Exploring the use of compound-specific carbon isotopes as a palaeoproductivity proxy off the coast of Adélie Land, East Antarctica

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Abstract

The Antarctic coastal zone is an area of high primary productivity, particularly within coastal polynyas where large phytoplankton blooms and drawdown of CO2 occur. Reconstruction of historical primary productivity changes, and the associated driving factors, could provide baseline insights on the role of these areas as sinks for atmospheric CO2, especially in the context of projected changes in coastal Antarctic sea ice. Here we investigate the potential for using carbon isotopes (δ13C) of fatty acids in marine sediments as a proxy for primary productivity. We use a highly resolved sediment core from off the coast of Adélie Land spanning the last ~400 years and monitor changes in the concentrations and δ13C of fatty acids along with other proxy data from the same core. We discuss the different possible drivers of their variability and argue that C24 fatty acid δ13C predominantly reflects phytoplankton productivity in open water environments, while C18 fatty acid δ13C reflects productivity in the marginal ice zone. These new proxies have implications for better understanding carbon cycle dynamics in the Antarctica coastal zone in future paleoclimate studies.

1 Introduction

Antarctic coastal zones are important players in the global carbon cycle. The deep ocean is ventilated in these regions as part of the Southern Ocean overturning circulation, allowing waters rich in nutrients and CO2 to be upwelled to the surface. In the absence of biological activity, most of the CO2 would be leaked to the atmosphere. However, coastal polynyas within the Antarctic margin are areas of very high primary productivity during the spring and summer months (e.g. Arrigo et al., 2008) that rapidly reduces CO2 to low levels through photosynthesis (Arrigo and van Dijken, 2003; Arrigo et al., 2008), resulting in surface water CO2 undersaturation with respect to atmospheric CO2 (Tortell et al., 2011). The subsequent export and burial of the organic carbon produced during these intense phytoplankton blooms can significantly lower atmospheric CO2 concentrations (Sigman and Boyle, 2000). Therefore, any change in the consumption of these nutrients by
phytoplankton, or any change in phytoplankton community structure, may affect the air-sea CO₂ exchange in this region.

Records of past phytoplankton productivity offer an opportunity to document the drivers of primary productivity at different timescales from pluri-decadal to millennial. In the Antarctic coastal zone past work has focused on records of organic carbon, biogenic silica and diatom abundances (Leccaroni et al., 1998; Frignani et al., 1998; Denis et al., 2009; Peck et al., 2015). These proxies however may provide a biased view of phytoplankton productivity as they only record a signal of siliceous productivity and may suffer from alteration during settling and burial (Beucher et al., 2004; Tréguer et al., 2017). As such, there is no robust understanding of how such records respond to surface water CO₂ which is of major importance in the context of Antarctic coastal sea ice changes.

Here we investigate the use of compound specific carbon isotope analysis (δ¹³C) of free (solvent extractable using ultrasonication), saturated algal fatty acids (FAs) in marine sediments as a potential integrative proxy for reconstructing primary productivity in a polynya environment. Fatty acids have the potential to be a useful palaeoproduction tool in this region due to their ubiquitous presence within marine sediments, while other commonly used compounds, such as alkenones, are absent, Fatty acids are also able to persist within the sediments for several thousand years, meaning they have the potential to be applied over long time spans in contrast to more labile compounds such as highly branches isoprenoid alkenes (HBIs). Furthermore, fatty acids are amenable to isotope analysis allowing them to yield more detailed information about the environment.

Previous studies in the highly-productive regions of the Southern Ocean have highlighted the potential for using compound-specific isotopes from algal biomarkers in sediments to track primary productivity changes both spatially and temporally. Villinski et al. (2008) found that the spatial variation in pCO₂ in the Ross Sea was associated with a variation in the δ¹³C of sedimentary organic carbon and sterol biomarkers, most likely due to a change in isotopic fractionation associated with the photosynthetic drawdown of CO₂. Their results demonstrate that the spatial variation in surface water CO₂ is recorded in sedimentary organic matter and algal biomarkers. We explore this further as well as looking into other potential drivers of compound-specific carbon isotopes.

We use samples from core DTGC2011, a 4.69 m sediment core recovered from offshore Adélie Land, East Antarctica, spanning the last ~400 years. The core chronology is based on radiocarbon dates and confirmed by ²¹⁰Pb excess activity measurements, which indicate that DTGC2011 spans the 1580-2000 C.E. period with a mean sedimentation rate of ~1 cm yr⁻¹ (Supplementary Information S1). In order to understand the signal recorded by the FAs, we estimate the most likely biological source of these compounds and the habitat and season of production. Moreover, we compare downcore changes in FA concentrations and δ¹³C with other proxy data from the same core.

Environmental setting

The Adélie drift is located in the Dumont D’Urville Trough in the Adélie Basin, ca. 35 km offshore from Adélie Land (Fig. 1). This is a 1000 m deep, glacially scoured depression on the East Antarctic continental shelf, bounded to the east by the Adélie Bank. Sea ice plays a key role on the dynamics of the region, with both fast
ice and pack ice present off the coast of Adélie Land. A large bank of fast ice forms annually between 135 and 142°E, and extends up to 120 km away from the coast (Massom et al., 2009). On the north edge of this fast ice buttress is an inlet of open water forming a polynya, an area of open water surrounded by sea ice (Bindoff et al., 2000).

The Adélie Coast is characterized by extremely high primary productivity, with phytoplankton assemblages dominated by diatoms (Beans et al., 2008). The site itself is located close to the Dumont D’Urville polynya (DDUP), with an annual net primary productivity (NPP) of 30.3 g C m⁻² a⁻¹, but is also directly downwind and downcurrent of the much larger and highly productive Mertz Glacier polynya (MGP) to the east, with an annual NPP of 39.9 g C m⁻² a⁻¹ (Arrigo et al., 2015). Various factors are known to drive productivity trends in the Southern Ocean, including open water area, glacial melt and mixed layer depth (Arrigo et al., 2015). In the MGP, Arrigo (2007) found light and nutrient availability to be the most important factors, which will in turn be modulated by changes in mixed layer depth, ice cover and glacial ice melt. Physiological differences in Phaeocystis antarctica compared to diatoms mean it can thrive in lower nutrient conditions and lower CO₂ levels.

The region is affected by various water masses. High Salinity Shelf Water (HSSW) is formed on the shelf in coastal polynyas as a result of sea ice production and the associated brine rejection. HSSW flows out of the shelf through the Adélie sill at 143°E (Fig. 1). Modified Circumpolar Deep Water (mCDW) is a warm, macronutrient-rich and salty water mass which upwells onto the continental shelf through channels in the shelf break. mCDW has been observed to upwell across the shelf break near the Mertz Glacier at 144°E (Williams et al., 2008) (Fig. 1). The Antarctic Coastal Current, also known as the East Wind Drift, flows westward often adjacent to ice shelves (Thompson et al., 2018). The Antarctic Surface Water (AASW) is a widespread water mass which extends across the continental shelf and has a surface mixed layer varying from a shallow (ca. 10 m), warmer and fresher layer in summer to a deeper (ca. 100 m), colder layer in winter. This is also transported westward along with the Antarctic Coastal Current (Martin et al., 2017). Surface waters along the Adélie coast have relatively high concentrations of nitrate, silica and phosphorus, with spatially variable levels of Fe which may be due to re-suspension of sediments and calving of ice (Vaillancourt et al., 2003; Sambrotto et al., 2003).

2 Materials and Methods

Fatty acids

One hundred and thirty-five sediment samples were taken for organic geochemical analyses, sampled at 1 cm intervals in the top 50 cm, 2 cm intervals between 50 and 100 cm, and 5 cm intervals until 458 cm. Lipid extractions were completed at the University of Birmingham. 2 to 5 grams of dried and homogenized sediment was extracted using 20 ml of dichloromethane:methanol (3:1 v/v) and ultrasonication. Specifically, samples were ultrasonicated for 20 mins and then heated at ~50°C for 1 hour, centrifuged and the supernatant pipetted off. The ultrasonication step and recovery of supernatant was repeated a further 2 times. The acid and neutral fractions were separated using an aminopropyl-silica gel column and the FAs eluted using diethyl ether with 4% acetic acid. The acid fraction was derivatized using boron trifluoride (14 % in methanol (v/v)) and subsequently cleaned up using a silica gel column and the fatty acid methyl esters (FAMEs) eluted with dichloromethane.
FAs were identified using an Agilent 7890B gas chromatograph (GC) coupled to an Agilent 5977A mass selective detector, with a BP5-MS (SGE) column (60m, 320µm internal diameter, 0.25µm film thickness). Helium was used as the carrier gas set at a constant flow rate of 2 ml/min. The MSD was run in scan mode with a scan width of 50 to 800 mass units. Concentrations were quantified using an Agilent 7890B GC-flame ionization detector, using Hydrogen as the carrier gas with a constant flow rate of 2 ml min⁻¹. An Rtx™-200 column (105 m, 250µm internal diameter, 0.25µm film thickness) which has a poly(trifluoropropylmethylsiloxane) stationary phase was used for FAME analyses to enable the best separation possible. The oven programme was: 70°C, held for 1 min, increased to 150°C at a rate of 30°C/min, increased to 320°C at a rate of 3°C/min, then held for 10 minutes. FAME concentrations were quantified by addition of a C₁₉ alkane as an internal standard, prepared in-house to the concentration of 10 ng/µl. The peak areas of FAMEs and the internal standard were used to calculate the concentration of each compound.

The δ¹³C composition of fatty acids are described in delta notation:

\[ δ^{13}C (\%o) = \left( \frac{(^{12}C/^{13}C)_{\text{sample}}}{(^{12}C/^{13}C)_{\text{standard}}} - 1 \right) \times 1000 \]

whereby the standard is Vienna Pee Dee Belemnite. Carbon isotopes were measured using an Agilent 7890A GC coupled to an Isoprime GC5 furnace and an Isoprime 100 isotope ratio mass spectrometer (IRMS). The Isoprime GC5 furnace contained a CuO furnace tube kept at 850°C. Helium was used as the carrier gas set at a constant flow of 1.7 ml/min and CO₂ was used as the reference gas. The GC had a VF-200ms column (60 m, 250µm internal diameter, 0.25µm film thickness) which also has a poly(trifluoropropylmethylsiloxane) stationary phase. The oven programme was: 70°C, held for 1 min, increased to 150°C at a rate of 30°C/min, increased to 320°C at a rate of 3°C/min, then held for 5 minutes. Most samples were run using an Agilent 7693 autosampler from dilutions of 10 – 100 µl. Where concentrations were very low, samples were dissolved in <10 µl and were manually injected. Most samples were run in duplicate except for a few cases where the sample concentration was so low that the entire sample had to be injected in one run.

Machine performance was routinely checked using a FAME ester mix (F8; Indiana University) containing eight FAME compounds. This was run before the start of analysis and after every five duplicate samples. Errors are based on the difference between duplicate measures and are all within 0.26‰. To correct for the additional carbon added during MeOH derivatization, three FA standards were analysed for their bulk carbon isotope value using an Elementar Pyrocube at the University of Birmingham. Samples were combusted at 920°C before being passed through a reduction column and the isotopic composition of sample gases was determined on an Isoprime continuous flow mass-spectrometer. These samples were then derivatized and then analysed on the GC-IRMS for the δ¹³C value of the FAME. The δ¹³C of the FA (δ¹³CFA) and FAME (δ¹³CFAME) were used to calculate the δ¹³C of the MeOH (δ¹³CMEOH) as follows:

\[ δ^{13}C_{\text{MeOH}} = (n_{\text{FAME}} \times δ^{13}C_{\text{FAME}}) - (n_{\text{FA}} \times δ^{13}C_{FA}) \]

whereby nFAME is the number of carbons in the FAME and nFA is the number of carbons in the FA. δ¹³CMEOH was calculated to be ca. -40.8‰ and the δ¹³CFA values were corrected using:

\[ δ^{13}C_{FA} = \left( \frac{(n_{\text{FAME}} \times δ^{13}C_{\text{FAME}}) + 40.8}{n_{\text{FA}}} \right) \]
Two hundred and thirty-four samples were taken every 2 cm over the whole core for highly branched isoprenoids (HBI) analysis. HBIs were extracted at Laboratoire d'Océanographie et du Climat: Expérimentations et Approches Numériques (LOCEAN), separately from the fatty acids, using a mixture of 9 mL CH$_2$Cl$_2$/MeOH (2:1, v:v). 7 hexyl nonadecane (m/z 266) was added as an internal standard during the first extraction steps, following the Belt et al. (2007) and Massé et al. (2011) protocols. Several sonication and centrifugation steps were applied in order to fully extract the selected compounds (Etourneau et al., 2013). After drying with N$_2$ at 35°C, the total lipid extract was fractionated over a silica column into an apolar and a polar fraction using 3 mL hexane and 6 mL CH$_2$Cl$_2$/MeOH (1:1, v:v), respectively. HBIs were obtained from the apolar fraction following the procedures reported by Belt et al. (2007) and Massé et al. (2011). After removing the solvent with N$_2$ at 35°C, elemental sulfur was removed using the TBA (Tetrabutylammonium) sulfite method (Jensen et al., 1977; Riis and Babel, 1999). The obtained hydrocarbon fraction was analyzed within an Agilent 7890A gas chromatograph (GC) fitted with 30 m fused silica Agilent J&C GC column (0.25 mm i.d., 0.25 µm film thickness), coupled to an Agilent 5975C Series mass selective detector (MSD). Spectra were collected using the Agilent MS-Chemstation software. Individual HBIs were identified on the basis of comparison between their GC retention times and mass spectra with those of previously authenticated HBIs (Johns et al., 1999) using the Mass Hunter software. Values are expressed as concentration relative to the internal standard.

Diatoms

One hundred and eighteen samples were taken every 4 cm over the whole core for diatom analyses. Sediment processing and slide preparation followed the method described in Crosta et al. (2020). Diatom counting followed the rules described in Crosta and Koç (2007). Around 350 diatom valves were counted in each sample at a 1000X magnification on a Nikon Eclipse 80i phase contrast microscope. Diatoms were identified to species or species group level. Absolute abundances of diatoms were calculated following the equation detailed in Crosta et al. (2008). The relative abundance of each species was determined as the fraction of diatom species against total diatom abundance in the sample.

3 Fatty acids within DTGC2011

Analysis by GC-MS identified seven dominant saturated FAs within the DTGC2011 samples (Fig. S2). These have carbon chain lengths of C$_{16}$ to C$_{26}$ and only the saturated forms (i.e. no double bonds) were identified. These are predominantly even chain length FAs, with only minor amounts of the C$_{17}$ compound measured (Gilchrist, 2018).

3.1 Fatty acid concentrations

The C$_{19}$ alkane was used as an internal standard to aid quantification of fatty acid concentrations. However, it should be noted that since this standard was added to samples post-extraction, our concentration estimates are semi-quantitative but can be used to compare concentration changes in different FA compounds.
Down core analysis of FA concentrations reveals clear groupings in concentration changes. In the upper part of the core (ca. 3 – 90 cm depth), spanning the last ~78 years, all FA compounds show a similar pattern, with elevated concentrations, broadly decreasing down-core (Fig. 2). Below this, however, two groups clearly diverge. These can be broadly divided into short-chained fatty acids (C\textsubscript{16} to C\textsubscript{20}; SCFAs) and long-chained fatty acids (C\textsubscript{22} to C\textsubscript{26}; LCFAs). Within these groups, the concentrations of different compounds show similar trends, but the two groups (SCFAs vs LCFAs) show different trends to each other (Gilchrist, 2018). This is confirmed by R\textsuperscript{2} values calculated for the linear regression of concentrations of each FA against each other throughout the core (Fig. 3; n = 135, p <0.001). Correlations between the SCFAs have R\textsuperscript{2} values between 0.97 and 0.99, while R\textsuperscript{2} values of LCFAs range between 0.88 and 0.95. Between the two groups, however, R\textsuperscript{2} values are all lower, ranging between 0.50 and 0.77.

These distinct groupings suggest that compounds within each group (SCFAs and LCFAs) likely have a common precursor organism or group of organisms, but the two groups themselves have different producers from each other. These producers may in turn thrive during different seasons or within different habitats and thus, the isotopic composition of compounds from these different groups may record different environmental signals.

R\textsuperscript{2} values were also calculated for samples below 25 cm only (ca. 1587 – 1978 C.E.), to remove correlations associated with preservation changes in the top part of the core (discussed below). Although the R\textsuperscript{2} values are not quite as high, they broadly confirm these groupings, with the R\textsuperscript{2} values generally being greater within the two groups (n = 73). R\textsuperscript{2} values range from 0.93 for the C\textsubscript{18} with C\textsubscript{20}, down to 0.07 for the C\textsubscript{18} and C\textsubscript{24} (Fig. 4).

The C\textsubscript{18} and C\textsubscript{24} FAs are the most abundant compounds within the SCFA and LCFA groups, respectively, and also the least correlated with each other both in the whole core (R\textsuperscript{2} = 0.5) and below 25 cm (R\textsuperscript{2} = 0.07), which suggests they are the most likely to be produced by different organisms. Furthermore, these two compounds yielded the highest quality isotope measurements, due to their greater concentrations, clean baseline and minimal coeluting peaks (Fig. S2). Thus, these two compounds (C\textsubscript{18} and C\textsubscript{24}) will be the focus of analysis and discussion.

### 3.2 Potential sources of the C\textsubscript{18} fatty acid

Potential sources for the C\textsubscript{18} FA in core U1357 (recovered from the same site as DTGC2011) are discussed in Ashley et al. (2021) who suggest the prymnesiophyte *Phaeocystis antarctica* to be the most likely main producer. This is based on a) previous studies of FAs produced by microalgae (Dalsgaard et al., 2003), b) the high observed abundance of *P. antarctica* within modern Adélie surface waters (Riaux-Gobin et al., 2011; Sambrotto et al; 2003) and c) comparison between the measured δ\textsuperscript{13}C values and those reported in the literature for *P. antarctica* (Kopczynska et al., 1995; Wong and Sackett, 1978). Unfortunately, the absence of *P. antarctica* in sediments, as it does not biomineralize any test, precludes the direct comparison of down core trends of this species with FAs. *Phaeocystis antarctica* has been found to live within and underneath sea ice before its break up, as well as in open ocean waters (Riaux-Gobin et al., 2013; Poulton et al., 2007), due to its ability to use a wide range of light intensities for energy production (Moisan and Mitchell, 1999).
Furthermore, Skerratt et al. (1998) compared the FAs produced by *P. antarctica* and two Antarctic diatoms, in culture samples, and showed that *P. antarctica* produced a much higher percentage of both saturated FAs (C₁₄-C₂₀) and C₁₈ FAs than the diatoms. This supports the hypothesis of *P. antarctica* being a dominant and abundant source of the saturated C₁₈ FA in the Adélie basin though minor contributions of C₁₈ from other phytoplankton species such as the diatoms and dinoflagellates or even bacteria cannot be excluded (Table S2).

### 3.3 Potential sources of the C₂₄ fatty acid

Long-chain n-alkyl compounds, including FAs, are major components of vascular plant waxes and their presence within sediments has commonly been used as a biomarker of terrestrial plants (Pancost and Boot, 2004). Although plants such as bryophytes (e.g. mosses) which are present in the Antarctic do also produce LCFAs (Salminen et al., 2018), it is unlikely that FAs from terrestrial plants make a significant contribution to the water column, due to their extremely limited extent on the continent, and the significant distance of the site from other continental sources.

However, there is much evidence in the literature for various aquatic sources of LCFAs, a few of which are summarized in Table S2. Although not all of these sources are likely to be present within the coastal waters offshore Adélie Land, it highlights the wide range of organisms which can produce these compounds, and thus suggests that an autochthonous marine source is likely, especially considering the highly productive nature of this region.

### 3.4 Microbial degradation and diageneric effects on fatty acid concentration

Both the C₁₈ and C₂₄ FAs show an overall decrease in concentrations down-core, with significantly higher concentrations in the top 80 cm (representing ~70 years) compared to the rest of the core. Below this point, FAs concentrations variations are attenuated (Fig. 2).

Many studies have shown that significant degradation of FAs occurs both within the water column and surface sediments as a result of microbial activity, and that there is preferential break down of both short-chained and unsaturated FA, compared to longer-chained and saturated FA (Haddad et al., 1992; Matsuda, 1978; Colombo et al., 1997). Haddad et al. (1992) studied the fate of FAs within rapidly accumulating (10.3 cm yr⁻¹) coastal marine sediments (off the coast of North Carolina, USA) and showed that the vast majority (ca. 90%) of saturated FAs were lost due to degradation within the top 100 cm (representing ~10 years). Similarly, Matsuda and Koyama (1977) found FA concentrations decrease rapidly within the top 20 cm of sediment (accumulating at 4 mm yr⁻¹) from Lake Suwa, Japan. Assuming similar processes apply to the DTGC2011 sediments, this suggests the declining concentrations within the upper part of the core are largely the result of diageneric effects such as microbial activity occurring within the surface sediments, and thus do not reflect a real change in production of these compounds in the surface waters.

The complete lack of both unsaturated and short chained (fewer than 16 carbon atoms) FA compounds identified within DTGC2011 samples, even within the top layers, suggests that selective breakdown of compounds has already occurred within the water column and on the sea floor (before burial). Wakeham et al. (1984) assessed the loss of FAs with distance during their transport through the water column at a site in the equatorial Atlantic Ocean and estimated that only 0.4 to 2% of total FAs produced in the euphotic zone reached a depth of 389 m, and even less reaching more than 1,000 m depth, the vast majority of material being recycled.
in the upper water column. Their results also show a significant preference for degradation of both unsaturated and short chained compounds over saturated and longer chain length compounds. Although no studies into the fate of lipids within the water column exist for the Adélie region, the >1,000 m water depth at the core site would provide significant opportunity for these compounds to be broken down during transportation through the water column. It is likely, therefore, that the distribution of compounds preserved within the sediments will not be a direct reflection of production in the surface waters, and explains the preference for saturated FAs with carbon chain lengths of 16 and more. It is also possible that some additional production and contribution of FAs by bacteria occurred during this process (Allen & Bartlett, 2002; Allen et al., 1999; Jónasdóttir, 2019).

Although FA concentrations in the top 80 cm of core DTGC2011 are much higher overall than the sediments below and show a broad decline over this section, there is a high level of variability. Concentrations do not decrease uniformly within the top part of the core, as may be expected if concentration change is a first order response to declining microbial activity. The peak in total FAs instead occurs at a depth of 21-22 cm with a concentration more than an order of magnitude higher than in the top layer. This variability creates difficulty in directly determining the effects of diagenesis. However, by 25 cm (ca. 1978 C.E.) the concentrations drop to below 1,000 ng g⁻¹ and remain so until 32 cm before increasing again. This may suggest that diagenetic effects of FA concentrations are largely complete by 25 cm (representing ca. 25 years), consistent with results from Haddad et al. (1992) and Matsuda and Koyama (1977), and that subsequent down-core concentration variations predominantly represent real changes in export productivity, resulting from environmental factors. However, the fluctuating nature of concentrations particularly in the youngest sediments means it is difficult to clearly unpick the effects of diagenesis from actual changes in production of these compounds, and a clear cut-off point for diagenetic effects cannot be determined.

3.5 Comparison of fatty acid concentrations with highly branched isoprenoid alkenes

We compare FA concentrations with other organic compounds (whose source is better constrained) in DTGC2011 to better understand FA sources. Direct comparison between different organic compound classes can be made since both are susceptible to similar processes of diagenesis, in contrast to other proxies such as diatoms. In core DTGC2011, concentrations of di- and tri-unsaturated highly branched isoprenoid (HBI) alkenes (referred to as HBI diene and HBI triene, respectively hereafter) were available.

In Antarctic marine sediments HBIs have been used as a tool for reconstructing sea ice (Belt et al., 2016, 2017). Smik et al. (2016) compared the concentrations of HBIs in sediment samples offshore East Antarctica from the permanently open-ocean zone (POOZ), the marginal ice zone (MIZ) and the summer sea-ice zone (SIZ). They found the HBI diene reached the highest concentrations in the SIZ and was absent from the POOZ. In contrast, the HBI triene was most abundant in the MIZ, i.e. at the retreating sea ice edge, with much lower concentrations in the SIZ and POOZ. This suggests that the two compounds are produced in contrasting environments but remain sensitive to changes in sea ice. The HBI diene biomarker (or IPSO₂₅ for Ice Proxy Southern Ocean with 25 Carbons) is mainly biosynthesised by Berkeleya adeliensis (Belt et al., 2016), a diatom which resides and blooms within the sea ice matrix, and thus can be used as a proxy for fast ice attached to the coast. In contrast, the presence of the HBI triene mostly in the MIZ is suggestive of a predominantly pelagic phytoplankton source (e.g. Rhizosolenia spp, Massé et al.,
2011; Smik et al., 2016; Belt et al., 2017), rather than sea-ice dwelling diatoms (Smik et al., 2016). The fact that
HBI triene reached its greatest abundance within the MIZ suggests its precursor organism may thrive in the
stratified, nutrient-rich surface waters of the sea-ice edge.

One key similarity between both the HBI diene and triene, and the FA concentrations is that the highest
concentrations are found in the youngest sediments. These compounds all show broad increases in concentration
from 110 cm depth (ca. 1900 C.E) until the top of the core (Fig. 2 and 5). Concentrations of HBIs are also
susceptible to degradation through the water column through visible light induced photo-degradation (Belt and
Müller, 2013) and diagenetic effects within the sediments including sulphurisation (Sinninghe Damstê et al.,
2007), isomerisation and cyclisation (Belt et al., 2000). Thus, it is likely that the elevated concentrations, and
thus the similarity between FA and HBI concentrations, is due to the material being fresher and thus less
affected by diagenesis, with diagenetic effects having an increasing and progressive impact down to ca. 25cm
depth.

However, despite an overall increase in HBI and FA concentrations above 110 cm depth, there are clear
deviations from this trend. Concentrations of the HBI triene show some broad similarities with FA
concentrations. In particular, both the HBI triene and the C18 FA have coeval concentration peaks around 1980-
88, 1967, 1938, 1961-72, 1848 and 1752 C.E. (Fig. 5). These peaks are offset from the HBI diene
concentrations, suggesting that they result from increased production in the surface waters rather than simply
changes in preservation. The HBI triene is more susceptible to degradation than the diene (Cabedo Sanz et al.,
2016), so while this could explain some of the differences between the diene and triene records, where the triene
increases independently of the diene, this is likely to be a genuine reflection of increased production of these
compounds at the surface rather than an artefact of preservation processes.

This close similarity between the C18 FA and HBI triene concentrations (Fig. 5) suggests that the C18 may also
be produced by an organism associated with the retreating ice edge. Phaeocystis antarctica has been proposed
as a potential producer of the C18 in core U1357B (Ashley et al., 2021). In the Ross Sea, P. antarctica has been
observed to dominate the phytoplankton bloom during the spring, blooming in deep mixed layers as the sea ice
begins to melt, after which diatoms tend to dominate during the summer (Arrigo et al., 1999; Tortell et al., 2011;
DiTullio et al., 2000). However, a few studies in the Adélie region suggest this is not the case there. Offshore
Adélie Land, P. antarctica has been found to only appear late in the spring/early summer, later than many
diatom species. During this time, it occurs preferentially within the platelet ice and under-ice water (Riaux-
Gobin et al., 2013). Furthermore, Sambrotto et al. (2003) observed a surface bloom of P. antarctica near the
Mertz Glacier (Fig. 1) during the summer months, in very stable waters along the margin of fast ice and Riaux-
Gobin et al. (2011) found P. antarctica to be abundant in the coastal surface waters eight days after ice break up.
This indicates an ecological niche relationship with cold waters and ice melting conditions. This might explain
the close similarity between the C18 and HBI triene concentrations, both produced by organisms occupying a
similar habitat at the ice edge.

The C24 FA record also shows some similarity with the HBI triene record. This appears to be mostly in the top
part of the core where the highest concentrations are found. The reason for this resemblance is unclear,
especially considering the lack of correlation between the C24 and C18 FA concentrations. However, it may relate
In contrast, the more negative δ13C values during early spring before ice break up. The more negative δ13C values suggest a pelagic phytoplankton source. Similarly, diatoms are being produced by different species with varying abundances and more susceptible to dissolution. For example, Fragilariopsis curta and Chaetoceros resting spores being the most abundant. However, trends in diatom concentrations, particularly in the upper part of the core. The known producer of the HBI diene, Berkeleya adeliensis, for example, was not recorded within the core, likely due to their lightly silified frustules which are more susceptible to dissolution (Belt et al., 2016). Therefore, despite the lack of a correlation between diatom abundances and FA concentrations, we cannot entirely rule out the possibility of a minor contribution of FAs by diatoms.

4 Carbon isotopes of fatty acids

Down-core changes in δ13C for the C18 and C24 FAs (δ13C18FA and δ13C24FA, respectively) (Fig. 7) clearly show different trends, with very little similarity between them (R² = 0.016). This further supports the idea that these compounds are being produced by different organisms, and thus are recording different information. The mean carbon isotope value of δ13C18FA of -29.8 ‰ in core U1357 from the same site (Ashley et al., 2021) is suggestive of a pelagic phytoplankton source (Budge et al., 2008). In core DTGC2011 the mean values of δ13C18FA and δ13C24FA are -26.2 ‰ and -27.6 ‰, respectively. Though more positive, these values are still within the range of a phytoplankton source. Additionally, we tentatively suggest that the 0.5‰ more positive δ13C18FA mean value over the δ13C24FA may indicate the contribution of sea-ice dwelling algae producers, since carbon fixation occurring within the semi-closed system of the sea ice will lead to a higher degree of CO2 utilisation than in surrounded open waters (Henley et al., 2012). Although no studies on FA δ13C of different organisms are available for the Southern Ocean, Budge et al. (2008) measured the mean δ13C value of C16 FA from Arctic sea-ice algae (-24.0 ‰) to be 6.7 ‰ higher than pelagic phytoplankton (-30.7 ‰) from the same region. The higher δ13C of the C18 FA could therefore be indicative of P. antarctica living partly within the sea ice, e.g. during early spring before ice break up. The more negative δ13C24FA suggests it is more likely to be produced by phytoplankton predominantly within open water.

4.1 Controls on δ13CFA

The δ13C18FA record shows a broadly increasing trend towards more positive values from ca. 1587 until ca. 1920 C.E., with short term fluctuations of up to ~4 ‰ superimposed on this long-term trend (Fig. 7). This is followed by a period of higher variability with a full range of 5.6 ‰ until the most recent material (ca. 1999 C.E.), with more negative δ13C values between 1921 and 1977 C.E. and a rapid shift toward more positive values thereafter. In contrast, the δ13C24FA record overall shows a weak, negative trend, with large decadal fluctuations of up to 4.6 ‰, with a more pronounced negative trend after ca. 1880 C.E. (Fig. 7).
Below we consider the various factors which may control the carbon isotope value of algal biomarkers produced in the surface waters. Down-core changes in FA δ¹³C are likely to be a function of either the δ¹³C of the dissolved inorganic carbon (DIC) source, changes in the species producing the biomarkers, diagenesis or changing photosynthetic fractionation (εp). The next section outlines the potential influence of these factors may have in order to assess the mostly likely dominant driver of FA δ¹³C.

4.1.1 Isotopic composition of DIC

The δ¹³C of the DIC source can be affected by upwelling or advection of different water masses, or the δ¹³C of atmospheric CO₂. Around the Antarctic, distinct water masses have unique carbon, hydrogen and oxygen isotope signatures and thus isotopes can be used as water mass tracers (e.g. Mackensen, 2001, Archambeau et al., 1998). In the Weddell Sea for example, Mackensen (2001) determined the δ¹³C value of eight water masses, which ranged from 0.41 ‰ for Weddell Deep Water, sourced from CDW, to 1.63 ‰ for AASW. A similar range of ~1.5 ‰ was identified in water masses between the surface and ~5,500 m depth along a transect from South Africa to the Antarctic coast (Archambeau et al., 1998). Assuming similar values apply to these water masses offshore Adélie Land, this range in values would be insufficient to explain the ~5 ‰ variation of δ¹³C recorded by both C¹₈ and C₂₄ FA, even in the situation of a complete change in water mass over the core site. Furthermore, site DTGC2011, located within a 1,000 m deep depression and bounded by the Adélie Bank to the north, is relatively sheltered from direct upwelling of deep water (Fig. 1). Though inflow of mCDW has been shown to occur within the Adélie Depression to the east of the bank (Williams and Bindoff, 2003) and possibly within the Dumont d’Urville Trough, only very small amplitude changes in δ¹³C of benthic foraminifera, tracking upper CDW, have been observed over the Holocene in Palmer Deep, West Antarctica (Shevenell and Kennett, 2002). Although from a different location, this argues against large changes in the isotopic composition of the source of mCDW.

Changes in the δ¹³C of atmospheric CO₂, which is in exchange with the surface waters could also have the potential to drive changes in the δ¹³C of algal biomarkers. Over the last ca. 200 years, the anthropogenic burning of fossil fuels has released of a large amount of CO₂ depleted in ¹³C, meaning that the δ¹³C of CO₂ has decreased by ca. 1.5 ‰, as recorded in the Law Dome ice core. Prior to this, however, the δ¹³C of CO₂ in the atmosphere remained relatively stable, at least for the last thousand years (Francey et al., 1999). Therefore, this could potentially drive the δ¹³C of algal biomarkers towards more negative values within the last 200 years, but this could not explain the full variation of ~5-6 ‰ in FA δ¹³C measured throughout the core. Although the C²₄ δ¹³C shows a slight decrease over the last ca. 100 years, this is preceded by increasing δ¹³C, while the C¹₈ δ¹³C displays no clear trend over the last 200 years. If atmospheric CO₂ was a key driver of fatty acid δ¹³C, we would expect both compounds to respond together, showing a trend towards more negative values over the last 200 years which neither of them do. This suggests that the effect of changing δ¹³C of atmospheric CO₂ is insignificant compared to local and regional inter-annual variations as a result of other environmental drivers (discussed below).

4.1.2 Changing species

A shift in the organisms producing the FA could also affect δ¹³C where species have different fractionation factors. For example, changing diatom species have been shown to have an effect on bulk organic matter δ¹³C in core MD03-2601, offshore Adélie Land, over the last 5 ka (Crosta et al., 2005). However, the bulk organic
matter might have contained other phytoplankton groups than diatoms with drastically different δ13C values and fractionation factors. Here we measured δ13C of individual biomarkers, produced by a more restricted group of phytoplankton groups (possibly restricted to a few dominant species) compared to bulk δ13C. As discussed above, the C18 appears to be produced predominantly by *P. antarctica*, whereas diatoms do not tend to produce high proportions of this compound (Dalsgaard et al., 2003).

### 4.1.3 Effect of diagenesis on lipid δ13C

Sun et al. (2004) studied the carbon isotope composition of FAs during 100 days of incubation in both oxic and anoxic seawater. They observed a shift towards more positive values in FA δ13C, ranging between 2.6‰ for the C14:0 and as much as 6.9‰ in the C18:1, under anoxic conditions. This suggests that diagenesis could affect FA δ13C in core DTGC2011. However, these observed changes are rapid (days to months), occurring on timescales which are unresolvable in the FA δ13C record (annual to decadal), and thus may have no effect on the trends observed in our record. Based on concentration data discussed above, it seems that diagenetic overprint is largely complete by ~25 cm (Fig. 2). In the top 25 cm of the core (ca. 1978 – 1998 C.E.), the δ13C24FA values increase by ~2.5‰, downward (R2 = 0.63, n = 11) while the δ13C18FA values display a large variation with no overall trend (R2 = 0.12, n = 20). If diagenesis was driving the changes in δ13C, it is likely that this trend would be observed in all FA compounds.

Taken together, it appears that neither changes in the δ13C of the DIC, changing phytoplankton groups nor diagenesis can fully explain the variation of FA δ13C recorded within DTGC2011. Therefore, we hypothesise that changes in εp are the main driver of FA δ13C.

### 4.2 Controls on photosynthetic fractionation (εp)

There is a positive relationship between εp in marine algae and dissolved surface water CO2(aq) concentration (Rau et al., 1989). As a result, higher δ13C values are hypothesised to reflect lower surface water CO2(aq) and vice versa. Popp et al. (1999) showed a strong negative correlation between CO2(aq) and δ13C of suspended particulate organic matter across a latitudinal transect in the Southern Ocean, suggesting that changes in surface water CO2(aq) can explain a large amount of the variation in δ13C. Changes in surface water CO2(aq) concentration in turn may be driven by various factors, including changing atmospheric CO2 (Fischer et al., 1997), wind-driven upwelling of deep, carbon-rich water masses (Sigman and Boyle, 2000; Takahashi et al., 2009), sea-ice cover (Henley et al., 2012) and/or primary productivity (Villinski et al., 2008). Thus, determining the main driver(s) of surface water CO2 changes offshore Adélie Land should enable interpretation of the DTGC2011 FA δ13C records.

### 4.2.1 Sea ice

Brine channels within sea ice have very low CO2 concentrations and a limited inflow of seawater. Carbon isotopic fractionation of algae living within these channels has been shown to be greatly reduced compared to organisms living in the surrounding open waters (Gibson et al., 1999), leading to elevated δ13C values. It is thus possible that, under conditions of high sea-ice cover, enhanced FA contribution from sea-ice algae leads to elevated sedimentary δ13C values. HBI diene concentrations within DTGC2011 show a much greater presence of fast ice at the core site ca. 1960 C.E. (Fig. 5). However, during this time there is no clear elevation in δ13C concentrations in either δ13C18FA or δ13C24FA, both instead showing generally lower δ13C values. In fact, δ13C18FA
shows the lowest values of the whole record between 1925 and 1974 C.E., during which sea ice, as recorded by the HBI diene, is at its highest level. This suggests that inputs in sea-ice algae at this time are not driving changes in FA δ¹³C.

The DTGC2011 core site sits proximal to the Dumont D’Urville polynya, which has a summer area of 13.02 x 10⁸ km² and a winter area of 0.96 x 10⁸ km² (Arrigo and van Dijken, 2003). Changes in the size of the polynya both on seasonal and inter-annual time scales will affect air-sea CO₂ exchange and thus also surface water CO₂ concentration. A reduced polynya may lead to greater supersaturation of CO₂ in the surface waters due to reduced outgassing, allowing CO₂ to build up below the ice, leading to lower δ¹³C values of algal biomarkers produced in that habitat (Massé et al., 2011). Thus changes in the extent of sea ice may also effect FA δ¹³C.

4.2.2 Observed trends in surface water CO₂(aq)

If the trend in surface water CO₂(aq) paralleled atmospheric CO₂, with an increase of over 100 ppm over the last 200 years (MacFarling Meure et al., 2006), we might expect phytoplankton to exert a greater fractionation during photosynthesis in response to elevated surface water CO₂(aq) concentration, resulting in more negative δ¹³C values. Taking into account the decline in atmospheric δ¹³CO₂ over the same period would further enhance the reduction in phytoplankton δ¹³C. Fischer et al. (1997) looked at the δ¹³C of both sinking matter and surface sediments in the South Atlantic and suggested that, since the preindustrial, surface water CO₂(aq) has increased much more in the Southern Ocean than in the tropics. They estimated that a 70 ppm increase in CO₂(aq) in surface waters of 1°C would decrease phytoplankton δ¹³C by ca. 2.7‰, and up to 3.3‰ δ¹³CO₂ change are included, between preindustrial and 1977-1990. However, sea ice cover and summer primary productivity are likely to be much higher off Adélie Land than in the South Atlantic, both of which will affect air-sea gas exchange.

Shadwick et al. (2014) suggest that surface water CO₂ should track the atmosphere in the Mertz Polynya region, despite the seasonal ice cover limiting the time for establishing equilibrium with the atmosphere. They calculated wintertime CO₂ in the shelf waters of the Mertz Polynya region, offshore Adélie Land (Fig. 1), measuring ca. 360 ppm in 1996, ca. 396 ppm in 1999, and ca. 385 ppm in 2007, while atmospheric CO₂ at the South Pole was 360, 366 and 380 ppm, respectively (Keeling et al., 2005). Based on the 1996 and 2007 data only, an increase in CO₂ of ca. 25 ppm is observed over these 11 years, coincident with the 20 ppm atmospheric CO₂ increase over this time period. However, high interannual variability (± ca. 30 ppm) is evident (e.g. 396 ppm in 1999) suggesting that other factors, particularly upwelling, may override this trend. The latter was also suggested by Roden et al. (2013) based on winter surface water measurements in Prydz Bay, indicating that decadal-scale carbon cycle variability is nearly twice as large as the anthropogenic CO₂ trend alone.

During the austral winter, upwelling of deep water masses causes CO₂ to build up in the surface waters, and sea ice covers limits gas exchange with the atmosphere (Arrigo et al., 2008; Shadwick et al., 2014). Although only limited data, the measurements by Shadwick et al. (2014) suggest slight supersaturation, of up to 30 ppm, occurs in the winter due to mixing with carbon-rich subsurface water, but with high interannual variability. This is compared to undersaturation of 15 to 40 ppm during the summer as a result of biological drawdown of CO₂.

Roden et al. (2013) also observed varying levels of winter supersaturation in Prydz Bay, East Antarctica, with late winter CO₂ values of 433 ppm in 2011 (45 μatm higher than atmospheric CO₂), and suggested that
intrusions of C-rich mCDW onto the shelf may play a part in this. Similarly, winter surface water CO₂ of 425 ppm has been measured by Sweeney (2003) in the Ross Sea, before being drawn down to below 150 ppm in the summer as phytoplankton blooms develop.

Enhanced upwelling of deep carbon-rich waters in the Southern Ocean are thought to have played a key role in the deglacial rise of atmospheric CO₂, increasing CO₂ concentrations by ~80 ppm (Anderson et al., 2009; Burke and Robinson, 2012). Changes in upwelling offshore Adélie Land could therefore drive some interannual variability in surface water CO₂ and hence FA δ¹³C in DTGC2011. However, upwelling tends to be stronger during the winter months, when sea-ice formation and subsequent brine rejection drive mixing with deeper C-rich waters. At this time, heavy sea-ice cover limits air-sea gas exchange and enhances CO₂ supersaturation in regional surface waters (Shadwick et al., 2014). In contrast, the phytoplankton producing FA thrive during the spring and summer months during which CO₂ is rapidly drawn down and the surface waters become undersaturated. However, upwelling cannot be discarded as a possible contributor to surface water CO₂ change. However, the core site is in a relatively sheltered area and is probably not affected by significant upwelling.

Based on these studies, changes in atmospheric CO₂ concentration and δ¹³C of the source appear to be unlikely to be a dominant driver of the FA δ¹³C record, with interannual variations driven by other factors overriding any longer-term trend. There is also no clear anthropogenic decline in the FA δ¹³C record over the last 200 years, which supports this hypothesis.

4.2.3 Productivity

Given that changes in atmospheric CO₂, source signal, sea ice algae or diagenesis seem unable to explain the full range of variability seen in the FA δ¹³C record, the most plausible driver appears to be changes in surface water primary productivity. Coastal polynya environments in the Antarctic are areas of very high primary productivity (Arrigo and van Dijken, 2003). The DTGC2011 core site sits near to the Dumont D’Urville polynya, and is just downstream of the larger and more productive MGP (Arrigo and van Dijken, 2003). In large polynyas such as the Ross Sea, primary productivity leads to intense drawdown of CO₂ in the surface waters, resulting in reduced fractionation by the phytoplankton during photosynthesis (Villinski et al., 2008). In the Ross Sea, surface water CO₂ has been observed to drop to below 100 ppm during times of large phytoplankton blooms (Tortell et al., 2011) demonstrating that primary productivity can play a key role in controlling surface water CO₂ concentrations in a productive polynya environment. Arrigo et al. (2015) found the MGP to be the 8th most productive polynya in the Antarctic (out of 46) based on total net primary productivity during their sampling period, and Shadwick et al. (2014) observed CO₂ drawdown in the MGP during the summer months.

Therefore, we suggest that FA δ¹³C signals recorded in DTGC2011 is predominantly a signal of surface water CO₂ driven by primary productivity. Indeed, the potential for the δ¹³C of sedimentary lipids to track surface water primary productivity has been recognised in the highly productive Ross Sea polynya. High variability in surface water CO₂ values have been measured across the polynya during the summer months (December – January), ranging from less than 150 ppm in the western Ross Sea near the coast, to >400 ppm on the northern edge of the polynya. This pattern was closely correlated with diatom abundances, indicating intense drawdown of CO₂ in the western region where diatom abundances were highest (Tortell et al., 2011). This spatial variation in productivity is recorded in particulate organic carbon (POC) δ¹³C, and is also tracked in the surface sediments
by total organic carbon (TOC) $\delta^{13}$C and algal sterol $\delta^{13}$C, all of which show significantly higher values in the western Ross Sea. This spatial pattern in sterol $\delta^{13}$C was concluded to be directly related to CO$_2$ drawdown at the surface, resulting in average sterol $\delta^{13}$C values varying from -27.9‰ in the west, where productivity is greatest, down to -33.5‰ further offshore (Villinski et al., 2008).

A similar relationship is evident in Prydz Bay, where POC $\delta^{13}$C was found to be positively correlated with POC concentration and negatively correlated with nutrient concentration, indicating greater drawdown of CO$_2$ and nutrients under high productivity levels (Zhang et al., 2014).

This suggests it is possible to apply FA $\delta^{13}$C as a palaeoproductivity indicator in the highly productive Adélie polynya environment. However, it is important to constrain the most likely season and habitat being represented, since phytoplankton assemblages vary both spatially (e.g. ice edge or open water) and temporally (e.g. spring or summer). The incredibly high sedimentation rate (1-2 cm yr$^{-1}$) within the Adélie Basin is thought to result, on top of regional high productivity, from syndepositional focusing processes bringing biogenic debris from the shallower Adélie and Mertz banks to the ca. 1,000 m deep basin (Escutia et al., 2011). Thus, it is likely that core DTGC2011 contains material from a wide area, including both the Mertz and Dumont d’Urville polynyas, and areas both near the coast and further offshore, meaning it is quite possible that the C$_{18}$ and C$_{24}$ FAs are integrating palaeoproductivity changes weighted towards different regional environments, which would explain their different trends. Furthermore, surface water CO$_2$ can vary spatially, such as in the Ross Sea polynya where Tortell et al. (2011) measured surface water CO$_2$ values ranging between 100 and 400 ppm. Thus, it is likely that these two areas offshore Adélie Land where the C$_{18}$ and C$_{24}$ FAs are being produced will also have differing surface water CO$_2$ concentrations and trends.

4.3 Comparison of fatty acid $\delta^{13}$C with other proxy data

Comparison of down-core variations in FA $\delta^{13}$C with other proxy data can also be used to decipher the main signal recorded. Comparison between $\delta^{13}$C$_{24\text{FA}}$ and the major diatom species abundances within the core (Fragilariopsis kerguelensis, Fragilariopsis curta, Fragilariopsis rhombica, Fragilariopsis cylindrus, Chaetoceros resting spores) shows a reasonably close coherence with Fragilariopsis kerguelensis, particularly since ~1800 C.E. (Fig. 6). Fragilariopsis kerguelensis is an open water diatom species and one of the most dominant phytoplankton species offshore Adélie Land (Chiba et al., 2000), reaching its peak abundance in the summer (Crosta et al., 2007). This suggests that the C$_{24}$ FA is being produced during the summer months and, as such, is reflecting productivity in more open waters. The $\delta^{13}$C$_{24\text{FA}}$ record does not show any similarity to the sea-ice records, as inferred by HBI diene concentrations and abundances of Fragilariopsis curta (Fig. 6 and 7), here again suggesting that these compounds are being produced in open water during the summer months after sea ice has retreated.

As discussed above, P. antarctica is a likely producer for the C$_{18}$ FA, a prymnesiophyte algae which has been observed in the Adélie region in summer months residing predominantly along the margin of fast ice, but also further offshore (Riaux-Gobin et al., 2013, 2011; Vaillancourt et al., 2003). The aversion of F. kerguelensis to sea ice (and thus also the C$_{24}$ FA producer) in contrast to P. antarctica, may explain the clear lack of coherence in the down-core trends in $\delta^{13}$C$_{18\text{FA}}$ and $\delta^{13}$C$_{24\text{FA}}$ (Fig. 7). Thus, we hypothesise that $\delta^{13}$C$_{18\text{FA}}$ is recording surface
water CO₂ driven by productivity in the MIZ, whilst δ¹³C₁₈FA is recording surface water CO₂ in more open
water, further from the sea-ice edge.

HBI diene concentrations indicate elevated fast ice cover between ~1919 and 1970 C.E., with a particular peak
between 1942 and 1970 C.E., after which concentrations rapidly decline and remain low until the top of the core
(Fig. 7). Abundances of F. curta, used as a sea-ice proxy, similarly show peaks at this time indicate increased
sea-ice concentration (Campagne, 2015) (Fig. 7). δ¹³C₁₈FA indicates a period of low productivity between ~1922
and 1977 C.E., broadly overlapping with this period of elevated fast ice concentration (Fig. 7), with a mean
value of -27.12‰. This is compared to the mean value of -26.23‰ in the subsequent period (~1978 to 1998
C.E.) during which HBI diene concentration remain low (Fig. 7). This suggests that productivity in the coastal
region was reduced, while sea-ice concentrations were high. This might be expected during a period of
enhanced ice cover – perhaps representing a reduction in the amount of open water, or a shorter open water
season – since the majority of productivity generally takes place within open water (Wilson et al., 1986).

Furthermore, δ¹³C₁₈FA shows a broad similarity with Chaetoceros resting spores (CRS) on a centennial scale,
with lower productivity at the start of the record, ca. 1587 to 1662 C.E., followed by an increase in both proxies
in the middle part of the record, where δ¹³C₁₈FA becomes relatively stable and CRS reaches its highest
abundances of the record. This is then followed in the latter part of the record, after ca. 1900 C.E., by both
proxies displaying lower values overall. CRS are associated with high nutrient levels and surface water
stratification along the edge of receding sea ice, often following high productivity events (Crosta et al., 2008).
The broad similarity to CRS, with lower values recorded during periods of high sea-ice concentrations, suggests
that δ¹³C₁₈FA is similarly responding to productivity in stratified water at the ice edge. This supports the
hypothesis that δ¹³C₁₈FA is recording primary productivity in the MIZ. Little similarity is evident between the
fatty acid isotope records and F. cylindrus and F. rhombica.

5 Conclusions

FAs identified within core DTGC2011, recovered from offshore Adélie Land, were analysed for their
concentrations and carbon isotope compositions to assess their utility as a palaeoproductivity proxy in an
Antarctic polynya environment. The C₁₈ and C₂₄ compounds yielded the best isotope measurements and show
very different δ¹³C trends, suggesting they are being produced by different species in different habitats and/or
seasons. Although we have made parsimonious interpretations, there are clearly uncertainties in interpreting the
FA δ¹³C, and, as such various assumptions have been made. The primary producers of the C₁₈ and especially the
C₂₄ FAs are a key source of uncertainty. Because these are general biomarkers, produced by many organisms, it
is impossible to constrain entirely to one producer class. But with further work in the region, it could be possible
further elucidate the most likely contributors. The possibility of inputs of FAs from multiple sources, in
particular from organisms further up the food chain, has consequences for their interpretation since this could
mean the δ¹³C FA is not fully reflecting just surface water conditions. Other key uncertainties are the magnitude
of upwelling of CO₂ at the site in comparison to drawdown by phytoplankton, and the potential role of changes
in air-sea CO₂ exchange.
Despite this, we argue that FA δ\(^{13}\)C has the potential to be used as a productivity proxy, but would be best used in parallel with other environmental proxies such as diatoms abundances or HBIs. Comparison with other proxy data and information from previous studies suggests that the C\(_{18}\) compound may be predominantly produced by *P. antarctica*, with δ\(^{13}\)C\(_{18}\)FA reflecting productivity changes in the marginal ice zone, where it is sensitive to changes in ice cover. In contrast, δ\(^{13}\)C\(_{24}\)FA, which compares well with abundances of the open water diatom *F. kerguelensis*, may be reflecting summer productivity further offshore, in open waters where it is less sensitive to fast ice changes. The use of δ\(^{13}\)C analysis of multiple FA compounds, as opposed to individual compounds or bulk isotope analysis, allows a more detailed insight into the palaeoproductivity dynamics of the region, with the potential to separate productivity trends within different habitats.

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**Author contributions:** K.E.A. wrote the paper with contributions and guidance from J.B., X.C., J.E. and S.E.G.; K.E.A. carried out the fatty acid molecular analyses (with support from U.I. and H.G.) and isotope analysis; P.C. and X.C. generated the diatom assemblage data, P.C. and G.M. generated the HBI analyses; S.S. performed the 210Pb analyses; X.C. and S.S. developed the age model. All authors contributed to the interpretations of data and finalization of the manuscript.

**Competing interests:** The authors have no competing interests.

**Data availability:** There is no restriction on data availability. Upon manuscript acceptance, all previously unpublished data will be added to the Supplement and made freely available at the NOAA NCDC data-base: [https://www.ncdc.noaa.gov/data-access/paleoclimatology-data/datasets](https://www.ncdc.noaa.gov/data-access/paleoclimatology-data/datasets).

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Figure 1: Location of Site DTGC2011 on bathymetric map of the Adélie Land region (modified from Beaman et al., 2011), indicating positions of the main glaciers (prior to Mertz Glacier Tongue collapse in 2010) and pathways of the main water masses affecting the region: Antarctic Slope Current (ASC), Modified Circumpolar Deep Water (mCDW) and High Shelf Salinity Water (HSSW) (Williams and Bindoff, 2003).
Figure 3: $R^2$ values for fatty acid concentrations throughout core DTGC2011. Values are colour coded according to the key on the left. Black border denotes correlations within each group.

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Figure 4: $R^2$ values for fatty acid concentrations in core DTGC2011 below 25 cm only. Values are colour coded according to the key on the left. Black border denotes correlations within each group.

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<tr>
<th></th>
<th>C16</th>
<th>C17</th>
<th>C18</th>
<th>C20</th>
<th>C22</th>
<th>C24</th>
<th>C26</th>
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<tr>
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<td>0.73</td>
<td>0.93</td>
<td>0.21</td>
<td>0.07</td>
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Figure 5: Concentrations of the C$_{18}$ fatty acid (blue), the HBI triene (red), HBI diene (grey) (Campagne, 2015), C$_{24}$ fatty acid (orange) from core DTGC2011. The left-hand panels show 1550 to 1950 C.E. and the right hand panels show 1950 to 2000 C.E., plotted on different y-axes due to the elevated concentrations in the top part of the core. Grey vertical bands highlight coincident peaks in C$_{18}$ fatty acid and HBI triene records.
Figure 6: δ¹³C values of the C₂₄ fatty acid (orange) and relative abundances (%) of the open water diatom *Fragilariopsis kerguelensis* (green). Also shown are relative abundances of the four most abundant diatom groups in DTGC2011. *Chaetoceros* resting spores (CRS; grey line), *Fragilariopsis curta* group (dark blue line), *Fragilariopsis cylindrus* (purple line) and *Fragilariopsis rhombica* (light blue line). Thick line represents 3-point moving average for each. Grey vertical bands highlight periods where C₂₄ fatty acid δ¹³C is in phase with *F. kerguelensis*. 
Figure 7: $\delta^{13}C$ of the C$_{24}$ (orange) and C$_{18}$ (blue) fatty acid, HBI diene concentrations (green; plotted on a log scale) and relative abundances of Fragilariopsis curta plus Fragilariopsis cylindrus (purple). Latter two records reflect sea ice concentrations. Grey vertical band highlights period where low C$_{18}$ $\delta^{13}C$ overlaps with elevated HBI diene concentrations.