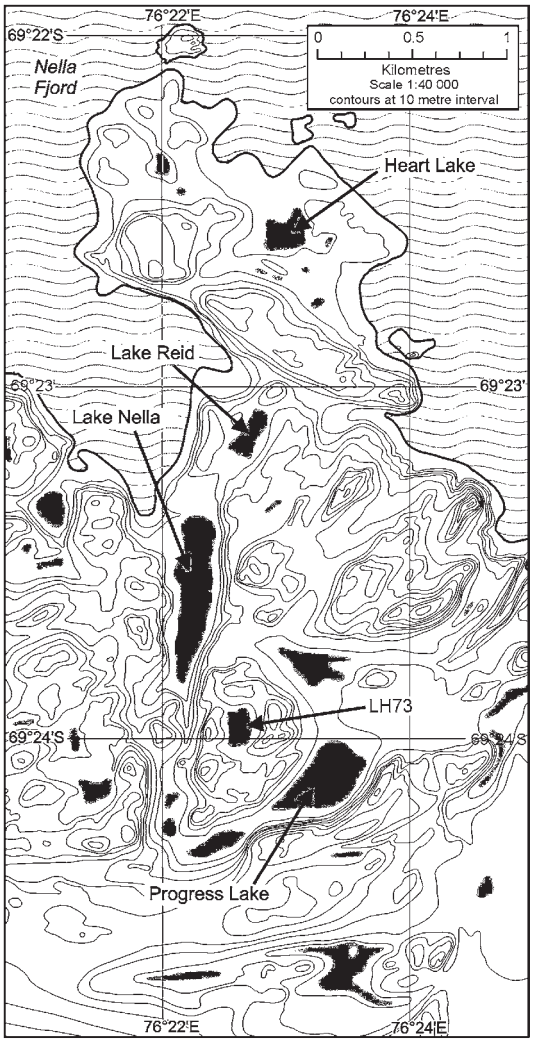

Fig. 3. Map of eastern Broknes, Larsemann Hills, Antarctica showing the location of Progress Lake.

preserve records from before the Last Glacial Maximum (LGM) and thus constitute some of the oldest continuous lacustrine sediment records in East Antarctica (Hodgson *et al*. 2001). The survival of these sediments is due to the region, at least in part, having remained ice-free throughout the LGM. The chronostratigraphy of a sediment core from Progress Lake (Hodgson *et al*. in press) suggests that the first sediments were deposited during the last interglacial, most likely Marine Isotope Stage 5e (MIS 5e). Sedimentological and geochronological evidence suggests that the lake was covered by a layer of *in situ* firnified snow and ice throughout the following glacial period, preserving the underlying sediment and causing a marked decline in the sedimentation rate. The sedimentation rate increased as deglaciation commenced, and ^{14}C dating shows that the upper layers of sediment are of late Holocene age (Marine Isotope Stage 1; MIS 1). The survival of the MIS 5e sediment record is unusual and the whole core spans an entire glacial cycle. A multi-proxy study of geochronological, sedimentological, biological and biogeochemical properties of the sediment core from Progress Lake showed systematic variations in the profiles of diatoms and the main pigments that correspond with the lithological units visible in the core (Hodgson *et al*. in press). Here, we present a detailed examination of the pigment distributions of selected samples from the Progress

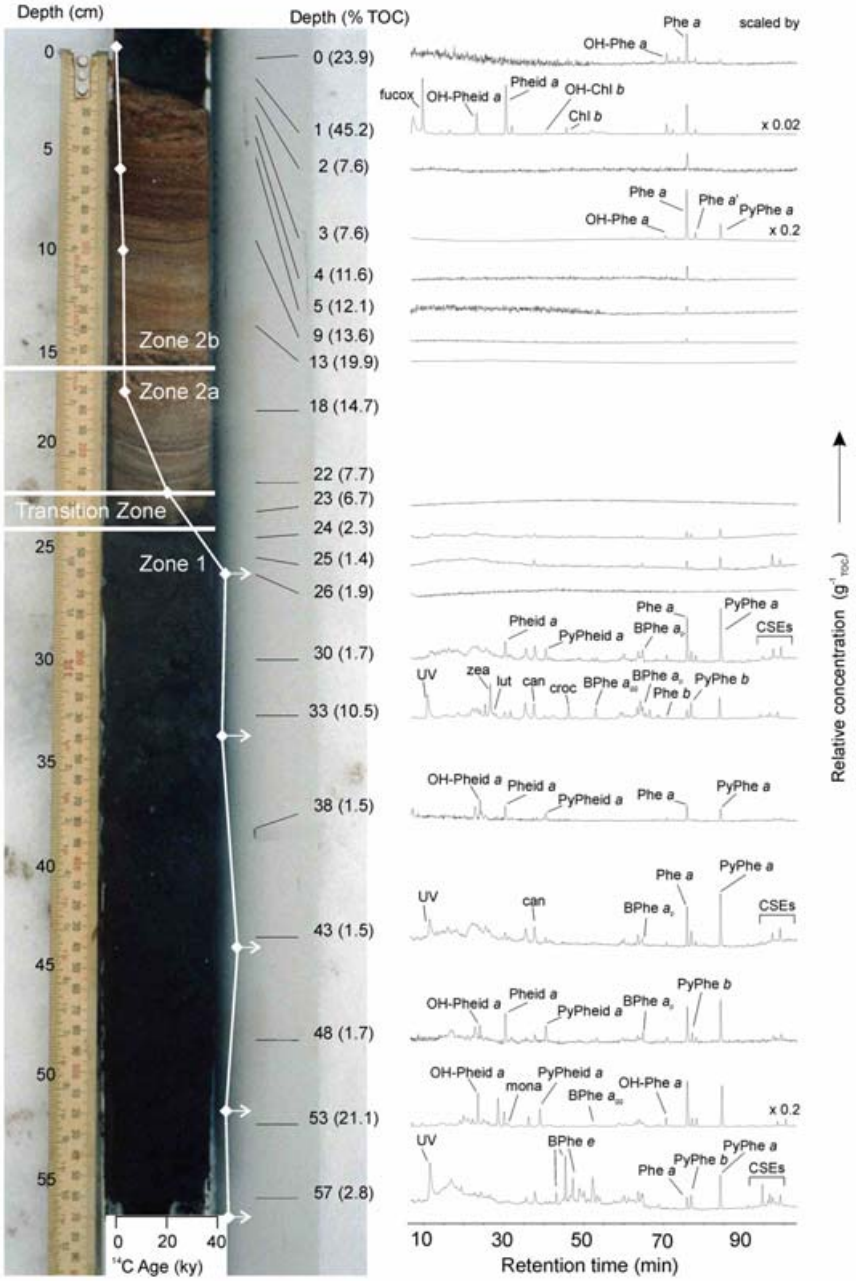

Fig. 4. Photograph of the Progress Lake sediment core indicating the sedimentological zones and HPLC chromatograms showing the pigment distributions in selected horizons. Chromatograms at 18 and 22 cm depth did not contain pigments and are not shown. Relative concentrations of pigments in individual horizons can be inferred from the scaling of the chromatograms. The radiocarbon chronology (reported elsewhere; Hodgson *et al*. 2001, in press) is superimposed on the photograph. Radiocarbon dates with right-facing arrows represent infinite radiocarbon ages or ages near the limits of detection. Key to pigment abbreviations: can = canthaxanthin, croc = crocoxanthin, fucox = fucoxanthin, lut = lutein, mona = monadoxanthin, UV = unidentified UV-absorbing compound (see text), zea = zeaxanthin. Pheid *a* and PyPheid *a* refer to the methyl esters. Other abbreviations as in text. The purpurins are minor components and can not be observed on HPLC chromatograms printed at this scale.

Lake sediment core based on a high performance liquid chromatography (HPLC) method that resolves a much wider range of Chls and BChls and their derivatives. Use of the HPLC method together with liquid chromatography-mass spectrometry (LC-MS) allows the pigments to be identified and quantified with a much higher degree of certainty. The objectives of the study were:

i) to provide a detailed biogeochemical characterization of the past photoautotrophic communities and infer the conditions in which they lived, and

ii) to compare the community composition at different stages of the last glacial-interglacial cycle.

Experimental

Site description

The Larsemann Hills (69°23'S, 76°53'E) are located approximately midway between the eastern extremity of the Amery Ice Shelf and the southern boundary of the Vestfold Hills in Prydz Bay. The area, occupying *c*. 50 km^2 and comprising the peninsulas of Stornes and Broknes and a number of offshore islands, contains over 150 freshwater lakes (Gillieson *et al*. 1990). Parts of Broknes remained ice-free throughout the LGM whereas Stornes did not become ice-free until the mid- to late-Holocene (Hodgson *et al*. 2001). Progress Lake (69°24'S, 76°24'E), situated on eastern Broknes (Fig. 3), is the deepest lake in the region (max. depth 38 m) and covers an area of 10.5 ha, with a catchment area of 39.1 ha. At an altitude of 65 m a.s.l., the lake is above the maximum relative sea level for the region (Verleyen *et al*. 2004) and there is no evidence for past shorelines at the site.

Field sampling

A 57 cm sediment core (Fig. 4) was recovered from a water depth of 34 m during the summer of 1997–98 with the logistical support of the Australian Antarctic Division. The core was divided into 1 cm sections in the field, sealed in sterile 'Whirlpak' bags and stored at -40ºC for transport to the UK.

Pigment extraction

Thawed samples were extracted by sonication in acetone. Following centrifugation (5 min at 2000 g) the supernatant was filtered through a pre-extracted cotton wool plug. The extraction procedure was repeated until the supernatant was colourless and the combined extracts were reduced to dryness *in vacuo* with further addition of acetone to remove residual water by azeotrope. Extracts were treated with an ethereal solution of diazomethane to methylate free acids (cf. Airs *et al*. 2001). Exposure of samples to light was minimised throughout the extraction procedure and dried extracts were stored in the dark at 4ºC.

HPLC and LC-MS/MS

High performance liquid chromatography (HPLC) was performed using two Waters Spherisorb 3µ ODS2 columns (4.6 x 150 mm) coupled in series. The 115 minute gradient elution using methanol, acetonitrile, ethyl acetate and 0.01M aqueous ammonium acetate and a flow rate of 0.7 mL min^{-1} is reported in detail elsewhere (Method A, Airs *et al*. 2001). Pigment concentrations were estimated using calibration lines for Phe *a* ($\varepsilon = 4.45 \times 10^4$ l mol^{-1} cm^{-1}), Phe *b* ($\varepsilon = 2.81 \times 10^4$ l mol^{-1} cm^{-1}; Jeffrey *et al*. 1997), and bacteriophaeophytins *a* (BPhe *a*; $\varepsilon = 4.46 \times 10^4$ l mol^{-1} cm^{-1}; Oleze 1985) and assuming equal molar absorbtivity for components having the same UV/vis spectra. Atmospheric pressure chemical ionization liquid chromatography-mass spectrometry/mass spectrometry (APCI LC-MS/MS) was performed as described previously (Airs & Keely 2000, Airs *et al*. 2001).

Results and discussion

Core description, lithology and geochronology

The detailed lithology and geochronology of the core has been described previously (Hodgson *et al*. in press). Briefly, the core was dominated by the remains of mats of filamentous cyanobacteria and appeared as two distinct zones separated by a transition zone. In the lower unit (Zone 1, 23/24–57 cm), decayed green/brown consolidated cyanobacterial mat remains occurred together with a coarse sediment fraction and some sandy layers that increased in proportion towards the basal sediments (53–57 cm). Mean organic carbon content was 3.9% and mean carbonate (inorganic) carbon 0.6%. Between 44 and 53 cm there were occasional moss layers and a minor layer of grit occurred at 29 cm. This zone was overlain by a transition zone (24–22 cm). In the upper unit (Zone 2; 22–0 cm) the gross morphological structure of the cyanobacterial mat was intact, with fine brown or orange laminated mats occurring from *c.* 22 cm to the top of the core. These laminae are believed to represent seasonal growth of the benthic microbial mat. The sediment surface, comprising a brown/orange mat layer, was underlain by an intensely green coloured layer. Beginning with weakly coloured laminae, interspersed with thin (< 1 mm) dark bands, the intensity of colour increased progressively towards the top of the core. The sediment was less compressed than Zone 1, with distinct sub-millimetre sandy layers at 22–23 cm and occasional sand layers elsewhere in the sequence. Mean organic carbon content was 14.7% and mean carbonate (inorganic) carbon 2%.

Table I. Radiocarbon (AMS ^{14}C) chronology of Progress Lake.

Laboratory No	Depth (cm)	Sample material*	^{14}C Enrichment (% Modern ± 1σ)	^{14}C Enrichment (% Modern absolute ± 1σ)#	Conventional radiocarbon age (yr BP ± 1σ)†	Carbon content # (% by wt.)	$\delta^{13}C_{PDB}$‰ ± 0.1	Calibrated age (cal yr BP)	Relative area under probability function
AA-35721	0	C	113.33 ± 0.53	112.66 ± 0.53	modern	21.0	-9.6	Modern	
AA-35754	6	C	80.54± 0.43		1740 ± 40	1.1	-17.7	1536–1737	0.990
								1760–1771	0.010
CAMS-64374	10	C	68.82 ± 0.25		3000 ± 30	0.5	-16.2	3077–3093	0.070
								3097–3131	0.119
								3136–3267	0.729
								3289–3321	0.082
AA-35755	17	C	65.93 ± 0.38		3345 ± 45	1.9	-18.8	3470–3643	0.917
								3656–3687	0.083
AA-41165	22–24	C	7.39 ± 0.14		20 920 ± 150	1.2	-26.0	24644–25571	1
AA-35756	26	C S	0.46 ± 0.11		43 200 ± 1900	0.3	-25.8		
AA-35757	34	C S	< 0.55		> 41 800	0.5	-26.0		
AA-35758	44	C M S	0.26 ± 0.11		47 800 ± 3300	0.8	-26.0		
AA-35759	52	C M S	< 0.45		> 43 400	2.3	-27.2		
CAMS-50384	56–58	C M S	n/a		> 44 400	1	-29.0		

† Results reported as > conventional radiocarbon age were indistinguishable from background at 2 σ, results are quoted at 2 σ lower limits.
# Absolute % Modern involves a mathematical adjustment to account for ongoing radioactive decay of the international reference standard (oxalic acid) since AD 1950 (Stuiver & Braziunas 1998).
* Sample material abbreviations: C = filamentous cyanobacteria, M = moss fragments, S = silt and sand.

The geochronology has been established using a combination of radiometric (^{137}Cs), radiocarbon (^{14}C) and thermoluminescence dating (Hodgson *et al*. 2001, in press). Radiometric measurements identified a ^{137}Cs activity peak of 103 Bq kg^{-1} at 4.5 cm depth that is presumed to record the 1964–65 fallout maximum from the atmospheric testing of nuclear weapons. The mean post-1964 surface sedimentation rate in the uppermost uncompressed

Table II. Analytical data for the major pigments identified in Progress Lake

Identification	t_R (min)	λ_{max} (nm)	$[M+H]^+$	Affinity / Interpretation
Chlorophyll *a* derivatives				all oxygenic photoautotrophs
OH-Pheid *a* methyl ester	24	410, 665	623	oxidising conditions
Pheid *a* methyl ester	29	410, 665	607	
PyPheid *a* methyl ester	40	410, 665	549	
OH-Phe *a*	71	410, 665	887	oxidising conditions
Purpurin-7 dimethyl phytyl ester	73	399, 676	917	oxidizing conditions in water column
Phe *a*	75	410, 665	871	
Phe *a* 13^2-epimer	77	410, 665	871	
Purpurin-18 phytyl ester	82	358, 407, 696	843	oxidizing conditions in water column
PyPhe *a*	84	410, 665	813	
CSE	94–100	406, 665	> 900	grazers of photoautotrophs
Chlorophyll *b* derivatives				Chlorophyta (mosses)
Phe *b*	70	436, 650	885	
PyPhe *b*	76	436, 650	827	
Bacteriochlorophyll *a* derivatives				purple photosynthetic bacteria (Chromatiaceae, Rhodospirillaceae)
BPhe a_{gg}	54	358, 747	883	*Rhodospirillum rubrum* (low oxygen tension, low sulfide conc.)
BPhe a_P	65	358, 747	889	purple photosynthetic bacteria (low oxygen tension)
Bacteriochlorophyll *e* derivatives				
Homologues of BPhe *e*	44–53	442, 661	799; 813; 827	brown species of green sulfur bacteria (Chlorobiaceae), water column anoxia
Carotenoids				
Fucoxanthin	11	449	641 $[M+H-H_2O]^+$, 581 $[M+H-H_2O-HCO_2Me]^+$	(diatoms) Bacillariophyta
Zeaxanthin	27	451, 480		Cyanophyta, chlorophyta
Lutein	28	419, 446, 474	551 $[M+H-H_2O]^+$	Chlorophyta
Monadoxanthin	32	417, 447, 475	567 $[M+H-H_2O]^+$	Cryptophytes
Canthaxanthin	38	476	565	Oxygenic photoautotrophs
Crocoxanthin	47	448, 475	551 $[M+H-H_2O]^+$	Cryptophytes
UV-absorbing compound	12	386		UV radiation screening

sediments was calculated to be 0.015 g cm^{-2} yr^{-1} (0.14 cm yr^{-1}). Radiocarbon (AMS ^{14}C) measurements show that the surface sediments are in near-equilibrium with modern $^{14}CO_2$, (absolute age 112.66 ± 0.53%; Table I), suggesting that a ^{14}C reservoir correction is not required (Hodgson *et al*. 2001). The ^{14}C measurements from the core yielded a conformable sequence of dates up to *c.* 43 200 ^{14}C yr BP, after which measurements were beyond detection limits, with the exception of one ^{14}C date at 44 cm (Table I, Fig. 4). Except where specifically stated, radiocarbon dates in the text are not calibrated. To establish a chronology for the lower unit of the core (Zone 1), thermoluminesence dating was applied to samples at 40–41 cm and 50–51 cm and returned approximate ages of 48–72 kyr BP and > 100 kyr BP, respectively.

Pigment identification and sources

Reversed-phase HPLC analysis of the acetone extracts of the twenty one stratigraphic horizons selected revealed marked variations in pigment abundance and composition throughout the Progress Lake sediment core and an absence of pigments in some sections (Fig. 4). Pigments and their transformation products were identified from their HPLC retention times (t_R), on-line UV/vis spectra, *m/z* value of the protonated molecule [M+H$^+$] and MS^n spectra (Table II; cf. Airs *et al*. 2001, Squier *et al*. 2002).

The pigment distributions are typically dominated by the Chl transformation products Phe *a* and PyPhe *a* (Figs 3 & 4). Two small peaks eluting immediately after Phe *a* were identified as PyPhe *b* and Phe *a* 13^2-epimer and small amounts (< 4% of total Chls) of Phe *b* were observed at 33, 53 and 57 cm depth (Fig. 4). Seven of the twenty one extracts contained Pheid *a* methyl ester and six of those also contained PyPheid *a* methyl ester (Fig. 4). Components that occur naturally as carboxylic acids are observed as the corresponding methyl esters following methylation with diazomethane, which is performed to enhance their preservation during sample storage and to improve chromatographic performance (Airs *et al*. 2001). The occurrence of components derived from Chls *a* and *b* (Figs 1 & 2) indicates the presence of oxygenic photoautotrophs at the time of sedimentation. Chl *b* derivatives are attributed to the presence of green algae (Chlorophyta) and, in selected horizons that are discussed below, a possible contribution from mosses has been considered. Late eluting compounds with UV/vis spectra characteristic of free-base Chl *a* derivatives and having protonated molecules in excess of 900 Da (Fig. 4, Table III) were identified as CSEs, widely regarded as markers for grazers operating on the photoautotrophic community. An indication of the nature of the sterols associated with the chlorin macrocycle was obtained by tandem mass spectrometry (MS/MS). In tandem MS the whole sterol moiety is lost as a neutral molecule and the charge-retaining chlorin macrocycle is observed in MS^2 as an ion at *m/z* 535 (cf. Harris *et al*. 1995, Airs *et al*. 2001). Thus, it was possible to identify SCEs in which eight different sterols were associated with the PyPheid *a* macrocycle (Table III). The formation of CSEs has been shown to include sterols from both the grazed organisms and the grazer (Harradine *et al*. 1996, Talbot *et al*. 1999a). The distributions of esterifying sterols were dominated by a $C_{27:1}$ and a $C_{29:1}$ sterol, the latter being consistent with an origin from lacustrine algae. Although some lacustrine algae do produce C_{27} sterols, sterols with twenty seven carbon atoms are associated mainly with marine organisms (see, for example, Volkman 2003). Furthermore, extensive incorporation of the animal sterol, cholest-5-en-3β-ol into CSEs has been reported in grazing experiments (Pearce *et al*. 1998). Accordingly, the $C_{27:1}$ sterol present in the CSEs in Progress Lake is most likely cholest-5-en-3β-ol originating from the

Table III. Sterols associated with PyPheid *a* in CSEs

CSE [M+H]$^+$	Esterifying sterol	Origin
887*	$C_{26:2}$	
901*	$C_{27:2}$	
915*	$C_{28:2}$	
915*	$C_{28:2}$	
929*	$C_{29:2}$	
903	$C_{27:1}$	grazing organisms
929*	$C_{29:2}$	
931	$C_{29:1}$	lacustrine algae

*denotes CSEs identified only at 57 cm depth

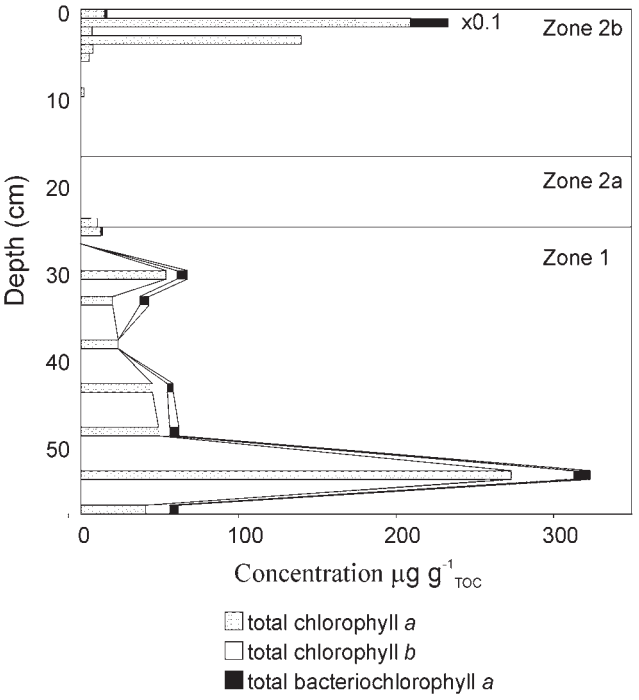

Fig. 5. Depth profiles showing the concentrations of components derived from Chls *a* and *b* and BChl *a* in the Progress Lake sediment core.

grazing organism. In the absence of rigorous structural characterization of the sterol components of the CSEs, and given the lack of species specificity of numerous sterols (Volkman 1986, 2003), it has not been possible to attribute sources to the sterols with any greater specificity.

Several samples in Zone 1 contained OH-Pheid *a* methyl ester and OH-Phe *a* (Fig. 4), assigned from their HPLC retention times, on-line UV/vis, MS and MS/MS spectra (Table II; cf. Airs *et al*. 2001, Squier *et al*. 2002). Further evidence of Chl oxidation, attributed to the existence of oxidising conditions in the water column at the time of deposition, is provided by minor amounts of purpurin-18 phytyl ester at 3 and 53 cm depth and purpurin-7 dimethyl phytyl ester at 3 cm depth. Although Chl *b* is susceptible to the same transformation reactions as Chl *a* (Daley 1973, Louda *et al*. 1998, Talbot *et al*. 1999b), it is notable that Phe *b* and PyPhe *b* were the only Chl *b* derivatives observed in Progress Lake. The failure to observe other components derived from Chl *b* might be accounted for by the lower overall Chl *b* concentrations, or might reflect differences in the degradative pathways experienced by different members of the primary producer community, for example, selective grazing on particular members of the community.

Bacteriophaeophytin (BPhe) *a* was identified (Table II) and found to be present throughout most of Zone 1 of the core (Fig. 4), accounting for between 2 and 13% of the total chlorin signal (Fig. 5). Although its precursor, BChl *a* (Fig. 1), occurs both in purple photosynthetic bacteria (Chromatiaceae or Rhodospirillaceae) and as an accessory pigment in green sulfur bacteria (Chlorobiaceae), previous studies have only found it to occur in significant abundance in sediments where purple bacteria are present (Borrego *et al*. 1993, Villanueva *et al*. 1994b, Vila *et al*. 1998). Accordingly, the occurrence of BPhe *a* in Progress Lake is interpreted as an indicator of the presence of purple photosynthetic bacteria. The identification of BPhe *a* in which the C-17[3] esterifying alcohol is geranylgeraniol (BPhe a_{gg}), as opposed to the more usual alcohol phytol (BPhe a_{p}), is described in detail elsewhere (Squier *et al*. 2004a). To date, the BChl from which this component is derived (BChl a_{gg} Fig. 1) has only been reported in the purple non-sulfur bacterium *Rhodospirillum rubrum* (Table II). Although BChl *a* is also susceptible to transformation (see, for example, Villanueva *et al*. 1994b, Ocampo & Repeta 2002, Wilson *et al*. 2004) its occurrence in oxygen depleted conditions provides an environment highly favourable to its preservation (Villanueva *et al*. 1994b). Thus, the limited extent of transformation of BChl *a* might indicate that the BChl *a*-producing community was not subjected to the same degradative pressures, for example grazing, as other members if the primary producer community (cf. Buffan-Dubau *et al*. 1996). Homologues of BPhe *e* in the sediments at 33 and 57 cm depth (Fig. 4, Table II) indicate the occurrence of brown species of green sulfur bacteria and thereby indicate

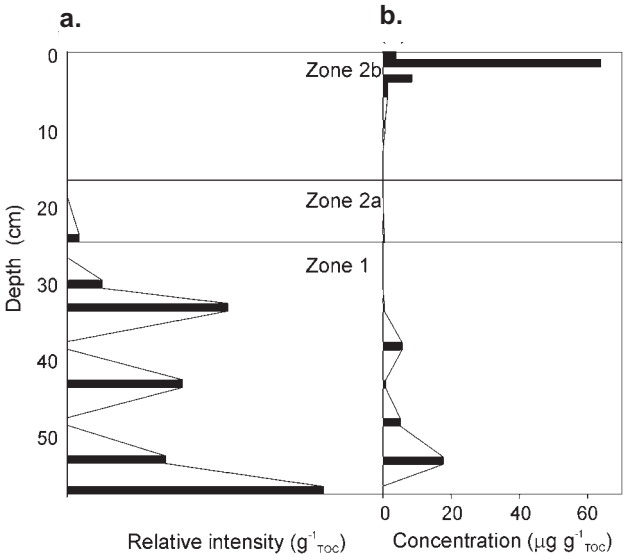

Fig. 6. Abundance depth profiles of **a.** an unidentified UV-absorbing compound, and **b.** 13[2]-hydroxychlorophyll derivatives in Progress Lake sediment.

euxinic conditions within the photic zone of the water-column. The absence of a wide range of BChl *e* (Fig. 1) derivatives, even at 57 cm depth where the abundance of BPhe *e* is greater than that of Chl *a* derivatives, is attributed both to environmental and structural factors. Firstly, absence of oxygen, a requirement for the growth of Chlorobiaceae, provides a depositional environment that favours pigment preservation. Secondly, absence of a carboxymethyl group at C-13[2] in BChl *e* (Fig. 1) precludes two transformations that occur for Chl *a* derivatives, namely decarbomethoxylation and oxidation centred on C-13[2].

An early eluting compound (UV in Fig. 4) exhibits chromatographic and UV/vis spectral characteristics (Table II) that are similar to those of the pigment scytonemin, a photoprotective pigment produced by certain species of cyanophyta as a defence against UV-induced cellular damage (Garcia-Pichel & Castenholz 1991, Proteau *et al*. 1993). Cyanophyta containing scytonemin occur in the shallower lakes in this region and in the margins of some of the deeper lakes (Ellis-Evans *et al*. 1998, Hodgson 2004b). Notably, however, this component did not produce the expected $[M+H]^+$ under APCI LC-MS conditions. The absence of an ion at *m/z* 545, readily observed for scytonemin by APCI LC-MS (Squier *et al*. 2004b), suggests that the component is not scytonemin. Further identification has not been possible to date. It is noteworthy, however, that the unidentified UV-absorbing compound is present in horizons where the levels of hydroxy-derivatives are low and absent where the hydroxy-derivatives are present in high relative abundance (Fig. 6). Exposure to elevated levels of UV radiation can result in the formation of oxygen-centred radicals, leading to increased levels of

cellular damage and formation of peroxygens. Such conditions would be expected to lead to higher proportions of Chl oxidation products, as indicated by their formation in model studies (Walker *et al*. 2002). Thus, although the structure of the UV-absorbing compound is unknown, it is possible that it performs a similar function to the UV-photoprotective function performed by scytonemin (Garcia-Pichel & Castenholz 1991, Dillon *et al*. 2002), as has been proposed for several other UV-absorbing compounds of unknown structure (Leavitt *et al*. 1997, Llewellyn & Mantoura 1997). This being the case, occurrence of the UV-absorbing compound would suggest adaptation of community composition or structure in response to elevated UV-levels. The variation in the abundance of 13^2-OH-Chl derivatives may indicate a varying capacity of the primary producer community to cope with the UV-induced stress over time (Fig. 6).

Carotenoids were observed, particularly within Zone 1, and were tentatively identified as zeaxanthin, lutein, canthaxanthin and crocoxanthin. Monadoxanthin was tentatively identified at 53 cm depth. Canthaxanthin was also observed in low abundances at depths of 24, 43, 48 and 57 cm. Zeaxanthin and lutein are major carotenoids in chlorophyta and the former is also abundant in cyanophyta. Canthaxanthin is widespread, albeit as a minor component, among oxygenic photoautotrophs and crocoxanthin and monadoxanthin occur as minor components in cryptophytes (Young & Britton 1993). An abundant early eluting component in the extract from 1 cm depth was tentatively identified as fucoxanthin, a major carotenoid in diatoms (Jeffrey *et al*. 1997). The carotenoids ββ-carotene, βγ-carotene, diatoxanthin and diadinoxanthin were also tentatively identified, on the basis of their UV/vis spectra, in the earlier study of 58 levels of this core (Hodgson *et al*. in press).

Pigment stratigraphy

Based on geochronological, sedimentological and biostratigraphic indicators, the sediment core has previously been divided into two main stratigraphic zones separated by a transition zone (Fig. 4; Hodgson *et al*. in press). The pigment distributions in the 21 samples analysed here support the demarcation, each zone recording markedly different conditions in the lake.

Zone 1: MIS 5e Interglacial (*c.* 57–24 cm, *c.*125–115 ky BP) The oldest unit of the core is characterized by relatively high, but varied, pigment concentrations. In general, pigments derived from Chl *a* dominate the distributions with lesser, but appreciable, contributions from Chl *b*- and BChl *a*-derived components (Fig. 5). Cyanophyta do not produce accessory chlorophyll pigments. Thus, the pigment composition suggests a photoautotrophic community comprising cyanophyta (Chl *a*, cyanobacterial carotenoids)

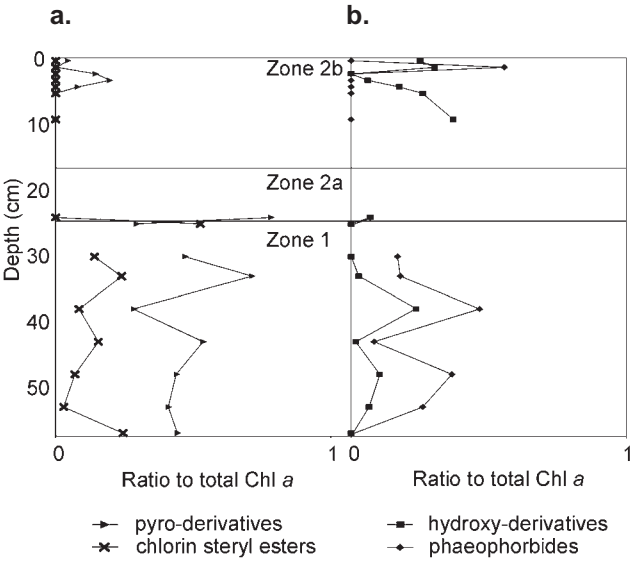

Fig. 7. Depth profiles of **a.** pyro-derivatives and CSEs, and **b.** 13^2-hydroxy-derivatives and Pheids relative to the total Chl *a* signal in the Progress Lake sediment.

and/or chlorophyta (Chls *a* and *b*) together with purple photosynthetic bacteria (BChl *a*). Although moss fragments were identified in the sediment between 44 and 53 cm depths, their presence is not accompanied by an increase in Chl *b*:*a* ratio as might be expected if they made an appreciable contribution to the pigment signal. Thus, it is likely that the moss pigments were degraded to colourless compounds during senescence and death, as is usual for the pigments of terrestrial plants (Hendry *et al.* 1987). BChl *a* derivatives record the presence of purple sulfur (Chromatiaceae) and/or non-sulfur (Rhodospirillaceae) photosynthetic bacteria and, hence, dysoxic conditions within the photic zone of the lake (Fig. 5). Such conditions can occur through thermal or chemical stratification of the water body (Pfennig 1978, Vila *et al*. 1998) or within benthic microbial mat systems. In the latter case, oxygen depletion beneath the uppermost zone of the mat, typically dominated by cyanophyta, can provide a suitable habitat for Chromatiaceae and/or Rhodospirillaceae (Stal 2001, Airs & Keely 2003).

CSEs were identified in all of the horizons analysed in this zone (Fig. 7) and their presence is interpreted as an indication of grazing of the photoautotrophic community at the time of deposition. The CSE sterol distributions are dominated by a $C_{27:1}$ sterol and a $C_{29:1}$ sterol which, as was discussed earlier, are probably derived from the grazing animal and lacustrine algae, respectively. It is noteworthy that grazers are relatively rare in the contemporary lake (Ellis-Evans *et al*. 1998) and relatively few remains of rotifers and tardigrades have been reported in palaeolimnological studies of the upper sediments (L. Cromer personal communication 2005). Thus, the presence of biomarkers of grazing activity attests to a marked change

in the community composition and lake during the last interglacial, when this sediment was deposited, and the present interglacial.

The horizons at 57, 53 and 33 cm depth show the presence of particular marker compounds, differentiating their pigment compositions from the other horizons within this zone. At 57 cm BPhe *e* homologues are present as significant components, indicating a substantial contribution to the sedimentary record from brown species of Chlorobiaceae. Their presence indicates at least some periods of euxinia within the photic zone of the lake. In particular, the presence of brown strains suggests deep water and/or an environment in which light-limitation was severe (Pfennig 1978, Montesinos & Esteve 1984, Borrego *et al*. 1993, Vila & Abella 1994). The distribution of CSE sterols is more complex at 57 cm, with higher relative abundances and a wider range of sterols. These include a major contribution from a $C_{28:2}$ sterol that was not observed elsewhere in the core, together with several structural isomers (see Table III). Although the distributions of sterols preserved within CSEs are considered to provide more accurate representations of the original sterol distribution than do the free sedimentary sterols (King & Repeta 1991, Pearce *et al*. 1998, Talbot *et al*. 1999a), some distributional differences can occur. Discrimination against incorporation of 4-methyl sterols into CSEs is suggested to arise from steric hindrance resulting from the presence of the 4-Me group (cf. Talbot *et al*. 2000). Furthermore, the dietary requirements of grazing organisms can result in the selective assimilation of sterols, for example the utilization by copepods of the diatom sterol, cholesta-5,24-dien-3β-ol for conversion to cholest-5-en-3β-ol (Talbot *et al*. 1999a). Nevertheless, it is likely that the observed complexity in the CSE composition at 57 cm depth reflects a greater diversity of the phytoplankton during the time represented by this horizon. Furthermore, the high abundance of CSEs at this depth relative to other horizons suggests a proportionally larger or more active grazing population was present at that time.

The total pigment abundance at 53 cm depth is much higher than in other horizons in Zone I and the distribution is dominated by Chl *a* derivatives (Fig. 4). Derivatives of Chl *b* and BPhe a_p were also present in appreciable amounts (Figs 4 & 5). Interestingly, BPhe a_{gg} was identified as a minor component, suggesting the presence of *Rhodospirillum rubrum*. Chromatiaceae inhabit environments where reduced sulfur species are available for use as electron donors for photosynthesis. By contrast, Rhodospirillaceae have a limited capacity to metabolise sulfur compounds and colonise habitats that combine low oxygen tension and low sulfide concentration. As photoorganotrophs, they inhabit environments in which there is appreciable recycling of organic matter (Pfennig 1978). Thus, the presence of a marker specific to Rhodospirillaceae suggests that heterotrophic recycling of organic matter was a significant process at this time. The high pigment concentrations that occur, in spite of such recycling, record a period of high photoautotrophic productivity during the time represented by this horizon. Such a situation probably arose either as a result of elevated input of nutrients or through efficient recycling of material present in the lake. In the absence of other markers, for example carotenoids specific to either family, it is not currently possible to attribute the BPhe a_p in this horizon to either Chromatiaceae or Rhodospirillaceae. Thus, two possible scenarios exist for the structure of the dysoxic region of the photic zone at this time: low sulfide concentrations supporting a Rhodospirillaceae community, or a stratified system where regions of both low and moderate sulfide concentrations supported separate communities of Rhodospirillaceae and Chromatiaceae, respectively.

Bphe *e* homologues and BPhes a_p and a_{gg} were identified at 33 cm depth together with Chl *a* and *b* derivatives (Fig. 4). This pigment assemblage suggests a complex stratified ecosystem with an oxygen gradient ranging from fully oxygenated to fully anoxic conditions and, within the oxygen depleted zone, further division into regions of high and low sulfide concentration. Alternatively, the range of photoautotrophs indicated to be present might reflect rapid (possibly seasonal) changes in the conditions during the time represented by this horizon.

The presence of brown species of Chlorobiaceae (homologues of BPhe *e*) is of particular interest. While the green species of Chlorobiaceae (containing BChls *c* and *d*) are reported to occur both in planktonic and benthic (microbial mat-dwelling) environments, literature reports of brown species are restricted to planktonic species (Abella *et al*. 1980, Vila & Abella 1994, Borrego *et al*. 1997, 1998, 1999, Vila *et al*. 1998, Stal 2001). Consequently, the presence of BPhe *e* homologues (Fig. 4, Table II) is interpreted to indicate the presence of a planktonic anaerobic photoautotrophic population. The water column anoxia necessary to support such an anaerobic population would be likely to prevent the growth of benthic microbial mats at depths below the chemocline. Another distinguishing feature of the BPhe *e*-containing horizons is the high proportion of Chl *b*-derived components relative to Chl *a* derivatives. This shift in proportion reflects a change in the oxygenic primary producer community towards a higher abundance of Chl *b*-producing organisms (Fig. 5). The horizons in question are both outside the zone in which moss fragments were present. Accordingly, and given the comparatively low Chl *b*:*a* ratios even where moss fragments were present, it is likely that the increased Chl *b*:*a* ratio at these depths reflects a greater contribution of chlorophyta relative to cyanophyta. Thus, the occurrence of BPhe *e* homologues and the coincident increase in the signal from chlorophyta marks a shift in the primary producer community composition, probably comprising

planktonic populations both of aerobic and anaerobic photoautotrophs. Primary production in the contemporary lake is dominated by benthic organisms without a significant contribution from plankton (Ellis-Evans *et al*. 1998, Sabbe *et al.* 2004). Thus, the presence of a dominant planktonic community in the palaeo-lake would represent a marked change in the lake ecology between the time of sediment deposition (MIS 5e) and the present (MIS 1). The development of water column anoxia is usually associated either with deep water, where the bottom layer is not susceptible to wind-induced mixing, or with eutrophication arising from fertilisation. In the case of Progress Lake a further possibility is that periods (multi-year) of ice-cover prevented uptake of oxygen from the atmosphere, leading to its depletion in the water column.

The relative contributions of Pheids, CSEs, pyro- and 13^2-hydroxy-derivatives to the total Chl *a*-derived signal reveal changes in the relative importance of the various transformation pathways of Chl *a* over the time period represented by Zone 1 (Fig. 7). As discussed above (see Introduction), the large number of variables that govern their formation limits the ecological significance that can be attributed to the presence of several of these transformation products. Nevertheless, some valuable inferences can be drawn. Assuming that the CSEs reflect a grazing community in the lake, changes in their abundance relative to the total Chl signal most likely reflect variations in the abundance of CSE-forming grazers. In horizons where CSEs are less abundant, Pheids are more prominent (Fig. 7). Given that Pheids can be formed both by heterotrophic ingestion and during senescence, their high relative abundance might reflect either the presence of a grazing community that effects hydrolysis to Pheids in preference to CSE formation, or high levels of chlorophyllase associated with senescent algae. It is noteworthy that 13^2-hydroxy-derivatives are present in their highest relative abundances in the same horizons as the Pheids (Fig. 7b) and make a smaller contribution to the total Chl pool where CSEs are most abundant. While these oxidation products have been observed to form during senescence and digestion, their formation has also been associated with prolonged residence times in oxygenated water columns (Naylor 1997, Walker *et al*. 2002, Walker & Keely 2004). The sinking of zooplankton faecal pellets provides a mechanism for the rapid sedimentation of detritus, efficiently removing pigments or transformation products from the water column. Furthermore, the dense nature of the faecal material provides an element of shielding and, hence, some protection from oxidation (Nelson 1993). By contrast, dead and senescent cells have a much longer residence time in the oxygenated waters, either in the water column or at the sediment surface, and have no such protection from oxidative transformation. Consequently, if the major process affecting the photoautotrophs is senescence, the significance of Chl oxidation is likely to be greater than when consumption by grazers is dominant. In summary, the diverse and changing pigment compositions within this zone provide evidence of a number of different limnological environments in the lake during the previous interglacial, including the development of periods of anoxia, grazing and phytoplankton activity and the presence of diverse communities of primary producers.

Transition Zone (24–22 cm, *c.* 115 k–20 920 yr BP)

The upper part of Zone 1 is characterized by weak or absent signals from pigments and between 24–22 cm there is a distinct transition zone in the core. Chronostratigraphic studies suggest that a layer of *in situ* firnified snow and ice covered the lake ice during part of this time, similar to snow-covered lakes on the nearby Stornes today (Hodgson *et al*. 2001, in press). The thickness of the firnified snow/ice and lake ice is not known, but the survival of laminae in the sediments suggests that the lower part of the water column remained unfrozen. Prolonged snow and ice cover persisting through the last glaciation would result in considerable suppression of primary productivity, thereby accounting for the limited pigment signal and sediment accumulation in this zone. Visual inspection of this section of the core (Fig. 4) reveals very thin (*c.* 1 mm) dark bands interspersed with weakly coloured inorganic bands, possibly representing alternating periods of photoautotrophy occurring under the ice and very small pulses of inorganic material entering the lake, for example as a result of periods of glacier melt or interstadials. These allochthonous contributions, which are supported by the presence of aerophilic diatom taxa (Hodgson *et al*. in press), and occasional sandy layers would dilute the organic matter content of the sediment and may account for the weak pigment signals observed. The pigment profiles before and after the transition zone boundary (at 24 and 25 cm depth) exhibit substantial differences: CSEs are prominent at 25 cm yet absent at 24 cm depth, while at 24 cm there is an appreciable amount of PyPhe *b*, which is not observed at 25 cm depth. The lack of continuity in the community composition between these adjacent horizons (i.e. disappearance of grazers and appearance of signatures of chlorophyta) supports the interpretation that these sediments represent discrete periods of biological activity separated by unproductive periods that were associated with small pulses of fine-grained inorganic material into the lake.

Zones 2a and 2b. Late Glacial, Termination 1 (22–16 cm, 20 920–*c.* 3345 ^{14}C yr BP) and MIS 1 (16–0 cm, *c.* 3345 ^{14}C yr BP to present)

Zone 2a (calibrated 2σ age range 24 644–25 571 to 3470–3643 yr BP), representing the late glacial and Termination 1, is characterized by a very low pigment content. The increase in pigment content in Zone 2b (calibrated 2σ age range 3470–3643 y BP to present) is believed to be linked to the late-Holocene retreat of the firnified snow and ice and the

resumption of biological activity. The pigment composition in Zones 2a and 2b is much less complex than that observed in Zone I. Except for the horizon at 1 cm depth, only Phe *a*, and its 13^2-hydroxy- and pyro-derivatives were present. The 1 cm-depth horizon, distinct from the other horizons within this section because of its strong green colour (cf. brown/orange at the surface), has a much higher pigment concentration and a more complex distribution including Chl *b*, indicative of chlorophyta, and substantial contributions from Pheid *a* methyl ester, OH-Pheid *a* methyl ester and fucoxanthin, together with carotenoids that occur in some cyanobacteria. The predominance of Chl *a*-derived components and absence of derivatives of accessory Chl pigments is consistent with a microbial mat-forming community dominated by cyanophyta. Similar distributions, with high levels of Pheid *a*, have been observed in contemporary microbial mats (Villanueva *et al*. 1994a, Hodgson *et al.* 2004b) and, in a former study, co-occurring fucoxanthin was attributed to an input from diatoms. Interestingly, the high levels of Pheid in that environment were suggested to result from enzymatic hydrolysis of Chl from various algal sources, induced by diatom-derived chlorophyllase (Villanueva *et al*. 1994a). Louda *et al*. (1998) attributed the accumulation of Pheid *a* during the earliest stages of algal degradation, and subsequent decrease relative to Phe *a*, to a greater resistance of Phe *a* to further transformation to yield colourless products. Furthermore, it is known that fucoxanthin, due to it containing a 5,6-epoxide group, is particularly susceptible to transformation in sediments (Repeta 1989). Thus, the high abundances of Pheid *a* methyl ester, OH-Pheid *a* methyl ester and fucoxanthin in the horizon at 1 cm suggests that it represents recent growth and is at the earliest stages of degradation. Although Chl *b* derivatives were only detected at 1 cm depth, the differences in pigment concentrations throughout the zone (Figs 4 & 5), and consideration of detection limits, mean that contributions from chlorophyta at other depths cannot be ruled out.

Application of the high-chromatographic-resolution HPLC method and LC-MS/MS to the study of these Antarctic Lake sediments has significantly improved the identification and quantification of pigments, particularly the Chls and BChls, compared with the previous study (Hodgson *et al*. in press), increasing the amount of information available to reconstruct the palaeolimnology of Progress Lake. In general, this study shows an increase in species and habitat diversity in this region of east Antarctica during the last (MIS 5e) interglacial, consistent with the warmer than present conditions shown in climate models (Weaver & Hughes 1994) and Antarctic continental ice cores (Jouzel *et al*. 1993). Conversely, lower pigment diversity and content in Zone 2 suggests cooler conditions during the present (MIS 1) interglacial.

Climate models now predict rapid increases in temperature over the next decades (estimated rises of between 1.3 and 6.3°C by 2100; Houghton 2001). Based on this study, it is possible to predict continued increases in lacustrine species diversity and productivity in polar regions where such temperature increases are being experienced (see Quayle *et al*. 2002, Smol *et al*. 2005). By examining the photoautotrophic communities of a previous, and warmer, interglacial, this study provides evidence of the substantial extent of species changes and structural reorganisation of photoautotrophic and grazing communities that might be might expected in the coming decades.

Conclusions

Detailed HPLC and LC-MS^n analysis of the pigment distributions in selected sediment samples from Progress Lake, Larsemann Hills has permitted the identification of biomarkers for both oxygenic and anoxygenic primary production. Changes in the composition and abundances of pigments reveal changes in the lake ecology and species composition spanning the last glacial-interglacial cycle. The combined approach of HPLC and LC-MS/MS has provided a wealth of data for palaeoenvironmental assessment. The approach should provide a basis for pigment studies in palaeolimnology in the future and is applicable to a wide range of high latitude lakes in both polar regions. The lower zone of the core represents an interglacial period (likely to be MIS 5e) followed by a period of 'sub'-glacial conditions. The upper zone represents the late glacial and Termination 1, and the present MIS 1 Holocene interglacial. The changing distributions of a number of Chl transformation products and carotenoids in the two interglacial units of the core reflect marked differences in the ecology of the lake between MIS 5e and MIS 1. The high diversity of pigments and their transformation products in MIS 5e reflect a diverse photoautotrophic community with active grazing together with periods of stratification and euxinia, consistent with the warmer conditions experienced in continental Antarctica during MIS 5e. By contrast, the lower diversity and concentrations of pigment transformation products in the MIS 1 sediment provides evidence of more restricted biological sources, reflecting a less diverse photoautotrophic community. These detailed pigment analyses provide evidence of how lacustrine species diversity, productivity and ecosystem structure might change in the coming decades in areas of the polar regions experiencing rapid increases in temperature.

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