**Fatty acid carbon isotopes: a new indicator of marine Antarctic paleoproductivity?**

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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 C₃₄ 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 algal fatty acids (FAs) in marine sediments as a potential integrative proxy for reconstructing primary productivity in a polynya environment. 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), but is also directly downwind and downcurrent of the much larger and highly productive Mertz Glacier polynya (MGP) to the east (Arrigo and van Dijken, 2003).

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 in methanol and subsequently cleaned up using a silica gel column and the FAs eluted with dichloromethane. FAs were identified using an Agilent gas chromatograph coupled to an Agilent mass selective detector and concentrations were quantified using a gas chromatograph – flame ionization detector analysis with the inclusion of an internal standard (C19 alkane) of known concentration. Carbon isotopes were measured with an Isoprime 100 isotope ratio mass spectrometer coupled to an Agilent gas chromatograph–flame ionization detector and a GC5 furnace. Errors are based on the standard deviation of duplicate measures and are all within 0.26‰.

HBIs

Two hundred and thirty-four samples were taken every 2 cm over the whole core for highly branched isoprenoids (HBI) alkenes analysis. HBI were extracted at Laboratoire d’Océanographie et du Climat: Expérimentations et Approches Numériques (LOCEAN), separately from the fatty acids, using a mixture of 9mL CH2Cl2/MeOH (2:1, v:v) to which internal standards were added and applying several sonication and centrifugation steps in order to extract properly the selected compounds (Etourneau et al., 2013). After drying with N2 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 CH2Cl2/MeOH (1:1, v:v), respectively. HBIs were obtained from the apolar fraction by the fractionation over a silica column using hexane as eluent following the procedures reported by (Belt et al., 2007, Massé et al., 2011). After removing the solvent with N2 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 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

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. 4). 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. 2; 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, 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. 3).

The C_{16} 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 (C18 and C24) will be the focus of analysis and discussion.

3.2 Potential sources of the C18 fatty acid

Potential sources for the C18 FA in core U1357 (recovered from the same site as DTGC2011) are discussed in Ashley et al. (in review) who suggest the prymnesiophyte Phaeocystis antarctica to be the most likely main producer based on a) previous studies (Dalsgaard et al., 2003), b) the high observed abundance of P. antarctica within modern Adélie surface waters (Riaux-Gobin et al., 2011) and c) comparison between the measured δ13C 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).

Dalsgaard et al. (2003) looked at the FAs of eight major microalgal classes and showed that Prymnesiophyceae and Dinophyceae produce the highest proportions of the saturated C18 FA, the former to which P. antarctica belongs. They also showed that the majority of FAs produced were the unsaturated form which are preferentially broken down in the water column and sediments. As such, although the C18 FA represents only a small proportion of the total FA fraction, its higher preservation rate increases its proportion in the sediment.

Riaux-Gobin et al. (2011) found P. antarctica to dominate the surface waters offshore Adélie Land after spring sea-ice break-up, representing 16% of the phytoplankton assemblage. Although several species of the class Dinophyceae were also recorded, P. antarctica was more than 20 times more abundant than the 3 most abundant Dinophyceae taxa combined. Sambrotto et al. (2003) also observed large blooms of Phaeocystis sp. in stable, shallow mixed layer water along the edge of fast ice near the Mertz Glacier.

Furthermore, Skerratt et al. (1998) identified the FAs produced by P. antarctica and two Antarctic diatoms, Chaetoceros simplex and Odontella weissflogii, from culture samples. Of the FAs produced by P. antarctica, 52% were saturated FAs (C14–C20) compared to just 14 and 11% for the two diatoms, respectively, the latter instead producing much more of the mono- and polyunsaturated FAs. The percentage of C18 FA produced by P. antarctica was also 4.1 and 12.5 times greater than the percentage of C18 produced by C. simplex and O. weissflogii, respectively. 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 dinofflagellates cannot be excluded.

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 entirely possible, especially considering the highly productive nature of this region.

3.4 Microbial degradation and diagenetic effects on fatty acid concentration

Both the C₁₄ and C₁₆ 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. 4).

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 concentration 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.

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
correlation 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 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. 4 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, as well as reacting with sediments resulting in 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 better preservation at the
top of the core, with diagenetic effects having an increasing and progressive impact down to ca. 25 cm 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 (Cabezo 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., in review). 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_{18} 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 better preservation in younger samples. The weaker coherence between the C_{24} and the HBI triene, and also HBI diene, suggests that the C_{24} 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 adelensis, 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 δ¹³C for the C₁₈ and C₂₄ FAs (δ¹³C₁₈FA and δ¹³C₂₄FA, respectively) (Fig. 6 and 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., in review) 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, 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 C₁₈ 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 rapid a 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. 6 and 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 nCDW 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 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 lighter 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. No clear trend towards lighter values is evident in the last 200 years of the FA $\delta^{13}$C records, which suggests that this change 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 C18 appears to be produced predominantly by *P. antarctica*, whereas diatoms do not tend to produce 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 C14:0 and as much as 6.9 ‰ in the C18:1, 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 resolvable 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. 4). In the top 25 cm of the core, the $\delta^{13}$C$_{FA}$ values increase by ~2.5 ‰ downward ($R^2 = 0.63, n = 11$) while the $\delta^{13}$C$_{FA}$ 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 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. 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 10^4 km^2 and a winter area of 0.96 x 10^4 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 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 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 δ$^{13}$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 δ$^{13}$C of the source appear to be unlikely to be a dominant driver of the FA δ$^{13}$C record, with interannual variations driven by other factors overriding any longer-term trend. There is also no clear anthropogenic decline in the FA δ$^{13}$C 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 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) δ¹³C and algal sterol δ¹³C, all of which show significantly higher values in the western Ross Sea. This spatial pattern in sterol δ¹³C was concluded to be directly related to CO₂ drawdown at the surface, resulting in average sterol δ¹³C 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 δ¹³C was found to be positively correlated with POC concentration and negatively correlated with nutrient concentration, indicating greater drawdown of CO₂ and nutrients under high productivity levels (Zhang et al., 2014).

This suggests it is possible to apply FA δ¹³C as a palaeoproduction 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 from 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 C₁₈ and C₁₆ FAs are integrating palaeoproduction changes weighted towards different regional environments, which would explain their different trends. Furthermore, surface water CO₂ can vary spatially, such as in the Ross Sea polynya where Tortell et al. (2011) measured surface water CO₂ values ranging between 100 and 400 ppm. Thus, it is likely
that these two areas offshore Adélie Land where the C18 and C24 FAs are being produced will also have differing surface water CO2 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 $\delta^{13}C$FA and the major diatom species abundances within the core 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 C24 FA is being produced during the summer months and, as such, is reflecting productivity in more open waters. The $\delta^{13}C$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 C18 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 C24 FA producer) in contrast to *P. antarctica*, may explain the clear lack of coherence in the down-core trends in $\delta^{13}C$FA and $\delta^{13}C$FA (Fig. 7). Thus, we hypothesise that $\delta^{13}C$FA is recording surface water CO2 driven by productivity in the MIZ, whilst $\delta^{13}C$FA 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). $\delta^{13}C$FA 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, $\delta^{13}C$FA 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 $\delta^{13}C$FA 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.

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.

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.s keruelensis*, may be reflecting summer productivity further offshore, in open waters where it is less sensitive to fast ice changes. We argue that FA $\delta^{13}$C can be used as a productivity proxy, but should be used in parallel with other proxies such as diatoms abundances or HBIs. The use of $\delta^{13}$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.

However, there are clearly uncertainties in interpreting the FA $\delta^{13}$C, and although we have made parsimonious interpretations, many assumptions have been made here. The producers of the C$_{18}$ and especially the C$_{24}$ FAs is a key source of uncertainty and will require further work to further elucidate. 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.

References


Zhang, R., Zheng, M., Chen, M., et al. (2014) An isotopic perspective on the correlation of surface ocean carbon...

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 2: $R^2$ 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.
Figure 3: $R^2$ 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 4: Fatty acid concentrations (μg/g of dry sediment) with depth from core DTGC2011
a) C16 and C18 fatty acids b) C17 and C20 fatty acids c) C22, C24 and C26 fatty acids.
Figure 5: Concentrations of the C18 fatty acid (blue), the HBI triene (red), HBI diene (grey) (Campagne, 2015), C24 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 C18 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: δ¹³C of the C₂₄ (orange) and C₁₈ (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 C₁₈ δ¹³C overlaps with elevated HBI diene concentrations.