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The last forests on Antarctica: Reconstructing flora and temperature from the Neogene Sirius Group, Transantarctic Mountains

Rhian L. Rees-Owen [a,b,*], Fiona L. Gill [a], Robert J. Newton [a], Ruza F. Ivanović [a], Jane E. Francis [c], James B. Riding [d], Christopher H. Vane [d], Raquel A. Lopes dos Santos [d]

[a] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[b] School of Earth and Environmental Sciences, University of St Andrews, St Andrews KY16 9AL, UK
[c] British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK
[d] British Geological Survey, Environmental Science Centre, Keyworth, Nottingham NG12 5GG, UK

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ABSTRACT

Fossil-bearing deposits in the Transantarctic Mountains, Antarctica indicate that, despite the cold nature of the continent's climate, a tundra ecosystem grew during periods of ice sheet retreat in the mid to late Neogene (17–2.5 Ma), 480 km from the South Pole. To date, palaeotemperature reconstruction has been based only on biological ranges, thereby calling for a geochemical approach to understanding continental climate and environment. There is contradictory evidence in the fossil record as to whether this flora was mixed angiosperm-conifer vegetation, or whether by this point conifers had disappeared from the continent. In order to address these questions, we have analysed, for the first time in sediments of this age, plant and bacterial biomarkers in terrestrial sediments from the Transantarctic Mountains to reconstruct past temperature and vegetation during a period of East Antarctic Ice Sheet retreat. From tetraether lipids (MBT′/CBT palaeothermometer), we conclude that the mean continental summer temperature was ca. 5 °C, in agreement with previous reconstructions. This was warm enough to have allowed woody vegetation to survive and reproduce even during the austral winter. Biomarkers from vascular plants indicate a low diversity and spatially variable flora consisting of higher plants, moss and algal mats growing in microenvironments in a glacial outwash system. Abietane-type compounds were abundant in some samples, indicating that conifers, most likely Podocarpaceae, grew on the Antarctic continent well into the Neogene. This is supported by the palynological record, but not the macrofossil record for the continent, and has implications for the evolution of vegetation on Antarctica.

1. Introduction

Since the first appearance of angiosperms on Antarctica in the Cretaceous more than 100 million years ago (Ma), Antarctic vegetation has undergone a significant secular change from a diverse fern-conifer dominated ecosystem, to a podocarp-southern beech temperate rainforest during the Late Cretaceous, to a low diversity tundra flora dominated by angiosperms in the Neogene (Dettmann and Thomson, 1987; Francis et al., 2008; Bowman et al., 2014). The trend correlates broadly with long term cooling seen from the mid-Eocene and the expansion of the Antarctic Ice Sheet (Zachos et al., 2008).

Generally, the mid- to late-Neogene Period (17–2.5 Ma) was characterised by an atmospheric CO_2 level similar to or lower than present, and warmer and fluctuating temperature values relative to today (Beerling and Royer, 2011). The interval is of particular interest in Antarctic science because of the complexity of both cryosphere and biosphere dynamics in the region (e.g. Lewis et al., 2008; Cook et al., 2013; Pollard et al., 2015). The scarcity of Neogene terrestrial deposits on Antarctica makes reconstructing vegetation difficult. However, it appears that an extensive, low diversity mosaic tundra vegetation existed over a wide geographical range throughout the Oligocene to the mid Miocene (24–14 Ma; Hill, 1989; Raine, 1998; Askin and Raine, 2000; Prebble et al., 2006) and survived multiple episodes of glacial advance and retreat (Ashworth et al., 2007). Questions remain over both the timing of the disappearance of this tundra vegetation and its composition. In the McMurdo Dry Valleys at least, woody vegetation appears to have been rendered extinct by the expansion of

* Corresponding author at: School of Earth and Environment Sciences, University of St Andrews, St Andrews, KY16 9AL, UK.
E-mail address: rlro@st-andrews.ac.uk (R.L. Rees-Owen).

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the East Antarctic Ice Sheet around 13.8 Ma (Lewis et al., 2007, 2008). However, palynological data from Deep Sea Drilling Project (DSDP) Site 274 in the Ross Sea suggests that southern beech trees (*Nothofagus*) were present into the Pliocene (5–2.5 Ma; Fleming and Barron, 1996). The macrofossil record indicates that Antarctic flora was dominated by *Nothofagus* at that time. Nevertheless, some pollen records suggest that conifers existed on Antarctica until at least until ca. 15 Ma (Warny et al., 2009).

The Sirius Group in the Transantarctic Mountains has played a key role in the reconstruction of the Neogene flora of Antarctica. Fossil discoveries from Oliver Bluffs (Fig. 1; 85°S, 166°E; Francis and Hill, 1996; Hill et al., 1996) are some of the most important palaeobotanical discoveries on the continent in recent years. The age of these deposits has been the subject of a contentious debate (Barrett, 2013). The plant fossils have been biostratigraphically dated by close association with late Pliocene marine diatoms (Harwood, 1986; Webb et al., 1984), thought to indicate the incursion of seaways deep into the Antarctic interior. This relatively young age has been challenged by multiple studies that suggest the diatoms represent wind-blown contamination from the open ocean much further away (Burckle and Potter, 1996; Stroeven et al., 1996). Additionally, cosmogenic exposure dating suggests these sediments are much older (at least 5 Ma, but possibly as old as 17 Ma; Ackert and Kurz, 2004); further details of this ongoing debate are given by Barrett (2013). Nevertheless, it is clear that the deposits represent a period of late Neogene Antarctic deglaciation, where the East Antarctic Ice Sheet had retreated far enough to allow tundra shrubs to grow 480 km from the South Pole. Not only do these sediments provide rare data on the evolution of vegetation on the Antarctic continent during the Neogene, but also insight into the Antarctic terrestrial climate during a warmer world.

The macrofossil and palynomorph record at Oliver Bluffs represent a low diversity angiosperm flora, including exceptionally preserved leaves and wood of *Nothofagus* (Carlquist, 1987; Webb and Harwood, 1987; Hill and Trustwell, 1993; Francis and Hill, 1996; Hill et al., 1996) as well as flowers, fruit, seeds and the remains of vascular plants with a cushion habit (Ashworth and Cantrill, 2004). Furthermore, at least five species of moss have been identified (Hill et al., 1996; Ashworth and Cantrill, 2004). There is no macrofossil record of coniferous plants at Oliver Bluffs, but rare bisaccate pollen grains suggest their presence, perhaps as *Podocarpidites* (Askin and Markgraf, 1986; Askin and Raine, 2000). The question of whether there were conifers in the interior of Antarctica has not been unequivocally answered. Resolving the issue would greatly enhance our understanding of Antarctic floral evolution.

Biomarkers from plants provide valuable information on terrestrial environments and climate. Those from vascular higher plants can reconstruct past floras and depositional environments. Some, such as aliphatic lipids (e.g. *n*-alkanes, *n*-alkanols) are non-specific, whereas others, particularly of the terpenoid family, provide valuable chemotaxonomic information (e.g. Otto and Wilde, 2001). For example, tricyclic diterpenoids (e.g. abietanes) are characteristically produced by conifers, whilst non-steroidal pentacyclic triterpenoids (e.g. oleanane-type compounds) are specific to angiosperms (Otto and Simoneit, 2001; Otto et al., 2005). Using a biomarker approach to understand vegetation gives additional insight into past floral change, because preservation biases in the macro- and microfossil record differ from those in the biomarker record (Diefendorf et al., 2014).

The fossil discoveries at Oliver Bluffs are thought to represent warm interglacials that allowed the flora to be briefly re-established from coastal refugia (Askin and Markgraf, 1986). Temperature values for these warm periods have been reconstructed from analysis of the biological limits of fossil plants, weevils and freshwater molluscs found at Oliver Bluffs, suggesting values significantly higher than the modern ones, i.e. 5 °C during the summer vs. ca. −26 °C for the present day (Francis and Hill, 1996; Ashworth and Kuschel, 2003; Ashworth and Preece, 2003). The distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs), a suite of bacterial membrane lipids, can be used to empirically reconstruct soil pH and continental temperature (using the so-called MBT′/CBT palaeothermometer; Weijers et al., 2007; Peterse et al., 2012). No geochemical thermometers have been applied to terrestrial Antarctic deposits during this interval.

This study describes the first biogeochemical study of the Sirius Group at Oliver Bluffs. The use of a geochemical thermometer adds an additional and robust dimension to our understanding of continental temperature during Southern Hemisphere deglaciations.

Fig. 1. (A) Map of Beardmore glacier region with Oliver Bluffs marked. Grey areas denote outcrops and white areas ice-covered land and the Ross Ice Shelf. (B) Geological section at Oliver Bluffs, Dominion Range. The bluff in the picture consists of thick units of glacial diamictite, representing times when glaciers were present in the region. Interbedded between the diamictites is a layer up to 0.3 m thick of siltstones, sandstones and breccias, representing an interval of glacial retreat during which immature soils developed on the land surface, intermittently covered by outwash gravels. Small dwarf shrubs of southern beech and other plants grew in the soils, now preserved as mummified fossil plants within weakly developed palaeosols.

We also analysed biomarkers from higher plants to assess their preservation and potential as vegetation and palaeoenvironmental indicators. Whilst the precise age of the deposits is not known, the results from the study should inform our understanding of Antarctic climate and vegetation in a past warmer world.

2. Material and methods

2.1. Geological setting

The samples were from the Meyer Desert Formation glacigenic deposits, which comprise the upper part of the Sirius Group in the Meyer Desert and Dominion Range region of the Transantarctic Mountains (Fig. 1; Mercer, 1972). The material was collected from Oliver Bluffs, which is today at the northern end of the Oliver Platform at 85°07′S and 166°35′E, 1760 m above sea level (masl). The site was at a similarly high latitude during deposition (Lawver and Gahagan, 2003) and would have been at a considerably lower altitude (Mercer, 1986; Webb et al., 1996).

Samples consisted of a siltstone matrix containing small fragments of mummified wood and fossil plant material. They came from one specific horizon, up to 0.3 m thick, consisting of siltstone with mixed sand and gravel lenses, and pebbles, small pieces of mummified wood representing branches and roots of small dwarf shrubs (Francis and Hill, 1996) and other mummified plant material (Ashworth and Cantrill, 2004). Glacial diamictites occur above and below this layer. The horizon represents an immature soil horizon with in situ shrubs, developed on an exposed peri-glacial landscape and buried by a subsequent glacial advance. The fossil flora was likely spatially complex (Ashworth and Cantrill, 2004), so we selected samples to give as broad a spatial coverage as possible (n = 15; see Supplementary Table 2 for sample list).

2.2. Plant lipid analysis using gas chromatography-mass spectrometry (GC–MS)

Prior to use, all glassware was solvent-cleaned and baked in a furnace (400 °C, 4 h). Wood fragments were removed from the sediment before it was dried and ground to <200 μm. Internal standards of known concentration were added (5α-androstane, octadecanoic acid, hexadecan-2-ol). An aliquot of sediment (20–25 g) was extracted using a Soxhlet apparatus for 24 h in dichloromethane (DCM)/MeOH (9:1, v/v). Sulfur was removed from the total lipid extract (TLE) by the addition of activated Cu wire (24 h). The bulk of the solvent was removed using a rotary evaporator. Half of the extract was archived; the other half was fractionated into four fractions (apolar, aromatic, aldehydes/ketones, polar) using column chromatography with activated silica gel and elution with hexane (4 ml), hexane/DCM (2:1; 2 ml), DCM (4 ml) and MeOH (5 ml) respectively (adapted from Bendle et al., 2007). The polar fraction was derivatised by adding bis(trimethyl)trifluoroacetamide (BSTFA) in pyridine and heating at 60 °C for 1 h prior to analysis. Samples were dissolved in EtOAc before analysis using GC–MS.

GC–MS was conducted at the University of Leeds (2014–2015) using a Trace 1300 gas chromatograph coupled to an ISQ mass spectrometer (Thermo Scientific, UK) and equipped with a non-polar fused silica column (CPSil-5CB, 50 m × 0.32 mm × 0.12 μm; Agilent Technologies, USA). The temperature programme was: 40–130 °C at 20 °C/min, then to 300 °C (held 25 min) at 4 °C/min. He was the carrier gas. The sample was injected splitless with the injector temperature at 300 °C. The ion source and transfer line were maintained at 300 °C. The emission current was 50 μA and the electron energy 70 eV. The analyser was set to scan m/z 50–650 with a scan cycle time of 0.6 s. Data were collected and processed using the XCalibur software. Individual compounds were assigned by interpretation of MS fragmentation patterns and comparison of spectra and retention times with literature and library data. Alkanes, alkanols and alkanoic acids were quantified relative to internal standards.

2.3. GDGT analysis using high performance liquid chromatography-mass spectrometry (LC–MS)

Freeze-dried sediment was extracted using an automated solvent extractor (Dionex 200) operated at 100 °C and 7.6×10^6 Pa with DCM: MeOH (9:1, v:v) to provide the TLE. An internal standard (a C_{46} GDGT) was added and the TLE separated into an apolar and a polar fraction in an Al_2O_3 column using n-hexane/DCM 9:1 and MeOH/DCM 1:1. The polar fraction was filtered through a polytetrafluoroethylene filter (PTFE, 0.45 μm) and analysed using a Thermo TSQ Quantiva MS instrument coupled to an Ultimate 3000 series μHPLC instrument. The chromatographic and MS conditions are described by Lopes dos Santos and Vane (2016). GDGT distributions were determined relative to the internal standard.

Weijers et al. (2007) created two indices, methylation of branched tetraethers (MBT) and cyclisation of branched tetraethers (CBT), which describe the empirical relationship between the distribution of branched tetraether lipids and surface mean annual air temperature (MAAT) and soil pH. More recently, Peterse et al. (2012) recalibrated the proxy using an expanded global soil dataset, and refined the brGDGTs used in the calibration. Here, we used the CBT index (Eq. 1 after Weijers et al., 2007) and the revised MBT′ index (Eq. 2; Peterse et al., 2012). MAAT was calculated using the calibration equation from Peterse et al. (2012; Eq. 3).

$$\mathrm{CBT} = -\log(\mathrm{Ib} + \mathrm{IIb})/(\mathrm{Ia} + \mathrm{IIa}) \quad (1)$$

$$\mathrm{MBT'} = (\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic})/(\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic} + \mathrm{IIa} + \mathrm{IIb} + \mathrm{IIc} + \mathrm{IIIa}) \quad (2)$$

$$\mathrm{MAAT} = -0.64 + 22.9 \times \mathrm{MBT'} \quad (3)$$

Roman numerals refer to GDGT structures given by Weijers et al. (2007). The average standard deviation for MBT′ and CBT, based on duplicate injections, was 0.013 and 0.051. This resulted in an analytical error in temperature estimates of ca. 0.3 °C for MAAT. The root mean squared error of the mean annual temperature was 5.7 °C, estimated using the transfer function from Peterse et al. (2012). Several factors may contribute to the relatively large scatter in the calibrations, but the uncertainty in temperature estimates is likely mainly systematic. Application of the proxy on a local scale (such as here) would result in much lower uncertainty, though an exact estimate of the error is hard to constrain (Peterse et al., 2012).

3. Results

3.1. Plant-derived lipids

All lipid fractions were dominated by plant-derived biomarkers, including a range of n-alkyl and terpenoid components; compound assignments are shown in Fig. 2.

The apolar fraction was characterised by n-alkanes between C_{14} and C_{34} with concentrations between 0.02 and 84.3 μg/g dry sediment. The odd/even preference index (OEP) ranged between 1.2 and 55.8 and the average chain length (ACL) between 25.3 and 28.1. The majority of samples had an n-alkane maximum at C_{27} (n = 11); however, the remainder (n = 4) were dominated by short chain alkanes (C_{17}).

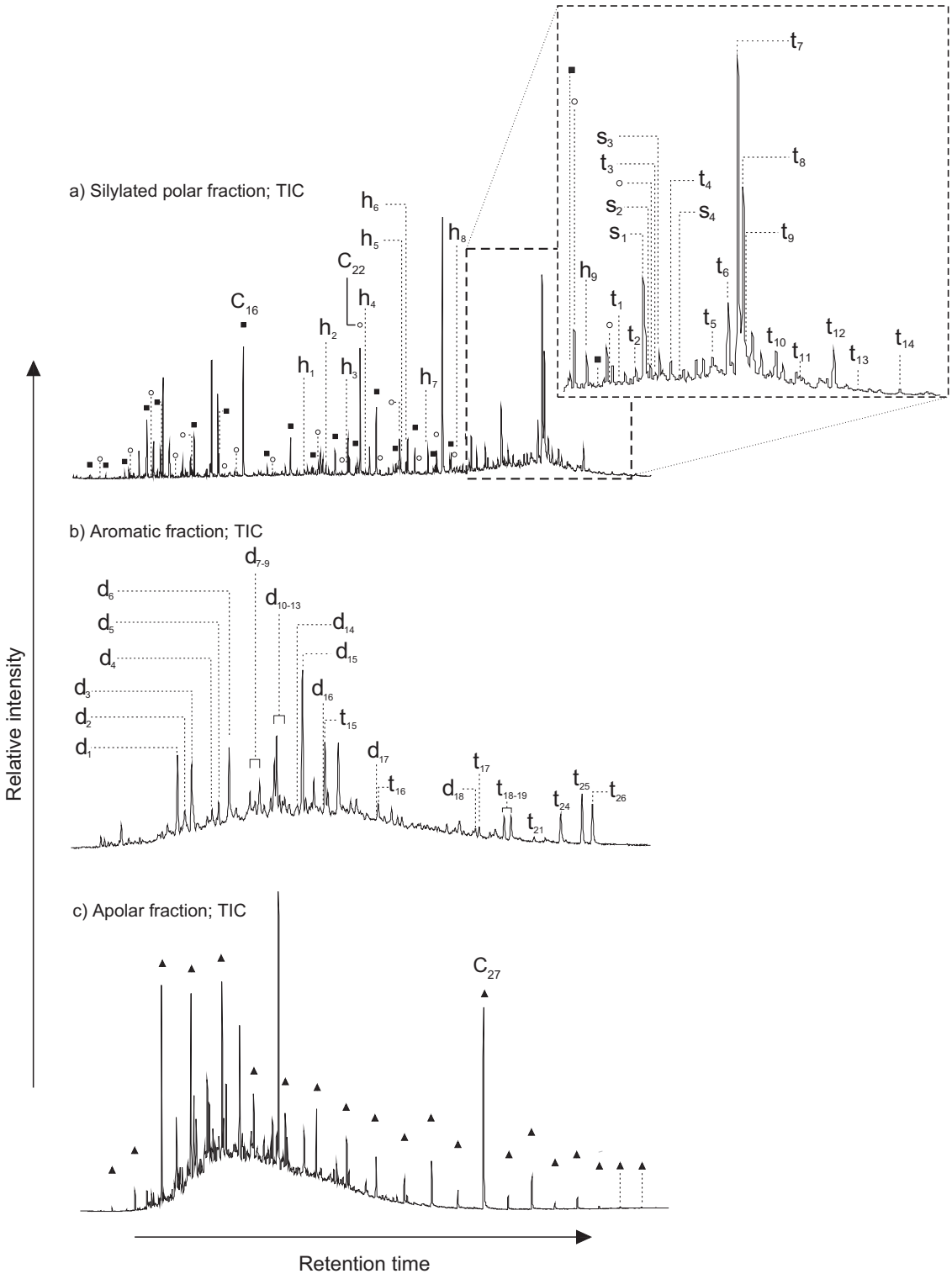

Fig. 2. Total ion current (TIC) traces of the polar (a) aromatic (b) and apolar (c) fractions from a representative sample from Oliver Bluffs, Transantarctic Mountains. In a: open circles, alkanols; filled squares, alkanoic acids; s, steroids; t, triterpenoids; h, diacids. In b: d, aromatic diterpenoids; t, aromatic triterpenoids. In c: filled triangles, alkanes. For peak assignments, see main text and Supplementary data.

The polar fraction contained *n*-alkanols and *n*-alkanoic acids, ranging from C_{10} to C_{30} and C_9 to C_{28}, respectively. The *n*-alkanols exhibited a strong even/odd predominance and the ACL ranged between 22.7 and 25.3. The dominant alkanol was C_{22} in all samples. The *n*-alkanoic acids exhibited a weaker even/odd predominance and had an average chain length from 22.9 to 25.6. The majority of samples exhibited a bimodal distribution of *n*-alkanoic acids, maximising at C_{16} and C_{22}, with C_{21} the most abundant lipid in one sample (OBFL-04-14). In addition to the fatty acid (FA) series, a series of α,ω-alkanedioic acids (C_{14}–C_{23}) and several hydroxy FAs were found in numerous samples. The polar fraction also contained numerous triterpenoid (t) and sterol (s) components

indicative of higher vascular plants, including 5β-sitosterol and campesterol (s1–4), as well as lupeol, olean-12-en-3,11-dione, β-amyrin (t1–3), uvaol? (t6), betulin (t7), α-amyrin (t10), betulinic acid and oleanolic acid (t12, t14) and several non-steroidal triterpenoids with no assigned structure.

The aromatic fraction contained a variety of aromatic diterpenoids and six di- and tri-aromatic *des*-A-triterpenoids (t18–20 and t22–24, respectively), as well as four unidentified aromatised triterpenoids (t15–17, t21). Diterpenoid (d) components of the abietane class, typical of conifers (Otto and Wilde, 2001; Yamamoto et al., 2006), were relatively abundant, particularly tetrahydroretene (d2), norsimonellite (d4), dehydroabietane (d14) and two dehydroabietins (18-norabieta-8,11,13-triene and 19-norabieta-8,11,13-triene; d8 and d10). 19-Norabieta-3,8,11,13-tetraene and 19-norabieta-4,8,11,13-tetraene were present in lower abundance (d9 and d13), as well as four trisnorabietatriene isomers (d1, d3, d5-6) and four isomers of an unidentified diterpenoid (d7, d11-12, d14).

3.2. Bacterial tetraether lipid distributions

BrGDGTs were present in all samples. The total concentration of brGDGTs per sample ranged between 0.23 and 61.5 ng/g dry sediment and averaged 7.12 ng/g. WSU-13-6 was a major outlier (outside the outer fence; 3x interquartile range added to the third quartile) with markedly higher brGDGT abundance than other samples (total 61.5 ng/g). GDGTs Ia and IIa were the most abundant (mean of 37% and 31% respectively), followed by IIIa (mean 17%), IIb (6%) and Ib (5%) (Fig. 3). BrGDGTs IIc and IIIc were below detection limit in several samples. The CBT index ranged between 0.30 and 1.21, and MBT′ between 0.16 and 0.59.

Using the revised calibration of Peterse et al. (2012; Eq. 3), reconstructed temperature ranged between 3.1 and 12.7 °C, with a mean of 5.0 ± 2.5 °C. One sample was identified as contributing to the wide range: WSU-13-6 was a major outlier (greater than the outer fence; outer fence = 3x interquartile range added to the third quartile) with a calculated temperature of 12.7 °C. This could not be attributed to analytical error so was included in our analysis.

4. Discussion

4.1. Reconstructing vegetation from plant biomarkers

4.1.1. Aliphatic lipids

The high molecular weight (HMW) aliphatic lipids were *n*-alkanes, *n*-alkanols and *n*-alkanoic acids in the range C_{22} to C_{34}, with high ACL and OEP, characteristic of epicuticular wax from higher plants (Eglinton and Hamilton, 1967). The *n*-alkanes maximised strongly at either C_{25} or C_{27}; longer chain alkanes were in lower abundance. It is difficult to ascribe unambiguous origins to HMW aliphatic distributions, because large ranges have been documented within genera and species (e.g. Stránský et al., 1967; Bush and McInerney, 2013). The aliphatic lipid record may be biased towards angiosperm representation; typically, leaf wax abundances are much higher in angiosperms than conifers (Diefendorf et al., 2011; Bush and McInerney, 2013). However, certain families and groups of conifers (such as Podocarpaceae and Araucariaceae) are known to synthesize leaf wax components in similar concentration to angiosperms (Diefendorf et al., 2015; Diefendorf and Freimuth, 2017). The *Podocarpidites* pollen recorded at Oliver Bluffs means we cannot exclude a significant Podocarpaceae contribution to the HMW aliphatic lipid distribution.

At our site, the *n*-alkane ACL index is at the lower end of the range reported for deciduous angiosperms and conifers (Diefendorf et al., 2011; Diefendorf and Freimuth, 2017), which could suggest a mixed input from other higher plants or mosses. High abundances of C_{27} have been reported in some sedges (graminoids; Ficken et al., 1998a), such as those at Oliver Bluffs, although most graminoids are typically dominated by higher MW alkanes (Bush and McInerney, 2013). Mid-chain homologues (C_{23} and C_{25}) are typically derived from *Sphagnum* moss (Baas et al., 2000; Nott et al., 2000; Pancost et al., 2002; Bush and McInerney, 2013) and freshwater macrophytes (Ficken et al., 2000). Both are a likely source for the abundant mid-chain alkanes here.

Similar to the alkane record, the dominant chain length in the alkanol and alkanoic acid series (C_{22} *n*-alkanol for all and C_{22} *n*-alkanoic for most samples) was low relative to those in modern leaf wax and the sedimentary archive, and most likely reflects

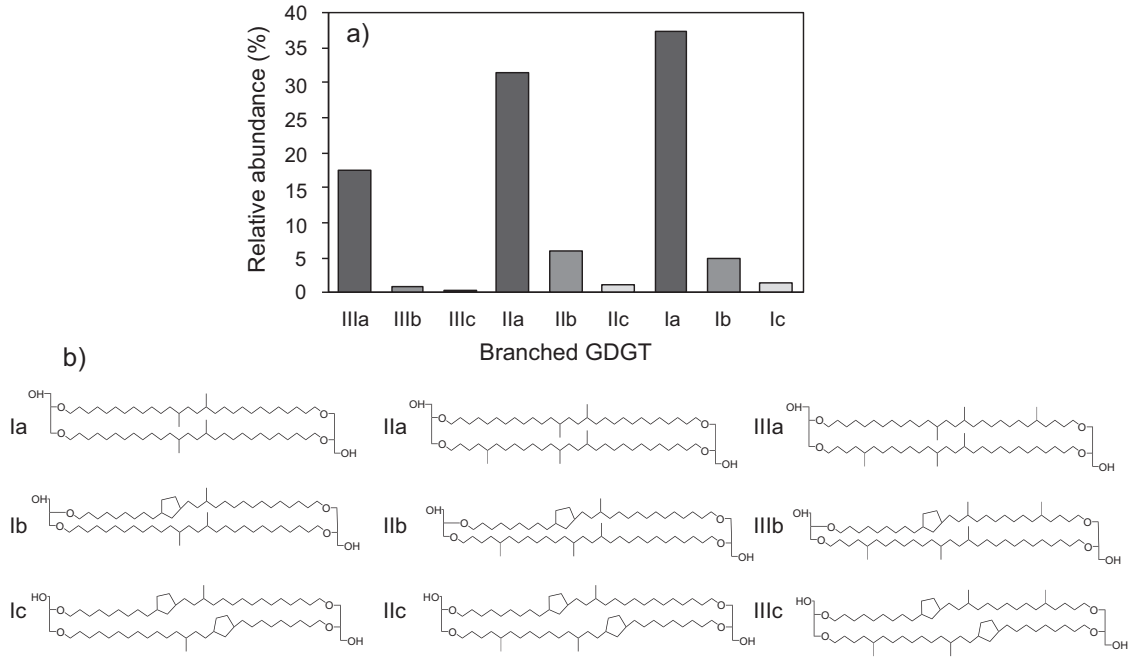

Fig. 3. (a) Average brGDGT distribution in sediment samples (n = 15); (b) structures of the branched GDGTs.

input from other plant types (Kolattukudy et al., 1976). Volkman et al. (1999) documented alkanol distributions dominated by C_{22} in freshwater microalgae, and high levels of C_{16} *n*-alkanoic acid, seen in several samples, are commonly attributed to algal sources (Cranwell, 1974; Cranwell et al., 1987). Alternatively, fairly abundant levels of mid-chain length alkanols and alkanoic acids have been recorded in both moss and moss-dominated soils, supporting a possible peat bog bryophyte source for the lipids (Ficken et al., 1998b; Nierop et al., 2006), although they are also documented in aquatic macrophytes (Ficken et al., 1998a, 2000). Fairly abundant diacids in these samples (relative to alkanoic acids) may also suggest a strong bryophyte input. These compounds may derive from the oxidation of ω-hydroxyalkanoic acids, which are significant components of some cutin acids from liverworts, as well as macromolecules in *Sphagnum* (Caldicott and Eglinton, 1976; Pancost et al., 2002).

The multiple lines of evidence suggest a mixed input of vegetation here, consisting of higher vascular plants, peat-bog forming plants and possibly some graminoids. This interpretation is consistent with the Oliver Bluffs macrofossil record, which, as well as abundant fossils from woody angiosperm shrubs and grasses, contains at least five poorly defined moss species as well as peat lenses (Ashworth and Cantrill, 2004). These are either a product of algal mats or mire deposits from poorly drained soil (Ashworth and Cantrill, 2004).

4.1.2. Terpenoids

The most abundant steroid was β-sitosterol (mainly from higher plants, but also possibly from algae; Volkman et al., 1999) and the others were in much lower abundance. Polar triterpenoids of the lupane, oleanane and ursane classes were abundant in the majority of samples, with betulin and a compound tentatively assigned as uvaol being the most abundant. Triterpenoids of these classes are characteristic of angiosperms and suggest an angiosperm input to the soils (Simoneit et al., 1986). Triterpenyl acids (tentatively assigned as betulinic acid and oleanolic acid) were in high abundance in some samples. Triterpenyl acids have been found in very high abundance in some *Sphagnum* mosses (Pancost et al., 2002); we speculate a possible moss source for them, although given their widespread distribution among angiosperm taxa, it is not possible to give a precise taxonomic assignment. Several di- and triaromatic triterpenes of the oleanane, ursane and lupane classes with A-ring (*des*-A) cleavage were present, and are also characteristic of angiosperms (Karrer, 1958; Karrer et al., 1977; Hürlimann and Cherbuliez, 1981; Simoneit et al., 1986). The presence of *des*-A-triterpenoids suggests microbially mediated formation (Trendel et al., 1989; Huang et al., 1996). The compounds found here are similar to those identified in Late Cretaceous and Paleocene (100–56 Ma) angiosperm fossils from Japan (Nakamura et al., 2010). This is consistent with the low level of oxidative degradation in our material and further supports an angiosperm input to the soil.

Diterpenoids are good chemotaxonomic biomarkers as they are major compounds in gymnosperms, and can have relatively high chemotaxonomic specificity (Simoneit et al., 1986; Otto and Wilde, 2001), although others have found with much less specificity between conifer groups (Diefendorf et al., 2015). The majority of the diterpenoids identified in the aromatic fraction were abietane-class compounds, which are widespread among conifers (Otto and Wilde, 2001). Tetrahydroretene (d2) and the dehydroabietins 18-norabieta-8,11,13-triene and 19-norabieta-8,11,13-triene (d5, d6) have been identified as points on the diagenetic pathway for the degradation of abietic acid to retene (Simoneit et al., 1986; Otto and Simoneit, 2001, 2002; Marchand-Geneste and Carpy, 2003). Additionally, dehydroabietane and the norabietatetraenes are also thought to form during the diagenesis of abietic acid (Hautevelle et al., 2006), so it seems likely these compounds originated from abietic acid. Under more reducing conditions, abietic acid can undergo transformation to norabietanes like fichtelite (Otto and Simoneit, 2001) and bacterial degradation results in diterpenoid ketones and carboxylic acids (Biellmann et al., 1973a, 1973b; Tavendale et al., 1997a, 1997b). Their absence suggests an oxidative diagenetic pathway for diterpenoids, which may or may not be biotic.

4.1.3. Depositional microenvironments

Substantial variability is noted in the distributions of the classes of aliphatic lipids between samples. In general, our samples cluster into three groups based on aliphatic lipid distributions (Fig. 4), which appear to represent several highly spatially heterogeneous distinct vegetation types, and support a complex sedimentary depositional regime consisting of microenvironments within a wide glacial outwash plain (Table 1, Fig. 4). Group 1 consists of an input dominated by higher vascular plants (high C_{27} alkane, few low MW alkanes), although high abundances of the C_{22} alkanoic acid may indicate an input from moss or microalgae (Nierop et al., 2006; Ficken et al., 1998b; Volkman et al., 1999). High abundances of triterpenoids suggests high angiosperm input, whilst low abundances of diterpenoids suggest very low input from conifer plants; these samples possibly correlate with the plant-colonized ridges of an outwash plain as described by Ashworth and Cantrill (2004). Samples in groups 2 and 3 exhibited high abundances of the C_{16} alkanoic acid, and low MW alkanes are also abundant in group 3 samples, which suggests that these samples have either a significant moss input, or an algal input (Han and Calvin, 1969; Ficken et al., 1998b; Cranwell, 1974), possibly from waterlogged locations in abandoned meltwater channels. Low abundances of diterpenoids in group 2 samples imply little coniferous input, and group 3 samples have abundant triterpenoids and diterpenoids, indicating a mixed coniferous-angiosperm input. The variability in lipid distributions suggests that the palaeovegetation grew in a mosaic pattern of mires, cryptogram-herb and tundra shrub as seen today on Arctic islands and at Tierra del Fuego, Chile, where the distribution of vegetation is a product of temperature, soil water balance and topography (Bliss and Matveyeva, 1992).

4.1.4. Coniferous input to soils

The terpenoid record provides interesting insights into Antarctic vegetation. The high abundance of unaltered triterpenoids is consistent with both the macrofossil record and palynomorph record, which indicates a vegetation dominated by angiosperms, particularly *Nothofagus*. However, conifer-derived diterpenoids are reported at Oliver Bluffs for the first time, supporting the presence of conifers on Antarctica well into the Neogene, as suggested by the pollen record. While the abietane-class diterpenoids are generally not considered to be chemotaxonomically indicative beyond distinguishing between angiosperms and conifers (Otto and Wilde, 2001), all coniferous pollen at Oliver Bluffs has been identified as Podocarpaceae (Askin and Raine, 2000), implying a possible podocarp origin for these diterpenoids.

The uncertainty in the age of the strata (likely mid- to late Miocene but possibly younger) makes it difficult to draw direct comparisons with other vegetation records. Earlier palynomorph records suggest that *Podocarpidites* species were the dominant Antarctic conifer throughout the Oligocene and early Miocene (33–14 Ma; Kemp and Barrett, 1975; Askin and Raine, 2000; Prebble et al., 2006), and abundant *Podocarpidites* pollen has been found between 17 Ma and 12 Ma in ANDRILL core AND-2A (Warny et al., 2009), supporting our interpretation. It is suggested that the *Podocarpidites* would have grown with a shrub or prostrate habit, similar to the prostrate *Nothofagus* fossils discovered at the same

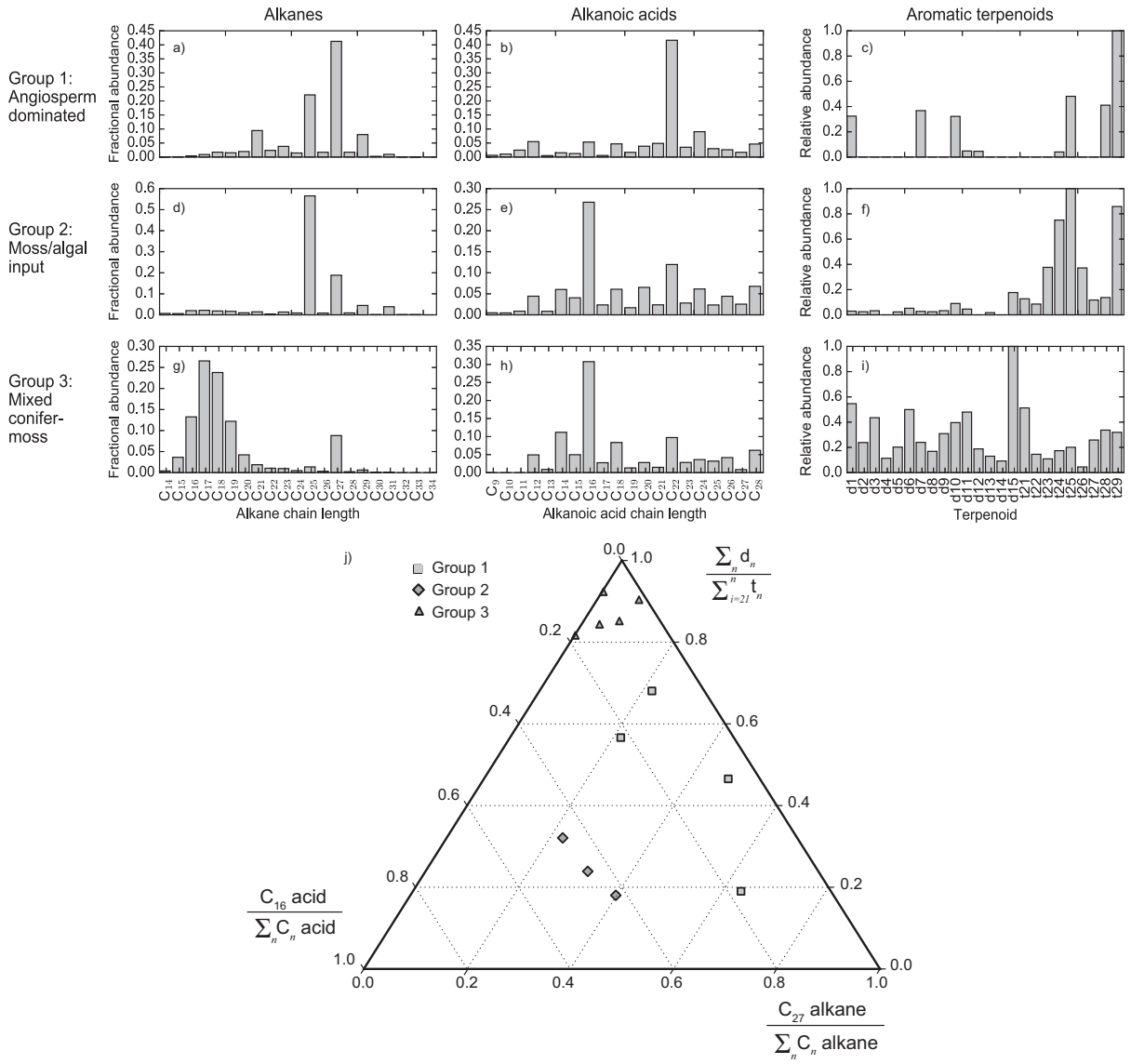

Fig. 4. Panels a–i. Distributions of lipid classes. Each row is a representative dataset for a single sample from each of the three environmental groups (group 1, sample LCBA-05-5; group 2, LCBA-05-17; group 3, OBFH-02-1). Each column represents a particular lipid group: the first gives *n*-alkane distributions, the second *n*-alkanoic acid distributions and the third aromatic terpenoids (comprising di- and triterpenoids). Thus, panel a shows the typical *n*-alkane distribution for environmental group 1. Note that *n*-alkanes and *n*-alkanoic acids are given as a fraction of the total homologous series (weighted to total organic carbon), whilst the terpenoids are calculated as abundances normalised to the largest peak in the fraction (=1). Panel j shows three selected metrics which differentiate the proposed microenvironments: C_{27} alkane/total alkanes (bottom axis), C_{16} alkanoic acid/total alkanoic acids (left axis), and aromatic diterpenoids/aromatic triterpenoids (right axis). Ratios are normalised to 1.

Table 1
Summary of mean biomarker class abundances and metrics for each proposed group. LMW and HMW alkanes, and polar triterpenoids are normalised to total organic carbon content. Aromatic triterpenoids and diterpenoids are given as abundances relative to the largest peak in the fraction (=1).

	LMW alkanes (μg/g C)	HMW alkanes (μg/g C)	Polar triterpenoids (μg/g C)	Aromatic triterpenoids	Diterpenoids	CPI	ACL
Group 1	6. 7	50.8	0.09	0.20	0.05	4.1	26.9
Group 2	4.3	45.3	0.05	0.41	0.04	5.2	26.5
Group 3	11.1	1.9	0.1	0.18	0.23	3.1	27.0

site (Francis and Hill, 1996). Whilst it is possible that the Oliver Bluffs sediments are Pliocene (2.5–5.3 Ma) in age, the sole Pliocene palynomorph record (from DSDP Site 274; Fleming and Barron, 1996), only discusses *Nothofagus* pollen.

We note an apparent discrepancy between the preservation of the macrofossil and lipid records. Many of the angiosperm-derived triterpenoids are unaltered natural products, with some evidence of diagenetic degradation, whilst we did not find any natural product precursors of the conifer-derived aromatic diterpenoids. Furthermore, only two grains of coniferous pollen and no coniferous macrofossils have been recorded at Oliver Bluffs, in contrast to the abundant *Nothofagus* macrofossil record. We suggest three possible explanations for the difference between the macrofossil and biomarker record:

(i) The presence of relatively degraded diterpenoids alongside better preserved angiosperm-derived triterpenoids is due to the reworking of older organic matter from sediments with a high input of coniferous plant material.
(ii) The diterpenoids are geologically contemporaneous with the triterpenoids, but are transported from a distal site with coniferous vegetation.
(iii) Different ecological niches for angiosperms and conifers existed within the glacial outwash plain (i.e. a mosaic of poorly- and well-drained soils; Ashworth and Cantrill, 2004), which could have had variable preservation potential relative to biomarker and macrofossil degradation.

The palynomorph record may support the first hypothesis; Askin and Markgraf (1986) suggested that some of the *Nothofagus* (angiosperm) pollen was reworked older Cenozoic palynomorphs. However, all pollen was deemed to be contemporaneous during later examinations (Ashworth and Cantrill, 2004). Furthermore, there is no indication in other biomarker classes of any reworking (very high abundances of FAs, strong OEP in the *n*-alkane record), suggesting that this hypothesis is unlikely. Therefore, it seems likely that the diterpenoids were contemporaneous, but preferentially degraded relative to triterpenoids. Preferential preservation of diterpenoids over triterpenoids has been documented in multiple geological settings, and has been attributed to either the preferential taphonomic degradation of angiosperm over coniferous plant material (Otto et al., 2005), or perhaps the preservation of diterpenoids in resins (Diefendorf et al., 2014). Abundant fossil angiosperm leaves, wood, seeds and fruit have been identified at Oliver Bluffs (Askin and Markgraf, 1986; Hill et al., 1996; Francis and Hill, 1996; Ashworth and Cantrill, 2004). We speculate that the well-preserved fossils shield triterpenoids from degradation, and are therefore likely the source of the abundant functionalised triterpenoids in our setting. Furthermore, diterpenoids are thought to undergo rapid preferential loss relative to triterpenoids in modern soil systems (Giri et al., 2015).

In contrast, no conifer macrofossils and only rare *Podocarpidites* pollen are recorded, which could be explained by either remaining hypothesis (2, 3). The lack of conifer pollen is unlikely to be due to preferential degradation. Conifers and angiosperm pollen grains appear to have similar preservation potential; they have similar wall thickness, and sporopollenin (the robust biopolymer from which spores and pollen grains are made) is relatively chemically similar across the plant kingdom (Hemsley et al., 1993; Wilmesmeier et al., 1993; Domínguez et al., 1999). Although other studies have noted abundant conifer biomarkers coinciding with a sparse pollen record (Bechtel et al., 2008; Diefendorf et al., 2014), it is difficult to understand why *Podocarpidites* pollen should be substantially less abundant than angiosperm pollen if the two coexisted at the same site, given their similarly recalcitrant nature. Hence, we would favour the explanation that a Podocarpaceae-dominated vegetation grew some distance from the Oliver Bluffs depositional site (hypothesis 2). The plant biomarkers may have been transported from the distal site as litter washed across the outwash plain, or alternatively on leaf surfaces by wind. The shape, size, and weight of leaves affects distance travelled (Spicer, 1981); most extant *Podocarpaceae* growing in high latitudes have relatively small needles (<2 cm long), and bark scarring on the Oliver Bluffs *Nothofagus* wood fossils indicates a system with high wind energy (Francis and Hill, 1996). This could conceivably provide a mechanism for the preferential degradation and alternative degradation mechanism of conifer biomarkers, as well as a lack of conifer macrofossils and a lower abundance of conifer pollen.

4.2. Temperature reconstruction

Using the brGDGT based proxy MBT′/CBT palaeothermometer, our results suggest a MAAT for the strata at Oliver Bluffs of 5 °C, with a possible range of 3–12 °C. As the majority of the samples (11 of 15) showed temperature values in the range 3–5 °C, we speculate that this is the temperature range that mainly characterised this interval. The large calibration errors for the proxy mean that absolute temperature calculations must be interpreted cautiously (Peterse et al., 2012). However, our results are consistent with other temperature reconstructions from the Oliver Bluffs succession (Fig. 5) and freshwater molluscs (Ashworth and Preece, 2003). Our reconstructions are significantly higher than a MAAT estimate of ca. −12 °C based on palaeosol analysis (Retallack et al., 2001). A further constraint on the application of the MBT′/CBT proxy to high latitude soils could be the decoupling of air and soil temperatures by winter snow (Cline, 1997). This decoupling could result in reconstructed soil temperature values that differ markedly from the MAAT. However, brGDGT temperature calculations from modern high latitude soils closely match measured MAAT distributions (Peterse et al., 2009), supporting our absolute temperature reconstruction.

The palaeolatitude of Oliver Bluffs is considered to have been very similar to today's (Lawver and Gahagan, 2003), which implies that, during winter months, (a) the polar light regime would have caused the surface temperature to drop well below freezing (supported by the presence of periglacial sediments in which the plants grew) and (b) soil water availability would have been severely limited. Temperature during these months may have dropped to −20 °C or lower (Francis and Hill, 1996), meaning that vegetation likely remained dormant for much of the year and soil bacterial activity decreased, although it would have continued under the snow (Männistö et al., 2012). We envisage that temperature values warmed enough to induce snowmelt were reached in summer, allowing vegetation to grow and soil bacteria activity to increase. Today, plant root and shoot growth in the Antarctic and the Arctic can occur at low temperature (0–5 °C; Shaver and Billings, 1977) and plants are adapted to a rapid burst of growth following snowmelt. Since brGDGTs are membrane lipids produced by an unknown group of soil bacteria, likely Acidobacteria (Weijers et al., 2007; Sinninghe Damsté et al., 2011), it is possible that

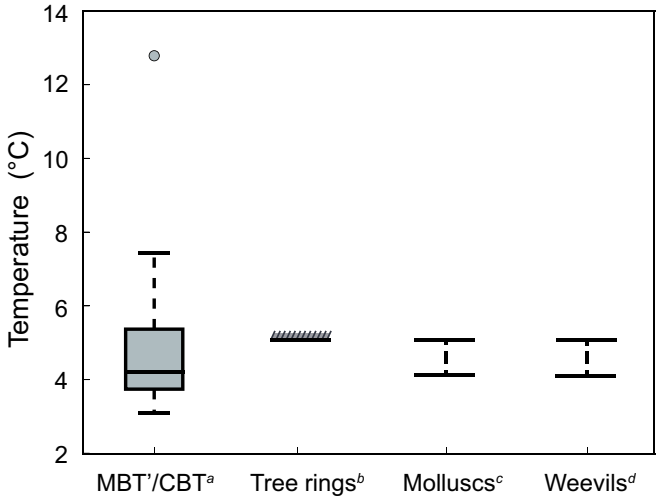

Fig. 5. Summer temperature reconstructions from Oliver Bluffs from four proxies. Range data from (a) this study, giving the maximum, minimum, first and third quartiles, and the median temperature (major outlier also shown – see Section 0); (b) Francis and Hill (1996), giving the minimum estimated summer temperature; (c) Ashworth and Preece (2003) and (d) Ashworth and Kuschel (2003).

brGDGT-producing bacteria at Oliver Bluffs had a preferential summer growing season during the late Neogene. No seasonal pattern has been found in brGDGT distributions at modern mid-latitudes (Weijers et al., 2011). However, at high latitude, the MBT/CBT temperature reconstructions from a core containing brGDGTs originating from coastal soils of the Wilkes Land sector of Antarctica showed a bias towards summer temperatures for the early and mid-Eocene (Pross et al., 2012). Similarly, MBT/CBT based reconstruction for the Arctic during the early Eocene is in good agreement with the warmest month temperature reconstruction based on oxygen isotopes from biogenic phosphate of co-occurring terrestrial vertebrates (Weijers et al., 2007; Eberle et al., 2010). Taking all this into consideration, we suggest that the temperature calculations here reflects a strong summer-seasonal or even warm monthly bias, meaning that MAAT over Antarctica was much cooler than 5 °C. Indeed, the vegetation reconstruction supports this conclusion as it indicates, consistent with the macrofossil record, a vegetation mixture similar to tundra shrub flora growing in present day cold high latitude environments.

5. Conclusions

This initial biogeochemical study of the Sirius Group at Oliver Bluffs provides new climate and flora results. Reconstructed temperature values are consistent with those reported from other temperature proxies recovered from the same site. Specifically, Antarctic summer surface air temperature values reconstructed using the MBT′/CBT proxy were around 5 °C, significantly higher than at present. This is consistent with multiple temperature reconstructions from the same site, and is in agreement with longer term temperature records throughout the Neogene, which suggest that continental summer temperature ranged between 4 and 12 °C (Prebble et al., 2006; Warny et al., 2009). The bacterially-derived temperature values show that, during the mid to late Neogene, Antarctica was perhaps 30 °C warmer than today. This was a cold, periglacial environment, as supported by the sedimentology and fossil flora at Oliver Bluffs (Retallack et al., 2001; Ashworth and Cantrill, 2004). The climate would have been strongly seasonal, where the onset of summer melt would have had a significant impact on the biological and hydrological regime of the outwash plain.

The aliphatic lipid record indicates a mixed vegetation consisting of moss, angiosperms and microalgal mats existing in a periglacial environment. The presence of aromatised diterpenoids provides the first geochemical evidence for the presence of conifers at or near the site, probably Podocarpaceae. The results contrast with the macrofossil record, which suggests that angiosperms were the only vascular higher plants present at the time, and support the palynomorph record from the same site (Askin and Raine, 2000). Our results emphasise the importance of using a multiproxy approach when reconstructing vegetation because of taphonomic and transport biases in both the fossil and molecular record. Undoubtedly, the work demonstrates that chemotaxonomy is a useful and complementary tool to palynology and palaeobotany.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.orggeochem.2018.01.001.

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