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 CO_2 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 CO_2, especially in the context of projected changes in coastal Antarctic sea ice. Here we investigate the potential for using carbon isotopes ($\delta^{13}C$) 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 $\delta^{13}C$ of fatty acids along with other proxy data from the same core. We discuss the different possible drivers of their variability and argue that C_{24} fatty acid $\delta^{13}C$ predominantly reflects phytoplankton productivity in open water environments, while C_{18} fatty acid $\delta^{13}C$ 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 CO_2 to be upwelled to the surface. In the absence of biological activity, most of the CO_2 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 CO_2 to low levels through photosynthesis (Arrigo and van Dijken, 2003; Arrigo et al., 2008), resulting in surface water CO_2 undersaturation with respect to atmospheric CO_2 (Tortell et al., 2011). The subsequent export and burial of the organic carbon produced during these intense phytoplankton blooms can significantly lower atmospheric CO_2 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 CO_2 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 CO_2 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 ($\delta^{13}C$) of freely extractable (using a standard solvent extraction protocol), 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 palaeoproductivity 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 pCO_2 in the Ross Sea was associated with a variation in the $\delta^{13}C$ of sedimentary organic carbon and sterol biomarkers, most likely due to a change in isotopic fractionation associated with the photosynthetic drawdown of CO_2. Their results demonstrate that the spatial variation in surface water CO_2 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 ^{210}Pb 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 $\delta^{13}C$ 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 CO_2 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 using dichloromethane/methanol (3:1 v/v) and ultrasonication. 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 FA 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. FA 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 FAs and the internal standard were used to calculate the concentration of each compound.

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

$$\delta 13C\ (‰) = ((12C/13C)\mathrm{sample}\ /\ (12C/13C)\mathrm{standard}\ -1) \times 1000$$

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 FA ester mix (F8; Indiana University) containing eight FA 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 δ^{13}C value of the FAME. The δ^{13}C of the FA (δ^{13}CFA) and FAME (δ^{13}CFAME) were used to calculate the δ^{13}C of the MeOH (δ^{13}CMeOH) as follows:

$$\delta^{13}\mathrm{CMeOH} = (\mathrm{nFAME} * \delta^{13}\mathrm{CFAME}) - (\mathrm{nFA} * \delta^{13}\mathrm{CFA})$$

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 δ^{13}CFAME values were corrected using:

$$\delta^{13}\mathrm{CFA} = ((\mathrm{nFAME} * \delta^{13}\mathrm{CFAME}) + 40.8)\ /\ \mathrm{nFA}$$

HBIs

Two hundred and thirty-four samples were taken every 2 cm over the whole core for highly branched isoprenoids (HBI) alkenes analysis. HBIs were extracted at Laboratoire d'Océanographie et du Climat: Experimentations et Approches Numériques (LOCEAN), separately from the fatty acids, using a mixture of 9mL CH_2Cl_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_2Cl_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 chomatograph (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

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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_{16} to C_{20}; SCFAs) and long-chained fatty acids (C_{22} to C_{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^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^2 values between 0.97 and 0.99, while R^2 values of LCFAs range between 0.88 and 0.95. Between the two groups, however, R^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^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^2 values are not quite as high, they broadly confirm these groupings, with the R^2 values generally being greater within the two groups (n = 73). R^2 values range from 0.93 for the C_{18} with C_{20}, down to 0.07 for the C_{18} and C_{24} (Fig. 4).

The C_{18} and C_{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 ($R^2 = 0.5$) and below 25 cm ($R^2 = 0.07$), 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_{18} and C_{24}) will be the focus of analysis and discussion.

3.2 Potential sources of the C_{18} fatty acid

Potential sources for the C_{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 $\delta^{13}C$ 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 C$_{18}$ FA in the Adélie basin though minor contributions of C$_{18}$ from other phytoplankton species such as the diatoms and dinoflagellates or even bacteria cannot be excluded (Table S2).

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3.3 Potential sources of the C$_{24}$ 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 diagenetic effects on fatty acid concentration

Both the C$_{18}$ and C$_{24}$ 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 diagenetic 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).

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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 IPSO$_{25}$ 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 thesediments including sulphurisation (Sinninghe Damsté 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 C_{18} 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 C_{18} FA and HBI triene concentrations (Fig. 5) suggests that the C_{18} may also be produced by an organism associated with the retreating ice edge. *Phaeocystis antarctica* has been proposed as a potential producer of the C_{18} 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 C_{18} and HBI triene concentrations, both produced by organisms occupying a similar habitat at the ice edge.

The C_{24} 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 C_{24} and C_{18} FA concentrations. However, it may relate to the progressive effect of diagenesis through the core. There is less similarity between the C24 and both the HBI triene also HBI diene, (compared to the coherence between C18 FA and HBI triene), which suggests that the C24 FA is predominantly produced by an organism which is not associated with sea ice, and thus instead with more open waters. Seventy-three diatom species were encountered in core DTGC2011 (Campagne, 2015), with *Fragilariopsis curta* and *Chaetoceros* resting spores being the most abundant. However, trends in diatom abundances do not show any clear correlations with the C_{18} or C_{24} FA concentrations. While this would lend support to the hypothesis that diatoms are not the main producers of these compounds, the differing effects of diagenesis on the preservation of diatoms and lipids could also explain some of the differences in observed 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 silicified 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 $\delta^{13}C$ for the C_{18} and C_{24} FAs ($\delta^{13}C_{18FA}$ and $\delta^{13}C_{24FA}$, respectively) (Fig. 7) clearly show different trends, with very little similarity between them ($R^2 = 0.016$). 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 $\delta^{13}C_{18FA}$ 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 $\delta^{13}C_{18FA}$ and $\delta^{13}C_{24FA}$ 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 $\delta^{13}C_{18FA}$ mean value over the $\delta^{13}C_{24FA}$ 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 CO_2 utilisation than in surrounded open waters (Henley et al., 2012). Although no studies on FA $\delta^{13}C$ of different organisms are available for the Southern Ocean, Budge et al. (2008) measured the mean $\delta^{13}C$ value of C_{16} FA from Arctic sea-ice algae (-24.0 ‰) to be 6.7 ‰ higher than pelagic phytoplankton (-30.7 ‰) from the same region.

The higher $\delta^{13}C$ of the C_{18} 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 $\delta^{13}C_{24FA}$ suggests it is more likely to be produced by phytoplankton predominantly within open water.

4.1 Controls on $\delta^{13}C_{FA}$

The $\delta^{13}C_{18FA}$ 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 $\delta^{13}C$ values between 1921 and 1977 C.E. and a rapid shift toward more positive values thereafter. In contrast, the $\delta^{13}C_{24FA}$ 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 $\delta^{13}C$ are likely to be a function of either the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) source, changes in the species producing the biomarkers, diagenesis or changing photosynthetic fractionation (ε_p). The next section outlines the potential influence of these factors may have in order to assess the mostly likely dominant driver of FA $\delta^{13}C$.

4.1.1 Isotopic composition of DIC

The $\delta^{13}C$ of the DIC source can be affected by upwelling or advection of different water masses, or the $\delta^{13}C$ of atmospheric CO_2. 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 $\delta^{13}C$ 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 $\delta^{13}C$ recorded by both C_{18} and C_{24} 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 $\delta^{13}C$ 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 $\delta^{13}C$ of atmospheric CO_2, which is in exchange with the surface waters could also have the potential to drive changes in the $\delta^{13}C$ of algal biomarkers. Over the last ca. 200 years, the anthropogenic burning of fossil fuels has released of a large amount of CO_2 depleted in ^{13}C, meaning that the $\delta^{13}C$ of CO_2 has decreased by ca. 1.5 ‰, as recorded in the Law Dome ice core. Prior to this, however, the $\delta^{13}C$ of CO_2 in the atmosphere remained relatively stable, at least for the last thousand years (Francey et al., 1999). Therefore, this could potentially drive the $\delta^{13}C$ 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 $\delta^{13}C$ measured throughout the core. Although the C_{24} $\delta^{13}C$ shows a slight decrease over the last ca. 100 years, this is preceded by increasing $\delta^{13}C$, while the C_{18} $\delta^{13}C$ displays no clear trend over the last 200 years. If atmospheric CO_2 was a key driver of fatty acid $\delta^{13}C$, 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 $\delta^{13}C$ of atmospheric CO_2 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 $\delta^{13}C$ where species have different fractionation factors. For example, changing diatom species have been shown to have an effect on bulk organic matter $\delta^{13}C$ 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 $\delta^{13}C$ values and fractionation factors. Here we measured $\delta^{13}C$ of individual biomarkers, produced by a more restricted group of phytoplankton groups (possibly restricted to a few dominant species) compared to bulk $\delta^{13}C$. As discussed above, the C_{18} 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 $\delta^{13}C$*

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 $\delta^{13}C$, ranging between 2.6 ‰ for the $C_{14:0}$ and as much as 6.9‰ in the $C_{18:1}$, under anoxic conditions. This suggests that diagenesis could affect FA $\delta^{13}C$ in core DTGC2011. However, these observed changes are rapid (days to months), occurring on timescales which are unresolvable in the FA $\delta^{13}C$ 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 $\delta^{13}C_{24FA}$ values increase by ~2.5 ‰, downward ($R^2 = 0.63$, n = 11) while the $\delta^{13}C_{18FA}$ values display a large variation with no overall trend ($R^2 = 0.12$, n = 20). If diagenesis was driving the changes in $\delta^{13}C$, it is likely that this trend would be observed in all FA compounds.

Taken together, it appears that neither changes in the $\delta^{13}C$ of the DIC, changing phytoplankton groups nor diagenesis can fully explain the variation of FA $\delta^{13}C$ recorded within DTGC2011. Therefore, we hypothesise that changes in ε_p are the main driver of FA $\delta^{13}C$.

4.2 Controls on photosynthetic fractionation (ε_p)

There is a positive relationship between ε_p in marine algae and dissolved surface water $CO_{2(aq)}$ concentration (Rau et al., 1989). As a result, higher $\delta^{13}C$ values are hypothesised to reflect lower surface water $CO_{2(aq)}$ and vice versa. Popp et al. (1999) showed a strong negative correlation between $CO_2(aq)$ and $\delta^{13}C$ of suspended particulate organic matter across a latitudinal transect in the Southern Ocean, suggesting that changes in surface water $CO_2(aq)$ can explain a large amount of the variation in $\delta^{13}C$. Changes in surface water $CO_{2(aq)}$ concentration in turn may be driven by various factors, including changing atmospheric CO_2 (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 CO_2 changes offshore Adélie Land should enable interpretation of the DTGC2011 FA $\delta^{13}C$ records.

4.2.1 *Sea ice*

Brine channels within sea ice have very low CO_2 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 $\delta^{13}C$ values. It is thus possible that, under conditions of high sea-ice cover, enhanced FA contribution from sea-ice algae leads to elevated sedimentary $\delta^{13}C$ 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 $\delta^{13}C$ concentrations in either $\delta^{13}C_{18FA}$ or $\delta^{13}C_{24FA}$, both instead showing generally lower $\delta^{13}C$ values. In fact, $\delta^{13}C_{18FA}$ 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 $\delta^{13}C$.

The DTGC2011 core site sits proximal to the Dumont D'Urville polynya, which has a summer area of 13.02 x 10^3 km^2 and a winter area of 0.96 x 10^3 km^2 (Arrigo and van Dijken, 2003). Changes in the size of the polynya both on seasonal and inter-annual time scales will affect air-sea CO_2 exchange and thus also surface water CO_2 concentration. A reduced polynya may lead to greater supersaturation of CO_2 in the surface waters due to reduced outgassing, allowing CO_2 to build up below the ice, leading to lower δ^{13}C values of algal biomarkers produced in that habitat (Massé et al., 2011). Thus changes in the extent of sea ice may also effect FA δ^{13}C.

4.2.2 Observed trends in surface water $CO_{2(aq)}$

If the trend in surface water $CO_{2(aq)}$ paralleled atmospheric CO_2, 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 $CO_{2(aq)}$ concentration, resulting in more negative δ^{13}C values. Taking into account the decline in atmospheric $\delta^{13}CO_2$ over the same period would further enhance the reduction in phytoplankton δ^{13}C. Fischer et al. (1997) looked at the δ^{13}C of both sinking matter and surface sediments in the South Atlantic and suggested that, since the preindustrial, surface water $CO_{2(aq)}$ has increased much more in the Southern Ocean than in the tropics. They estimated that a 70 ppm increase in $CO_{2(aq)}$ in surface waters of 1°C would decrease phytoplankton $\delta^{13}C_{org}$ by ca. 2.7‰, and up to 3.3‰ $\delta^{13}CO_2$ 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 CO_2 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 CO_2 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 CO_2 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 CO_2 of ca. 25 ppm is observed over these 11 years, coincident with the 20 ppm atmospheric CO_2 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 CO_2 trend alone.

During the austral winter, upwelling of deep water masses causes CO_2 to build up in the surface waters, and sea ice cover 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 CO_2. Roden et al. (2013) also observed varying levels of winter supersaturation in Prydz Bay, East Antarctica, with late winter CO_2 values of 433 ppm in 2011 (45 μatm higher than atmospheric CO_2), and suggested that intrusions of C-rich mCDW onto the shelf may play a part in this. Similarly, winter surface water CO_2 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 CO_2, increasing CO_2 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 CO_2 and hence FA $\delta^{13}C$ 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 CO_2 supersaturation in regional surface waters (Shadwick et al., 2014). In contrast, the phytoplankton producing FA thrive during the spring and summer months during which CO_2 is rapidly drawn down and the surface waters become undersaturated. However, upwelling cannot be discarded as a possible contributor to surface water CO_2 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 CO_2 concentration and $\delta^{13}C$ of the source appear to be unlikely to be a dominant driver of the FA $\delta^{13}C$ record, with interannual variations driven by other factors overriding any longer-term trend. There is also no clear anthropogenic decline in the FA $\delta^{13}C$ record over the last 200 years, which supports this hypothesis.

4.2.3 Productivity

Given that changes in atmospheric CO_2, source signal, sea ice algae or diagenesis seem unable to explain the full range of variability seen in the FA $\delta^{13}C$ 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 CO_2 in the surface waters, resulting in reduced fractionation by the phytoplankton during photosynthesis (Villinski et al., 2008). In the Ross Sea, surface water CO_2 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 CO_2 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 CO_2 drawdown in the MGP during the summer months.

Therefore, we suggest that FA $\delta^{13}C$ signals recorded in DTGC2011 is predominantly a signal of surface water CO_2 driven by primary productivity. Indeed, the potential for the $\delta^{13}C$ of sedimentary lipids to track surface water primary productivity has been recognised in the highly productive Ross Sea polynya. High variability in surface water CO_2 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 CO_2 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) $\delta^{13}C$, 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 δ^{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 δ^{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 δ^{13}C with other proxy data

Comparison of down-core variations in FA δ^{13}C with other proxy data can also be used to decipher the main signal recorded. Comparison between δ$^{13}C_{24FA}$ 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 δ$^{13}C_{24FA}$ 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 δ$^{13}C_{18FA}$ and δ$^{13}C_{24FA}$ (Fig. 7). Thus, we hypothesise that δ$^{13}C_{18FA}$ is recording surface water CO_2 driven by productivity in the MIZ, whilst δ$^{13}C_{24FA}$ is recording surface water CO_2 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). $\delta^{13}C_{18FA}$ 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, $\delta^{13}C_{18FA}$ 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 $\delta^{13}C_{18FA}$ 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 $\delta^{13}C_{18FA}$ is similarly responding to productivity in stratified water at the ice edge. This supports the hypothesis that $\delta^{13}C_{18FA}$ 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 C_{18} and C_{24} compounds yielded the best isotope measurements and show very different $\delta^{13}C$ 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 $\delta^{13}C$, and, as such various assumptions have been made. The primary producers of the C_{18} and especially the C_{24} 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 $\delta^{13}C$ FA is not fully reflecting just surface water conditions. Other key uncertainties are the magnitude of upwelling of CO_2 at the site in comparison to drawdown by phytoplankton, and the potential role of changes in air-sea CO_2 exchange.

Despite this, we argue that FA $\delta^{13}C$ 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 $\delta^{13}C_{18FA}$ reflecting productivity changes in the marginal ice zone, where it is sensitive to changes in ice cover. In contrast, $\delta^{13}C_{24FA}$, which compares well with abundances of the open water diatom *F*

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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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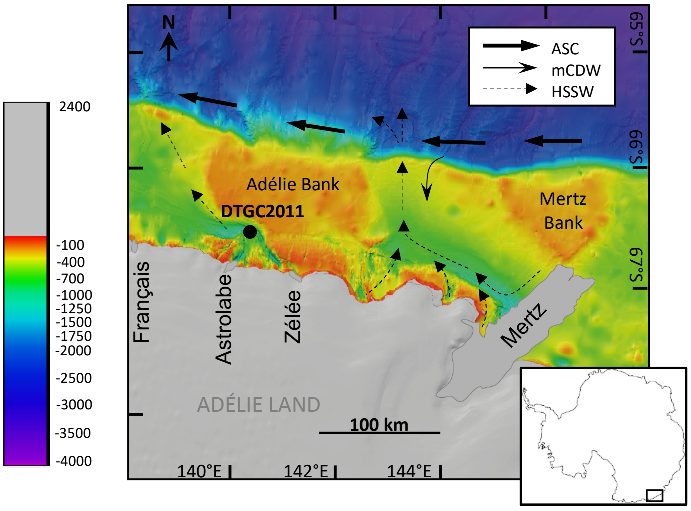
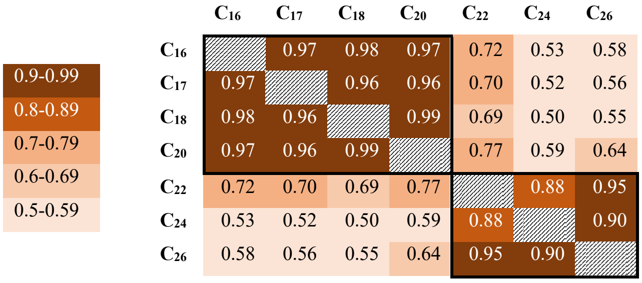


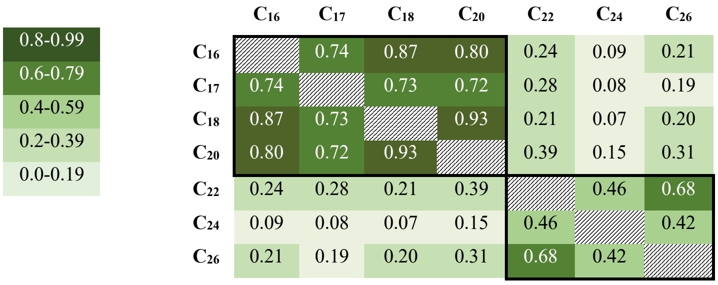
Figure 1: Location of Site DTGC2011 on bathymetric map of the Adélie Land region (modified from Beaman et al., 2011), indicating positions of the main glaciers (prior to Mertz Glacier Tongue collapse in 2010) and pathways of the main water masses affecting the region: Antarctic Slope Current (ASC), Modified Circumpolar Deep Water (mCDW) and High Shelf Salinity Water (HSSW) (Williams and Bindoff, 2003).



0.9-0.99
0.8-0.89
0.7-0.79
0.6-0.69
0.5-0.59

	C_{16}	C_{17}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}
C_{16}	▨	0.97	0.98	0.97	0.72	0.53	0.58
C_{17}	0.97	▨	0.96	0.96	0.70	0.52	0.56
C_{18}	0.98	0.96	▨	0.99	0.69	0.50	0.55
C_{20}	0.97	0.96	0.99	▨	0.77	0.59	0.64
C_{22}	0.72	0.70	0.69	0.77	▨	0.88	0.95
C_{24}	0.53	0.52	0.50	0.59	0.88	▨	0.90
C_{26}	0.58	0.56	0.55	0.64	0.95	0.90	▨

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.



0.8-0.99
0.6-0.79
0.4-0.59
0.2-0.39
0.0-0.19

	C_{16}	C_{17}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}
C_{16}	▨	0.74	0.87	0.80	0.24	0.09	0.21
C_{17}	0.74	▨	0.73	0.72	0.28	0.08	0.19
C_{18}	0.87	0.73	▨	0.93	0.21	0.07	0.20
C_{20}	0.80	0.72	0.93	▨	0.39	0.15	0.31
C_{22}	0.24	0.28	0.21	0.39	▨	0.46	0.68
C_{24}	0.09	0.08	0.07	0.15	0.46	▨	0.42
C_{26}	0.21	0.19	0.20	0.31	0.68	0.42	▨

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.

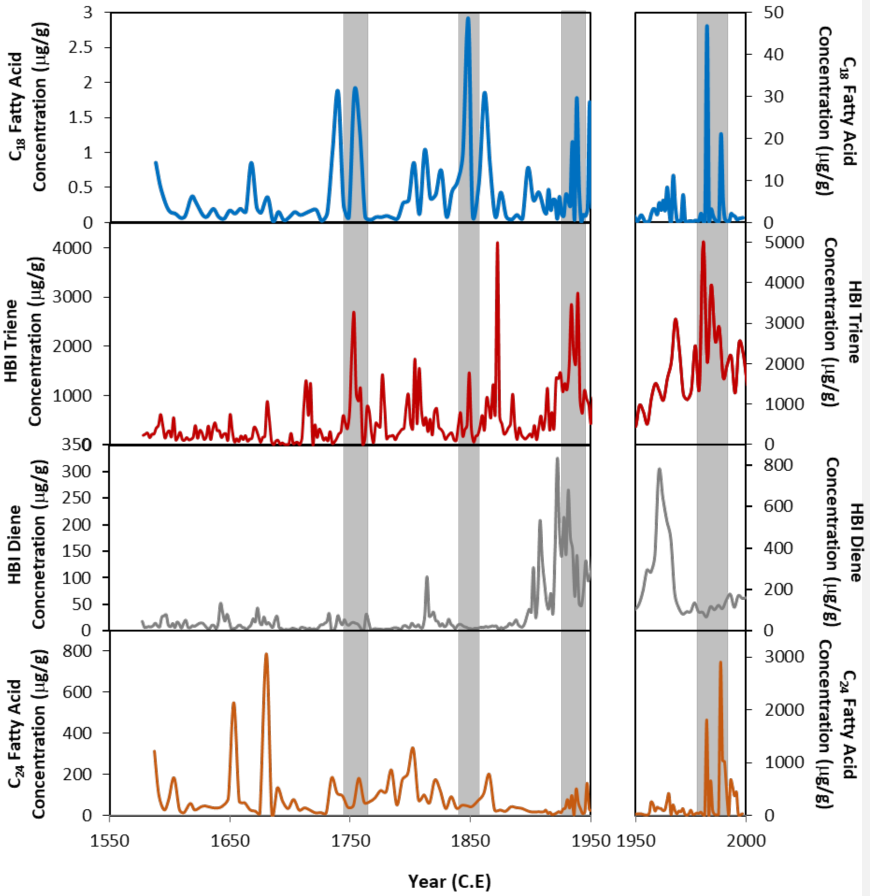


Figure 5: Concentrations of the C_{18} fatty acid (blue), the HBI triene (red), HBI diene (grey) (Campagne, 2015), C_{24} fatty acid (orange) from core DTGC2011. The left-hand panels show 1550 to 1950 C.E. and the right hand panels show 1950 to 2000 C.E., plotted on different y-axes due to the elevated concentrations in the top part of the core. Grey vertical bands highlight coincident peaks in C_{18} fatty acid and HBI triene records.

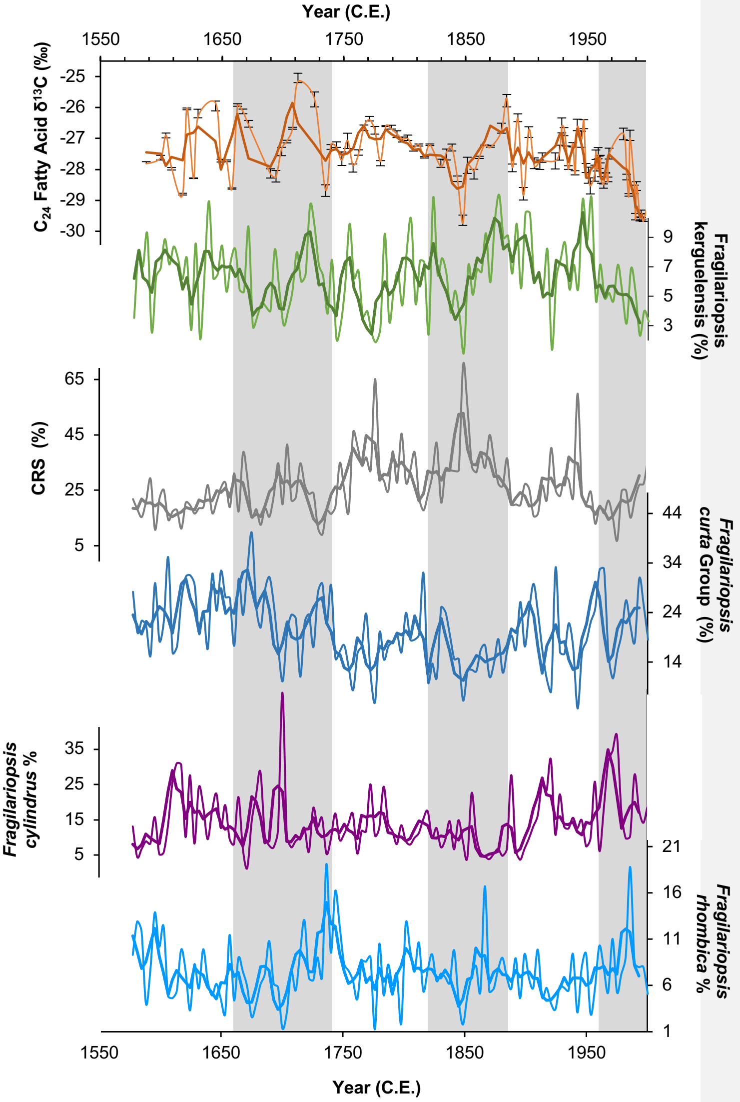


Figure 6: **δ^{13}C values of the C$_{24}$ fatty acid (orange) and relative abundances (%) of the open water diatom *Fragilariopsis kerguelensis* (green). Also shown are relative abundances of the four most abundant diatom groups in DTGC2011. *Chaetoceros* resting spores (CRS; grey line), *Fragilariopsis 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 C$_{24}$ fatty acid δ^{13}C is in phase with *F. kerguelensis*.**

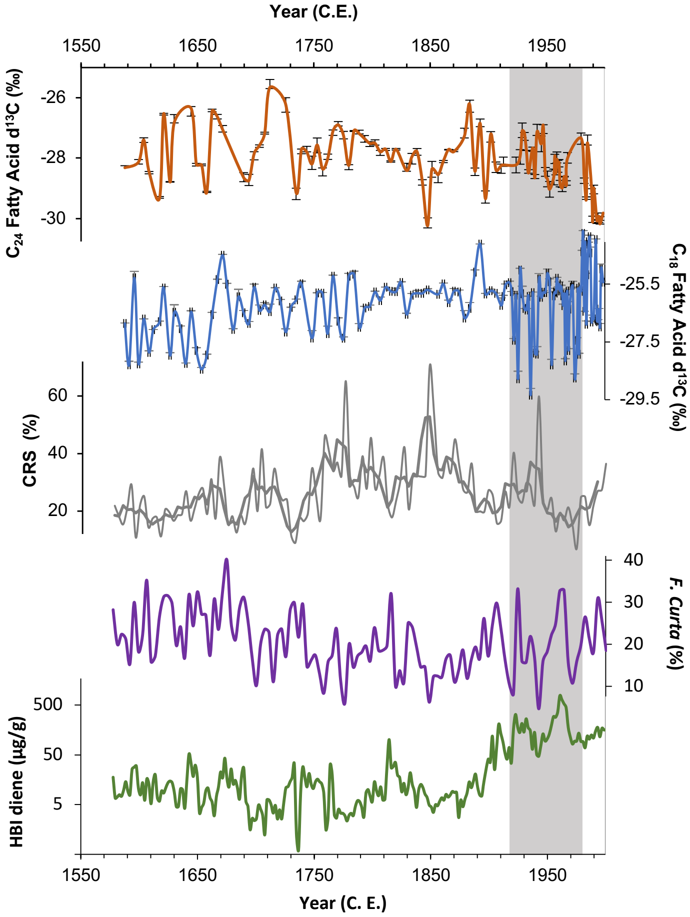


Figure 7: δ^{13}C of the C$_{24}$ (orange) and C$_{18}$ (blue) fatty acid, HBI diene concentrations (green; plotted on a log scale) and relative abundances of *Fragilariopsis curta* plus *Fragilariopsis cylindrus* (purple). Latter two records reflect sea ice concentrations. Grey vertical band highlights period where low C$_{18}$ δ^{13}C overlaps with elevated HBI diene concentrations.