2016-05

Distributions of highly branched isoprenoid alkenes and other algal lipids in surface waters from East Antarctica: Further insights for biomarker-based paleo sea-ice reconstruction

Smik, L

10.1016/j.orggeochem.2016.02.011
ORGANIC GEOCHEMISTRY
Elsevier BV

Distributions of highly branched isoprenoid alkenes and other algal lipids in surface waters from East Antarctica: further insights for biomarker-based paleo sea-ice reconstruction

Lukas Smik [a], Simon T. Belt [a,*], Jan L. Lieser [b], Leanne K. Armand [c], Amy Leventer [d]

[a] *School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK*

[b] *Antarctic Climate & Ecosystems Cooperative Research Centre, University of Tasmania, Hobart, Tasmania, Australia*

[c] *Department of Biological Sciences, Faculty of Science and Engineering, Macquarie University, North Ryde, NSW, 2109, Australia*

[d] *Department of Geology, Colgate University, Hamilton, New York, 13346, USA*

* Author for correspondence. Tel.: +44 (0)1752 584959; Fax: +44 (0)1752 584709.

E mail address: sbelt@plymouth.ac.uk (Simon Belt).

ABSTRACT

The occurrence and variable abundance of certain di- and tri-unsaturated C_{25} highly branched isoprenoid (HBI) biomarkers in Antarctic marine sediments has previously been proposed as a possible proxy measure of paleo sea-ice extent in the Southern Ocean. In the current study, we obtained 47 near-surface (ca. 0–10 m) water samples taken from locations in East Antarctica with different sea ice settings and analysed them for their HBI, sterol and fatty acid content. Sampling locations ranged from the permanently open-ocean zone (POOZ), with no seasonal sea-ice cover, the near-shore summer sea ice zone (SIZ), where sea ice remains long into the summer melt season, and the marginal ice zone (MIZ), located between the POOZ and the SIZ, and with a highly variable latitudinal sea-ice edge throughout the season. A di-unsaturated C_{25} HBI (diene II) was only identified in surface waters from the MIZ and the SIZ, consistent with a sea-ice diatom origin for this biomarker. In contrast, a tri-unsaturated C_{25} HBI (triene III) was detected in all samples from the POOZ, the MIZ and the SIZ, and with a stable isotopic composition ($\delta^{13}C = -35 \pm 1.5‰$) consistent with a phytoplankton source. The highest concentrations of diene II and triene III were in samples from the SIZ and the MIZ, respectively, thus providing further insights into the sea-ice conditions likely favourable for their production and how their relative abundances (the II/III ratio) in underlying sediments might be better interpreted for paleo sea-ice reconstruction. In this respect, relatively high II/III might be a good indicator of extended (into summer) seasonal sea-ice cover, while lower II/III may provide a better indicator of the MIZ. However, the observation of highly variable II/III within the polynya setting of the SIZ may also have

significant impacts on sedimentary values. Distributions of diatom sterols and fatty acids were also variable between the three sampling zones, but these were not as distinctive as those observed for the HBIs.

Keywords: Antarctic; Sea Ice; Proxy; Highly Branched Isoprenoid; HBI alkenes; Diatom

1. Introduction

Southern Ocean sea ice is critical to Earth's climate regulation. It is one of the most seasonal and variable features of the Earth's surface, and has a significant influence on key oceanic and atmospheric processes, which in turn drive global climate (Brandon et al., 2010; Comiso, 2010). Determining the paleo sea-ice record is widely recognised as critical to elucidating past (and future) climate conditions (Dieckmann and Hellmer, 2010; Vaughan et al., 2013). According to the Intergovernmental Panel on Climate Change, the lack of paleo sea-ice records from the Southern Ocean hinders modern climate modelling efforts, yet some models suggest that Antarctic sea-ice extent will reduce by 24% and more than a third in terms of total volume by 2100 (Turner et al., 2009; Vaughan et al., 2013). Further, Stammerjohn et al. (2012) have speculated that the duration of the sea-ice season (i.e., the time between seasonal sea-ice advance and retreat) might get shorter, meaning that sea ice would advance later and retreat earlier, with an overall increase in open ocean conditions, more generally. Although the analysis of fossil diatoms has been used with great success for reconstruction of Antarctic winter sea-ice extent over the last 220,000 years (Gersonde et al., 2005; Armand and Leventer, 2010; de Vernal et al., 2013), this approach is not applicable for longer timeframes and does not provide the complementary information on the occurrence of summer sea ice; a parameter critical in determining the net area of sea ice coverage and loss (Esper and Gersonde, 2014; Ferry et al., 2015). As such, there is a need to develop new and complementary proxies for reconstructing geophysical parameters associated with Antarctic sea ice.

In recent years, the organic geochemical lipid IP_{25} (Structure I; Fig. 1) (Belt et al., 2007) has emerged as a useful proxy for paleo Arctic sea-ice extent, in part, due to its selective production by certain diatoms residing in Arctic sea ice (Belt et al., 2007, 2013; Brown et al., 2014). Importantly, IP_{25} and other more unsaturated highly branched isoprenoid (HBI) alkenes are sufficiently stable in underlying Arctic sediments to permit paleo sea-ice reconstructions spanning recent decades (e.g., Müller et al., 2011; Navarro-Rodriguez et al., 2013; Stoynova et al., 2013; Xiao et al., 2013, 2015), the Holocene (Vare et al., 2009; Müller et al., 2012) and the Pliocene/Pleistocene boundary (Knies et al., 2014; Müller and Stein, 2014). Although IP_{25} has not been reported in the Antarctic, a structural analogue (an HBI diene; structure II; Fig. 1) has been identified in both sea-ice diatoms and sediments from the region (Nichols et al., 1988; Johns et al., 1999; Massé et al., 2011), with an isotopic ($\delta^{13}C$) signature that is also characteristic of a sea-ice origin (Johns et al., 1999; Sinninghe Damsté et al., 2007; Massé et al., 2011). Since this HBI diene is co-produced with IP_{25} by Arctic sea-ice diatoms (Brown et al., 2014) and is positively correlated with IP_{25} when quantified in sediments (Massé et al., 2011; Cabedo-Sanz et al., 2013), it too can be used as a proxy for Arctic sea ice, and also has the potential to provide the basis for paleo sea-ice reconstruction for the Southern Ocean.

A number of Antarctic sea-ice reconstruction studies based on the variable abundance of HBI diene II in Antarctic sediments have begun to appear (Barbara et al., 2010, 2013; Denis et al., 2010; Massé et al., 2011; Collins et al., 2013; Etourneau et al., 2013). A further HBI (an HBI triene; structure III; Fig. 1) has been reported in Antarctic phytoplankton and sediments, although this

isomer has not been identified in Antarctic sea ice. Further, its significantly lighter stable isotopic composition ($\delta^{13}C$) in phytoplankton ($\delta^{13}C = -40.2 \pm 0.5‰$) and sediments (e.g., $\delta^{13}C = -41.6 \pm 1.1‰$) (Massé et al., 2011), compared to diene II, indicates an exclusive origin in the pelagic phytoplankton (Trull and Armand, 2001), possibly from species that thrive within the marginal ice zone or retreating ice margin (Collins et al., 2013). As such, measurement of diene II in Antarctic sediments has generally been used to provide proxy evidence for variability in past sea-ice extent for the Southern Ocean (Barbara et al., 2010, 2013; Denis et al., 2010; Massé et al., 2011; Etourneau et al., 2013), while parallel quantification of triene III has been used to demonstrate open-water conditions and possibly changes in seasonality of Antarctic sea ice (Collins et al., 2013). The development of HBIs as proxies for Antarctic sea ice is much less advanced than that of IP_{25} for the Arctic (see Belt and Müller, 2013) and has relied almost entirely on their analysis in a small number of sediments, rather than within their source environments. Further, the specific diatoms responsible for HBI production in the Southern Ocean are not known, but the major species found in Antarctic winter sea ice and in phytoplankton (e.g., *Fragilariopsis* spp. in sea ice) are unlikely to be the sources (Collins et al., 2013).

Other common lipid biomarkers such as sterols and fatty acids have received less attention as possible sea-ice proxies, likely due to their ubiquity and low environmental specificity, at least compared to HBIs such as IP_{25}. However, some sterols, including epi-brassicasterol (24-methylcholesta-5,22E-dien-3β-ol) from phytoplankton and dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol) from dinoflagellates (Volkman, 1986; Volkman et al., 1993), have

been measured alongside IP_{25} to provide complementary evidence for open water conditions, especially for regions with seasonal sea-ice cover. Further, by combining IP_{25} and some sterol concentrations together, application of the so-called PIP_{25} index shows some potential for making IP_{25}-based sea-ice reconstructions more quantitative (e.g., Müller et al., 2011; Belt and Müller, 2013). In any case, the occurrence of sterols and fatty acids in all phytoplanktonic communities means that they can potentially provide useful qualitative estimates of marine primary productivity (e.g., Fahl and Stein, 2012), at least in surface waters.

In the current study, we aimed to obtain further insights into the use of certain HBIs as proxies for Antarctic sea ice by investigating their occurrence and abundance distributions in near-surface (ca. 0–10 m) water samples taken from a transect in the East Antarctic with contrasting sea ice settings. Samples were taken, and analysed, from three distinctively different regions with respect to sea-ice cover into summer: the permanently open-ocean zone (POOZ) with no seasonal sea-ice cover, the near-shore summer sea ice zone (SIZ) where sea ice remains long into the summer melt season, and the marginal ice zone (MIZ), located between the former two regions, and with a highly variable latitudinal sea-ice edge throughout the season. In particular, we assessed for the absolute and relative distributions of diene II and triene III within each zone and compared the outcomes with algal sterols, fatty acids and chlorophyll *a* (Chl *a*) as more generic indicators of marine primary productivity.

2. Experimental

2.1. Surface water samples

Water samples were obtained as part of the NBP1402 cruise aboard the RVIB *Nathaniel B Palmer* in February–March 2014 (see NBP1402 Scientific Cruise Report, 2014, Sabrina Coast: Marine record of cryosphere–ocean dynamics for details). At each sampling site, surface water (ca. 0–10 m water depth) was obtained either from the ship's intake line or from CTD rosettes. In total, sampling was carried out at 47 sites, with 38 locations within the polynya region (in the SIZ), west of the Dalton Iceberg Tongue (East Antarctica), and a further 9 locations representing a transect to ca. 56°S in the MIZ and the POOZ (Fig. 2). In each case, 1.5–3.0 l of sampled water was filtered onto 25 mm Whatman GF/F filters (used as supplied), wrapped in aluminium foil and stored frozen (–80 °C). Sample data and locations are detailed in Supplementary Table 1.

2.2. Lipid extraction and analysis

Filtered water samples were extracted and analysed as described previously for melted sea ice and water samples (Brown, 2011; Brown et al., 2011; Belt et al., 2013). In brief, internal standards (9-octyl-8-heptadecene (10 µl; 2 µg/ml), 5 -androstan-3β-ol (10 µl; 2 µg/ml), and nonadecanoic acid (10 µl; 1 mg/ml)) were added to filters prior to extraction for quantification of HBIs, sterols and fatty acids, respectively. Filters were then saponified (5% KOH; 70 °C; 60 min), after which, non-saponifiable lipids (including HBIs and sterols) were extracted with hexane (3 × 2 ml) and purified by open column chromatography (SiO_2). HBIs and sterols were eluted using hexane (5 column volumes) and

hexane/methyl acetate (4:1 v/v; 5 column columns), respectively. Fatty acids were obtained by adding concentrated HCl (1 ml) to the saponified solution (after extraction of non-saponifiable lipids) and re-extracted with hexane (3 × 2 ml). Fractions containing fatty acids and sterols were derivatized (BSTFA; 50 µl; 70 °C; 60 min) prior to analysis by gas chromatography–mass spectrometry (GC–MS).

All lipid fractions were analysed and quantified using GC–MS in total ion current (TIC) or single ion monitoring (SIM) mode using a Hewlett-Packard 5890 Series II gas chromatograph, fitted with a 30 m fused silica HP_{5ms} column (0.25 mm i.d., 0.25 µm film) coupled to a 5970 Series Mass Selective Detector (MSD) (Belt et al., 2012). Individual lipids (and their derivatized products) were identified on the basis of their characteristic GC retention indices and mass spectra, together with comparison of both parameters with those obtained from purified standards held in the University of Plymouth Biogeochemistry Research Centre laboratory. Quantification of individual lipids was also achieved using GC–MS. First, manually integrated GC–MS peak areas of individual lipids were divided by those of the respective internal standards. Second, in order to account for the differences in GC–MS responses between lipids and internal standards, integrated GC–MS lipid/internal standard ratios were normalised using instrumental response factors calculated from calibration curves obtained using purified standards of known concentration. Third, multiplication of these normalised lipid area ratios by the mass of the internal standard yielded the mass of lipid extracted in each case, and these were finally converted to their

corresponding seawater concentrations using the volume of water filtered. All analytical data can be found in Supplementary Table 1.

2.3. Sea-ice and chlorophyll a data

Mean monthly satellite-derived sea-ice extent and Chl *a* data were obtained from the National Snow and Ice Data Center (Fetterer et al., 2002) and NASA (http://oceandata.sci.gsfc.nasa.gov/), respectively. Sea-ice imagery was derived from MODIS (on-board Terra and Aqua spacecraft) and provided by NASA Worldview (https://earthdata.nasa.gov/earth-observation-data/near-real-time).

3. Results

3.1. HBIs in surface waters

HBI diene II could be identified and quantified in all of the surface water samples from the SIZ with a range in concentration of 0.10–0.48 pg/ml (mean 0.25 pg/ml, Fig. 3). The mean concentration of diene II in samples from the MIZ (0.10 pg/ml) was lower than that for the SIZ and this biomarker was absent (or below the limit of quantification; 0.025 pg/ml) in the sample from the most northerly location within the MIZ and in each of the four samples from the POOZ (Fig. 3). In contrast, triene III could be quantified in all samples from the three zones (Fig. 3). The concentration of triene III was 0.21–3.97 pg/ml in the SIZ with generally higher values in the MIZ (2.24–8.99 pg/ml). Indeed, the mean triene III concentration in the MIZ (6.00 pg/ml) was ca. six times higher than

that in the SIZ (1.06 pg/ml). However, triene III was present in much lower amounts (0.06–0.09 pg/ml) in samples from the POOZ, with a mean concentration (0.07 pg/ml) ca. 14 and 85 times lower compared to the SIZ and MIZ, respectively. Consistent with these differences in diene II and triene III distributions between zones, concentrations of these HBIs were not at all correlated (Table 1) and the mean II/III ratio was ca. 22 times larger in the SIZ (0.344) compared to the MIZ (0.016); all individual values were also higher in the SIZ (Fig. 3). Finally, although the abundances of both diene II and triene III were not sufficiently high in individual samples to enable us to obtain their stable isotopic composition ($\delta^{13}C$), we were able to determine a value for triene III ($\delta^{13}C = -35 \pm 1.5‰$) by combining several extracts together; however, the combined abundance of diene II was too low to enable us to obtain the corresponding value for this HBI.

3.2. Sterols and fatty acids in surface waters

The major sterols in all samples were 24-methylcholesta-5,22E-dien-3β-ol (epi-brassicasterol), 24-methylenecholesterol, 22-dehydrocholesterol and cholesterol, consistent with diatoms as the predominant microalgal source. Further, sterol concentrations were generally well correlated (Table 1), indicating consistency in the relative composition between sampling sites. Individual and combined sterol concentration data (Fig. 4) can be found in Supplementary Table 1. The mean total sterol (epi-brassicasterol + 24-methylenecholesterol + 22-dehydrocholesterol + cholesterol) concentration was 1190, 1400 and 4690 pg/ml in the SIZ, MIZ and POOZ, respectively, with

significantly less variation between the zones compared to the trends seen for diene II and triene III. The FA GC–MS chromatograms were dominated by C_{14}, C_{16} and $C_{16:1}$, again consistent with diatoms as the major components in the filtered biota (e.g., Opute, 1974; Volkman et al., 1989; Reuss and Poulsen, 2002). Concentrations of C_{14}, C_{16} and $C_{16:1}$ were also well correlated across all samples (Table 1) and there was some variation in mean concentrations of individual and total FAs (C_{14} + C_{16} + $C_{16:1}$) between the different sampling zones (Fig. 5; Supplementary Table 1). Thus, the mean total FA concentration was ca. 1.9 and 2.9 times higher in the MIZ (7759 pg/ml) compared to the SIZ (4014 pg/ml) and POOZ (2652 pg/ml), respectively.

4. Discussion

4.1. Lipid distributions within different sea ice settings

The occurrence of diene II in seasonally sea ice covered surface waters within the polynya, west of the Dalton Iceberg Tongue, and further offshore in the MIZ is consistent with production of this biomarker by sea-ice diatoms during the spring bloom (Nichols et al., 1988; Johns et al., 1999), followed by their release into the upper water column during sea-ice melt. In addition, the absence of diene II within the POOZ further supports the notion of selective production of this biomarker by certain (as yet unknown) diatoms affiliated with sea ice. Consistent with both of these observations, sympagic diatoms have previously been identified in near-coastal surface waters off Adélie Land (also

East Antarctica) soon after ice melt, while the species composition further offshore was dominated by pelagic counterparts (Riaux-Gobin et al., 2011).

Unfortunately, the abundance of diene II in the SIZ and MIZ samples was too low for us to determine its stable isotopic composition (and thus confirm its sea ice origin), although this HBI has been reported previously in sea ice from a nearby location (ca. 66°S; 110°E) (Massé et al., 2011) with an isotopic signature ($\delta^{13}C = -5.7‰$) characteristic of a sea-ice diatom source. In fact, HBI II identified previously in sea ice and sediments from other Antarctic locations is always isotopically heavy, and has not been reported in Antarctic phytoplankton, suggesting that its production is highly specific to certain sea-ice diatoms. The source of HBI II in our water samples is therefore believed to be sea-ice diatoms that were released into the surface waters during ice melt. Further, we interpret the overall increased concentration of diene II in the SIZ samples compared to those from the MIZ as reflecting more favourable conditions for sea-ice diatom growth due, mainly, to longer seasonal sea ice cover. Indeed, at the time of sampling (9 February–10 March 2014), remnant sea ice was still evident in the SIZ, but the MIZ was characterised by clear, open water conditions. The maximum winter sea ice extent in the region is normally reached during September and October (Fig. 2) with spring retreat occurring during November and December, coincident with (at least some) sea ice diatom growth (e.g., Arrigo et al., 2010). Although there have been no systematic time-series investigations of the production of diene II in Antarctic sea ice, the accumulation of IP_{25} in Arctic sea ice has been shown to closely parallel the spring bloom (Brown et al., 2011; Belt et al., 2013). As such, the corresponding accumulation of diene II in

Antarctic sea ice might be expected to be highest in regions of longer spring sea ice duration (i.e., within the SIZ), with lower amounts within the MIZ due to competing sea ice melt. Consistent with this suggestion, diene II was not detected in the most northerly sampling location within the MIZ, where the sea-ice margin had already retreated further south by December 2013 (Fig. 2). Finally, the selective production of diene II by sea ice diatoms likely explains the poor overall correlations between its concentration and those of the other lipids (Table 1), which could all be identified in each of the SIZ, MIZ and POOZ.

The distribution pattern of triene III is substantially different to that of diene II, indicating contrasting environmental control over its production. For example, triene III could be identified and quantified in samples from all locations, consistent with biosynthesis by phytoplankton rather than sea-ice diatoms, a conclusion supported further by an extremely light isotopic signature for this lipid in the current study ($\delta^{13}C = -35 \pm 1.5‰$) and in previous reports when measured in Antarctic phytoplankton (Massé et al., 2011) and sediments from both the Antarctic (Massé et al., 2011) and the Arctic (Belt et al., 2008). Although the sources of triene III in Antarctic (or Arctic) phytoplankton are not known, diatoms belonging to the *Pleurosigma* genus are likely candidates, since some of these, including planktonic species, are known producers of HBI trienes (including III) in culture (e.g., Belt et al., 2000, 2001; Grossi et al., 2004). Curiously, despite the ubiquity of triene III in samples from each zone, the mean concentration was markedly higher in the SIZ compared to the POOZ and even higher in the MIZ (Fig. 3). In previous paleo Antarctic sea-ice studies based on HBI lipids in marine sediments, the down-core variability of triene III has been

interpreted in terms of changes in the extent or duration of open-water conditions, with the corresponding abundances of diene II providing the complementary responses in terms of sea-ice duration (Barbara et al., 2010, 2013; Denis et al., 2010; Massé et al., 2011; Collins et al., 2013; Etourneau et al., 2013). In general, opposing trends in these two HBIs provides some support for such interpretations. However, in a study focussing on glacial age sediments from the Scotia Sea in the South Atlantic, Collins et al. (2013) observed in-phase changes in diene II and triene III concentrations and suggested that these might be better interpreted in terms of the latter being produced by phytoplankton that thrive at the ice edge, with low seasonality shifts favouring production of both biomarkers. Further, Etourneau et al. (2013) interpreted late Holocene increases in HBI II and HBI III within a western Antarctic Peninsula record as indicating increasing sea ice extent during colder winters (increased II) coeval with warmer summers (increased III). However, no in situ data have thus far been presented to test either hypothesis further. In the current study, our surface water data certainly indicate enhancement of triene III within the MIZ (relative to the POOZ) as the sea-ice edge retreats during spring, but with concentrations of diene II that are lower than for the SIZ. Conversely, a reduction in triene III in the SIZ (relative to the MIZ) is accompanied by the highest diene II concentrations as described earlier. Such shifts in the relative concentrations of the two HBIs are even more evident in the II/III ratio between the three zones with all values in the SIZ being larger than those for the MIZ (Fig. 3). Our surface water sample data thus indicate that relatively low II and high III (and

thus low II/III) are characteristic of the MIZ, while high II and low III (high II/III) reflect conditions of longer seasonal sea-ice cover found in the SIZ.

In order to investigate the sensitivity of triene III to the local sea-ice conditions in more detail and, in particular, to assess the significance of the enhancement in the MIZ compared to the POOZ, we also determined the concentrations of selected marine diatom sterols and FAs as more generic indicators of primary productivity. In contrast to the data for triene III, the concentrations of both lipid classes (individual and totals) were much more evenly distributed between the SIZ, the MIZ and the POOZ. The mean concentrations of total sterols and FAs were, however, highest in the MIZ, although the relative enhancements were not as large as those of triene III (Figs. 3, 4, and 5). As such, all three markers of marine diatom productivity (triene III, sterols, FAs) show increased values within the MIZ, and elevated mean (February/March) Chl *a* concentration was also evident within the MIZ (0.75 mg/m^3) compared to the POOZ (0.11 mg/m^3) and the SIZ (0.3 mg/m^3) (Supplementary Figure 1). The largest (clearest) change in mean lipid concentration between the different sampling zones is especially evident through inspection of triene III/total sterol and triene III/total FA ratios (Figs. 6a, b), with higher values within the MIZ due to enhanced triene III (Fig. 3b). At this stage, it is not clear what the reason behind the particular enhancement in triene III is, although it may, potentially, be attributed to a preference (or tolerance) of the species that biosynthesise this HBI to the stratified and nutrient-rich surface waters found at the sea ice edge which are well-known to promote phytoplankton productivity in the Antarctic (e.g., Niebauer and

Alexander, 1985; Smith and Nelson, 1985; Korb et al., 2005) and the Arctic (Sakshaug and Skjoldal, 1989; Sakshaug et al., 2009; Perrette et al., 2011). In contrast, the smaller changes in relative concentration of total sterols and total FAs between the different sampling regions likely reflect more general variations in diatom productivity, especially as these are lipids common to all diatoms. In addition, there may also be additional contributions to the FA budget from some other microalgae or bacteria (e.g., Volkman et al., 1989; Nichols et al., 1993) that further influence the distributions between zones, and this may explain, in part, the slightly different distributions of sterols and FAs between sampling regions (Figs. 4 and 5), most clearly observed through somewhat variable (mean and range) total FA/total sterol ratios (Fig. 6c).

The sensitivity of both diene II and triene III to the local sea-ice conditions, as demonstrated here, likely adds further value to their use as proxies for paleo sea-ice reconstruction when measured in Antarctic sediments. For example, on the basis of the variations in diene II and triene III identified in the current study, examination of sedimentary changes in both biomarkers and the ratio between them has the potential to provide further insights into sea-ice occurrence, duration and identification of winter/summer sea-ice limits and the MIZ. To date, however, there has not been a sufficiently detailed spatial assessment of the distributions of diene II and triene III in Antarctic surface (or down-core) sediments representing different overlying sea ice conditions, or a study of their behaviour within the water column prior to sedimentation, to evaluate whether the signature distributions identified here are preserved within the paleo record. In the meantime, we note that Belt et al. (2015) recently

observed an inverse relationship between IP_{25} and triene III in surface sediments from different regions of the Barents Sea (Arctic), which experiences a dynamic sea-ice advance and retreat cycle similar to that of the main transect in the current study. Thus, high (low) IP_{25} and low (high) triene III were observed in surface sediments with relatively long (short) seasonal sea-ice cover and the same relationships were preserved within three down-core records covering the Holocene and the Younger Dryas. As a result, Belt et al. (2015) concluded that combined measurement of IP_{25} and triene III could provide more detailed descriptions of seasonal Arctic sea-ice conditions (and temporal changes to these) than IP_{25} alone, and we suggest that the same may be true for diene II and triene III for the Antarctic. Testing this hypothesis will require a much greater examination of the spatial distributions of these two HBIs in Antarctic surface sediments and of their transit behaviour between surface waters and sediments. Both of these are currently being investigated in our laboratory.

4.2. The role of the polynya

Sea-ice cover within the SIZ typically reaches a maximum during late September/early October, with some partial break-up by the end of October (Fig. 7a). A distinctive feature of the SIZ within the current study, however, is the polynya, located west of the Dalton Iceberg Tongue (Fig. 7b). Polynya formation occurs as a consequence of a natural embayment between the Dalton Iceberg Tongue to the east and landfast ice off Law Dome to the west, which limits sea-ice export via the westward-flowing Antarctic Coastal Current. Together with katabatic winds that funnel along the Moscow University Ice Shelf, this

embayment results in recurrent ice formation and break-up leading to a 'sea-ice factory' scenario that is responsible for sea-ice retention even into summer, which contrasts with the advance/retreat cycle that occurs further north. Importantly, from a marine sediment-based proxy perspective, with horizons representing multi-year accumulation, a polynya scenario is a common feature for the SIZ on an annual basis, as evidenced from satellite records and reflected further by the median February sea-ice extent from 1980–2010 (Fig. 2). In any case, extended sea-ice duration within the polynya is likely favourable for enhanced sea-ice diatom growth and thus, production of diene II, as seen in the SIZ samples (Fig. 3a). On the other hand, the occurrence of transient phases of open water within the polynya (Fig. 7b) potentially explains the somewhat higher abundances of triene III (and of sterols and FAs; Figs. 3-5), at least when compared with values in the POOZ. Therefore, relatively high abundances of both HBIs in the sedimentary record, as observed here within the SIZ water samples, may reflect polynya-type conditions rather than long seasonal sea-ice cover followed by warmer summers, as has been suggested previously (Etourneau et al., 2013). In addition, II/III ratios within our SIZ samples span at least one order of magnitude (Fig. 3c), which is typical of the range seen in sedimentary records, and interpreted previously as indicating quite major shifts in either sea ice extent and/or open water conditions during summers (Barbara et al., 2010, 2013; Etourneau et al., 2013). Of course, whether sedimentary II/III ratios closely reflect those of the overlying water samples, or if the variation seen in the latter becomes homogenised within sediments, is in need of further investigation; however, on the basis of the data presented here, it is possible that

some control over substantial variations in sedimentary II/III may not be limited to large-scale changes in sea-ice extent, but may also be influenced by polynya-driven processes.

5. Conclusions

Distributions of an HBI diene (II) and triene (III) in surface waters from an offshore transect within the region north of the polynya west of the Dalton Iceberg Tongue (East Antarctica) were found to be extremely sensitive to the local sea-ice conditions. Thus, diene II was only detected at sampling sites that experienced seasonal sea ice, with highest concentrations found in coastal locations with longer-lasting ice cover and a recurrent polynya. In contrast, triene III was observed in surface waters from the POOZ, the MIZ and the SIZ, but with highest concentrations within the region of the retreating sea ice edge (the MIZ). Production of intermediate level concentrations of triene III within the SIZ likely reflects favourable conditions associated with the polynya. These observations are consistent with significant environmental control over the biosynthesis of II and III by sea ice diatoms and open water phytoplankton, respectively, with the production of III being especially favoured within the vicinity of the retreating ice-edge or the polynya. Although some environment-specific trends were also identified in the sterol and FA distributions, these were not as striking as those for II and III. Our data generally support various previous deductions based on sedimentary records of II and III in dated marine archives, especially the abundance of diene II as an indicator of seasonal sea-ice extent. The occurrence of triene III at all sites is consistent with the use of this

biomarker as an open water indicator, while enhanced concentrations within the MIZ supports the notion of a more specific indicator of increased productivity adjacent to the sea-ice edge, as suggested by Collins et al. (2013). However, additional local factors, such as those associated with polynya formation, may also exert significant control over the distribution of triene III and the relative concentrations of II and III, in particular.

Acknowledgments

We thank the US National Science Foundation's Polar Program in Antarctic Integrated System Science, the NBP1402 scientific party, ASC support staff, and ECO crew members led by Captain Sebastian Paoni on board the RVIB *N.B. Palmer*, whose support enabled us to obtain the samples described in this study. We thank the University of Plymouth for financial support to LS and STB. JLL was supported by the Australian Government's Cooperative Research Centre program through the Antarctic Climate & Ecosystem CRC (ACE CRC), and under Australian Research Council's Special Research Initiative for Antarctic Gateway Partnership (Project ID SR140300001). LA was supported by the Department of Biological Sciences in the Faculty of Science and Engineering at Macquarie University. AL was supported by NSF Grant number 1143836. We also thank Dr Kyle Taylor (ISOPRIME, UK) for determining the stable isotopic composition of HBI III. We are grateful to two anonymous reviewers who provided useful comments that helped improve this manuscript.

Associate Editor–**Sylvie Derenne**

References

Armand, L.K., Leventer, A., 2010. Palaeo sea ice distribution and reconstruction derived from the geological record. In: Thomas, D.N., Dieckmann, G.S. (Eds.), Sea Ice. Wiley-Blackwell Publishing Ltd, Oxford, UK, pp. 469–530.

Arrigo, K.R., Mock, T, Lizotte, M.P., 2010. Primary producers in sea ice. In: Thomas, D.N., Dieckmann, G.S. (Eds.), Sea Ice. Wiley-Blackwell Publishing Ltd, Oxford, UK, pp. 283–326.

Barbara, L., Crosta, X., Massé, G., Ther, O., 2010. Deglacial environments in eastern Prydz Bay, East Antarctic. Quaternary Science Reviews 29, 2731–2740.

Barbara, L., Crosta, X., Schmidt, S., Massé, G., 2013. Diatoms and biomarkers evidence for major changes in sea ice conditions prior the instrumental period in Antarctic Peninsula. Quaternary Science Reviews 79, 99–110.

Belt, S.T., Allard, W.G., Massé, G., Robert, J.-M., Rowland, S.J., 2000. Highly branched isoprenoids (HBIs): identification of the most common and abundant sedimentary isomers. Geochimica et Cosmochimica Acta 64, 3839–3851.

Belt, S.T., Massé, G., Allard, W.G., Robert, J.-M., Rowland, S.J., 2001. C_{25} highly branched isoprenoid alkenes in planktonic diatoms of the *Pleurosigma* genus. Organic Geochemistry 32, 1271–1275.

Belt, S.T., Massé, G., Rowland, S.J., Poulin, M., Michel, C., LeBlanc, B., 2007. A novel chemical fossil of palaeo sea ice: IP_{25}. Organic Geochemistry 38, 16-27.

Belt, S.T., Massé, G., Vare, L.L., Rowland, S.J., Poulin, M., Sicre, M.-A., Sampei, M., Fortier, L., 2008. Distinctive ^{13}C isotopic signature distinguishes a novel sea ice biomarker in Arctic sediments and sediment traps. Marine Chemistry 112, 158–167.

Belt, S.T., Brown, T.A., Navarro Rodriguez, A., Cabedo Sanz, P., Tonkin, A., Ingle, R., 2012. A reproducible method for the extraction, identification and quantification of the Arctic sea ice proxy IP_{25} from marine sediments. Analytical Methods 4, 705–713.

Belt, S.T., Brown, T.A., Ringrose, A.E., Cabedo-Sanz, P., Mundy, C.J., Gosselin, M., Poulin, M., 2013. Quantitative measurements of the sea ice diatom biomarker IP_{25} and sterols in Arctic sea ice and underlying sediments: Further considerations for palaeo sea ice reconstruction. Organic Geochemistry 62, 33–45.

Belt, S.T., Müller, J., 2013. The Arctic sea ice biomarker IP_{25}: a review of current understanding, recommendations for future research and applications in palaeo sea ice reconstructions. Quaternary Science Reviews 79, 9–25.

Belt, S.T., Cabedo-Sanz, P., Smik, L., Navarro-Rodriguez, A., Berben, S.M.P., Knies, J., Husum, K., 2015. Identification of paleo Arctic winter sea ice limits and the marginal ice zone: optimised biomarker-based reconstructions of late Quaternary Arctic sea ice. Earth and Planetary Science Letters 431, 127–139.

Brandon, M.A., Cottier, F.R., Nilsen, F., 2010. Sea ice and oceanography. In: Thomas, D.N., Dieckmann, G.S. (Eds.), Sea Ice. Wiley-Blackwell Publishing Ltd, Oxford, UK, pp. 79–112.

Brown, T.A., 2011. Production and Preservation of the Arctic Sea Ice Diatom Biomarker IP_{25}. PhD Thesis, University of Plymouth, UK.

Brown, T.A., Belt. S.T., Mundy, C., Philippe, B., Massé, G., Poulin, M., Gosselin, M., 2011. Temporal and vertical variations of lipid biomarkers during a bottom ice diatom bloom in the Canadian Beaufort Sea: further evidence for the use of the IP_{25} biomarker as a proxy for spring Arctic sea ice. Polar Biology 34, 1857–1868.

Brown, T.A., Belt, S.T., Tatarek, A., Mundy, C.J., 2014. Source identification of the Arctic sea ice proxy IP_{25}. Nature Communications 5, 4197.

Cabedo-Sanz, P., Belt, S.T., Knies, J.K., Husum, K., 2013. Identification of contrasting seasonal sea ice conditions during the Younger Dryas. Quaternary Science Reviews 79, 74–86.

Collins, L.G., Allen, C.S., Pike, J, Hodgson, D.A., Weckström, K., Massé, G. 2013. Evaluating highly branched isoprenoid (HBI) biomarkers as a novel Antarctic sea ice proxy in deep ocean glacial age sediments. Quaternary Science Reviews 79, 87–98.

Comiso, J., 2010. Variability and trends of the global sea ice cover. In: Thomas, D.N., Dieckmann, G.S. (Eds.), Sea Ice. Wiley-Blackwell Publishing Ltd, Oxford, UK, pp. 205–246.

Denis, D., Crosta, X., Barbara, L., Massé, G., Renssen, H., Ther, O., Giraudeau, J., 2010. Sea ice and wind variability during the Holocene in East Antarctica:

insight on middle-high latitude coupling. Quaternary Science Reviews 29, 3709–3719.

de Vernal, A., Gersonde, R., Goosse, H., Seidenkrantz, M.-S., Wolff, E.W., 2013. Sea ice in the paleoclimate system: the challenge of reconstructing sea ice from proxies – an introduction. Quaternary Science Reviews 79, 1–8.

Dieckmann, G.S., Hellmer, H.H., 2010. The importance of sea ice: an overview. In: Thomas, D.N., Dieckmann, G.S. (Eds.), Sea Ice. Wiley-Blackwell Publishing Ltd, Oxford, UK, pp. 1–22.

Esper, O., Gersonde, R., 2014. New tool for the reconstruction of Pleistocene Antarctic sea ice. Palaeogeography, Palaeoclimatology, Palaeoecology 399, 260–283.

Etourneau, J., Collins, L.G., Willmott, V., Kim, J.-H., Barbara, L., Leventer, A., Schouten S., Sinninghe Damsté, J.S., Bianchini, A., Klien, V., Crosta, X., Massé, G. 2013. Holocene climate variations in the western Antarctic Peninsula: evidence for sea ice extent predominantly controlled by changes in insolation and ENSO variability. Climate of the Past 9, 1431–1446.

Fahl, K., Stein, R., 2012. Modern seasonal variability and deglacial/Holocene change of central Arctic Ocean sea ice cover: New insights from biomarker proxy records. Earth and Planetary Science Letters 351–352, 123–133.

Ferry, A., Prvan, T., Jersky, B., Crosta, X., Armand, L.K., 2015. Statistical modeling of Southern Ocean marine diatom proxy and winter sea ice data: Model comparison and developments. Progress in Oceanography 131, 100–112.

Fetterer, F., Knowles, K., Meier, W., Savoie, M., 2002. *Sea Ice Index.* [sea ice extent]. Boulder, Colorado USA: National Snow and Ice Data Center. http://dx.doi.org/10.7265/N5QJ7F7W.

Gersonde, R., Crosta, X., Abelmann, A., Armand, L., 2005. Sea-surface temperature and sea ice distribution of the Southern Ocean at the EPILOG Last Glacial Maximum–a circum-Antarctic view based on siliceous microfossil records. Quaternary Science Reviews 24, 869–896.

Grossi, V., Beker, B., Geenevasen, J.A.J., Schouten, S., Raphel, D., Fontaine, M.-F., Sinninghe Damsté, J.S., 2004. C_{25} highly branched isoprenoid alkenes from the marine benthic diatom *Pleurosigma strigosum*. Phytochemistry 65, 3049–3055.

Johns, L., Wraige, E.J., Belt, S.T., Lewis, C.A., Massé, G., Robert, J.-M., Rowland, S.J., 1999. Identification of a C_{25} highly branched isoprenoid (HBI) diene in Antarctic sediments, Antarctic sea ice diatoms and cultured diatoms. Organic Geochemistry 30, 1471–1475.

Knies, J., Cabedo-Sanz, P., Belt, S.T., Baranwal, S., Fietz, S., Rosell-Melé, A., 2014. The emergence of modern sea ice cover in the Arctic Ocean. Nature Communications 5, 5608.

Korb, R.E., Whitehouse, M.J., Thorpe, S.E., Gordon, M., 2005. Primary production across the 30 Scotia Sea in relation to the physico-chemical environment. Journal of Marine Systems 57, 231–249.

Massé, G., Belt, S.T., Crosta, X., Schmidt, S., Snape, I., Thomas, D.N., Rowland, S.J., 2011. Highly branched isoprenoids as proxies for variable sea ice conditions in the Southern Ocean. Antarctic Science 23, 487–498.

Müller, J., Wagner, A., Fahl, K., Stein, R., Prange, M., Lohmann, G., 2011. Towards quantitative sea ice reconstructions in the northern North Atlantic: A combined biomarker and numerical modelling approach. Earth and Planetary Science Letters 306, 137–148.

Müller, J., Werner, K., Stein, R., Fahl, K., Moros, M., Jansen, E., 2012. Holocene cooling culminates in sea ice oscillations in Fram Strait. Quaternary Science Reviews 47, 1–14.

Müller, J., Stein, R., 2014. High-resolution record of late glacial sea ice changes in Fram Strait corroborates ice-ocean interactions during abrupt climate shifts. Earth and Planetary Science Letters 403, 446–455.

Navarro-Rodriguez, A., Belt, S.T., Brown, T.A., Knies, J., 2013. Mapping recent sea ice conditions in the Barents Sea using the proxy biomarker IP_{25}: implications for palaeo sea ice reconstructions. Quaternary Science Reviews 79, 26–39.

Nichols, P.D., Volkman, J.K., Palmisano, A.C., Smith, G.A., White, D.C., 1988. Occurrence of an isoprenoid C_{25} diunsaturated alkene and high neutral lipid content in Antarctic sea ice diatom communities. Journal of Phycology 24, 90–96.

Nichols, D.S., Nichols, P.D., McMeekin, T.A., 1993. Polyunsaturated fatty acids in Antarctic bacteria. Antarctic Science 5, 149–160.

Niebauer, H.J., Alexander, V., 1985. Oceanographic frontal structure and biological production at an ice edge. Continental Shelf Research 4, 367–388.

Opute, F.I., 1974. Lipid and fatty-acid composition of diatoms. Journal of Experimental Botany 25, 823–835.

Perette, M., Yool, A, Quartly, G.D., Popova, E.E., 2011. Near-ubiquity of ice-edge blooms in the Arctic. Biogeosciences 8, 515–524.

Reuss, N., Poulsen, L.K., 2002. Evaluation of fatty acids as biomarkers for a natural plankton community. A field study of a spring bloom and a post-bloom period off West Greenland. Marine Biology 141, 423–434.

Riaux-Gobin, C., Poulin, M., Dieckmann, G., Labrune, C., Vétion, G., 2011. Spring phytoplankton onset after the ice break-up and sea-ice signature (Adélie land, East Antarctica). Polar Research 30, 5910. doi: 10.3402/polar.v30i0.5910.

Sakshaug, E., Johnsen, G., Kristiansen, S., von Quillfeldt, C., Rey, F., Slagstad, D., Thingstad, F., 2009. Phytoplankton and primary production. In: Sakshaug, E., Johnsen, G., Kovacs, K. (Eds.), Ecosystem Barents Sea. Tapir Academic Press, Trondheim, Norway, pp.167–208.

Sakshaug, E., Skjoldal, H., 1989. Life at the ice edge. Ambio 18, 60–67.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Coolen, M.J.L., Schouten, S., Volkman, J.K., 2007. Rapid sulfurization of highly branched isoprenoid (HBI) alkenes in sulfidic Holocene sediments from Ellis Fjord, Antarctica. Organic Geochemistry 38, 128–139.

Smith, W.O., Nelson, D.M.,1985. Phytoplankton bloom produced by a receding ice edge in the Ross Sea: spatial coherence with the density field. Science 227, 163–166.

Stammerjohn, S., Massom, R., Rind, D., Martinson, D., 2012. Regions of rapid sea ice change: An inter-hemispheric seasonal comparison. Geophysical Research Letters 39, L06501.

Stoynova, V., Shanahan, T.M., Hughen, K.A., de Vernal, A., 2013. Insights into circum-Arctic sea ice variability from molecular geochemistry. Quaternary Science Reviews 79, 63–73.

Trull, T., Armand, L.K., 2001. Insights into Southern Ocean carbon export from the $\delta^{13}C$ of particles and dissolved inorganic carbon during the SOIREE iron release experiment. Deep-Sea Research II: Topical Studies in Oceanography 48, 2655–2680.

Turner, J., Comiso, J.C., Marshall, G.J., Lachlan-Cope, T.A., Bracegirdle, T., Maksym, T., Meredith, M.P., Wang, Z., Orr, A., 2009. Non-annular atmospheric circulation change induced by stratospheric ozone depletion and its role in the recent increase of Antarctic sea ice extent. Geophysical Research Letters 36, L08502.

Vaughan, D.G., Comiso, J.C., Allison, J., Allison, I., Carrasco, J., Kaser, G., Kwok, R., Mote, P., Murray, T., Paul, F., Ren, J., Rignot, E., Solomina, O., Steffen, K., Zhang, T., 2013. Observations: Cryosphere. In: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Bosching, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, and New York, USA. pp. 317–82.

Vare, L.L., Massé, G., Gregory, T.R., Smart, C.W., Belt, S.T., 2009. Sea ice variations in the central Canadian Arctic Archipelago during the Holocene. Quaternary Science Reviews 28, 1354–1366.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. Organic Geochemistry 9, 83–99.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C_{25} and C_{30} highly branched isoprenoid alkenes in laboratory cultures of two marine diatoms. Organic Geochemistry 21, 407–414.

Volkman, J.K., Jeffrey, S.W., Nichols, P.D., Rogers, G.I., Garland, C.D. 1989. Fatty acid and lipid composition of 10 species of microalgae used in mariculture. Journal of Experimental Marine Biology and Ecology 128, 219–240.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., Jeffrey, S.W., 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. Organic Geochemistry 20, 7–15.

Xiao, X., Fahl, K., and Stein, R., 2013. Biomarker distributions in surface sediments from the Kara and Laptev Seas (Arctic Ocean): Indicators for organic-carbon sources and sea-ice coverage. Quaternary Science Reviews 79, 40–52.

Xiao, X., Fahl, K., Müller, J., Stein, R. 2015. Sea-ice distribution in the modern Arctic Ocean: biomarker records from Trans-Arctic Ocean surface sediments. Geochimica et Cosmochimica Acta 155, 16–29.

Figures and Tables

Fig. 1. Structures of C_{25} HBI alkenes described in this study: (I) IP_{25}; (II) HBI diene; (III) HBI triene.

Fig. 2. Map of the main study region and location of individual sampling sites. Major ocean currents and other landmarks are also indicated. ACC: Antarctic Circumpolar Current; ACoC: Antarctic Coastal Current. Dated lines refer to mean satellite-derived sea-ice extent (NSIDC) and the regions designated as the permanently open ocean zone (POOZ), the marginal ice zone (MIZ) and the seasonal ice zone (SIZ) are also shown. The main polynya region described in the text includes samples located further south than ca. 66°S.

Fig. 3. Distributions of diene II, triene III and II/III in East Antarctic surface waters.

Fig. 4. Concentrations (pg/ml) of major (and total) sterols in East Antarctic surface waters.

Fig. 5. Concentrations (pg/ml) of major (and total) fatty acids in East Antarctic surface waters.

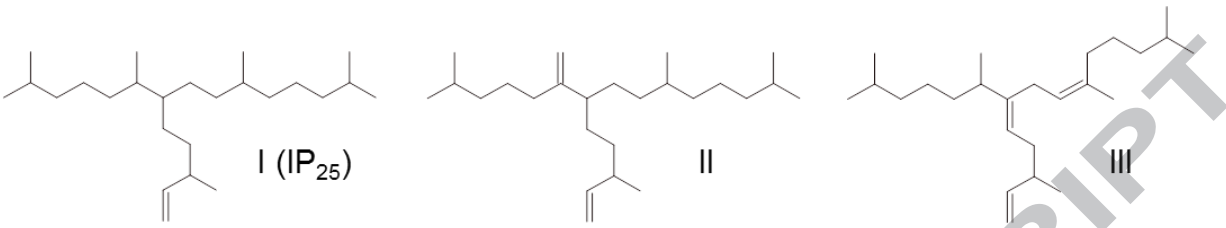
Fig. 6. Distributions of: (a) HBI III/Total sterol; (b) HBI III/Total FA; (c) Total FA/Total sterol in East Antarctic surface waters.

Fig. 7. Satellite-derived visible images of the study region (composite of data from the MODerate Resolution Imaging Spectroradiometer (MODIS), flown on

two NASA spacecraft (Terra and Aqua)). Imagery was recorded on: (a) 26 October 2013 and (b) 18 February 2014.

Table 1. Correlation between biomarkers in East Antarctic surface waters (values in bold indicate significant correlation (r) where $p < 0.05$).

Figure 1



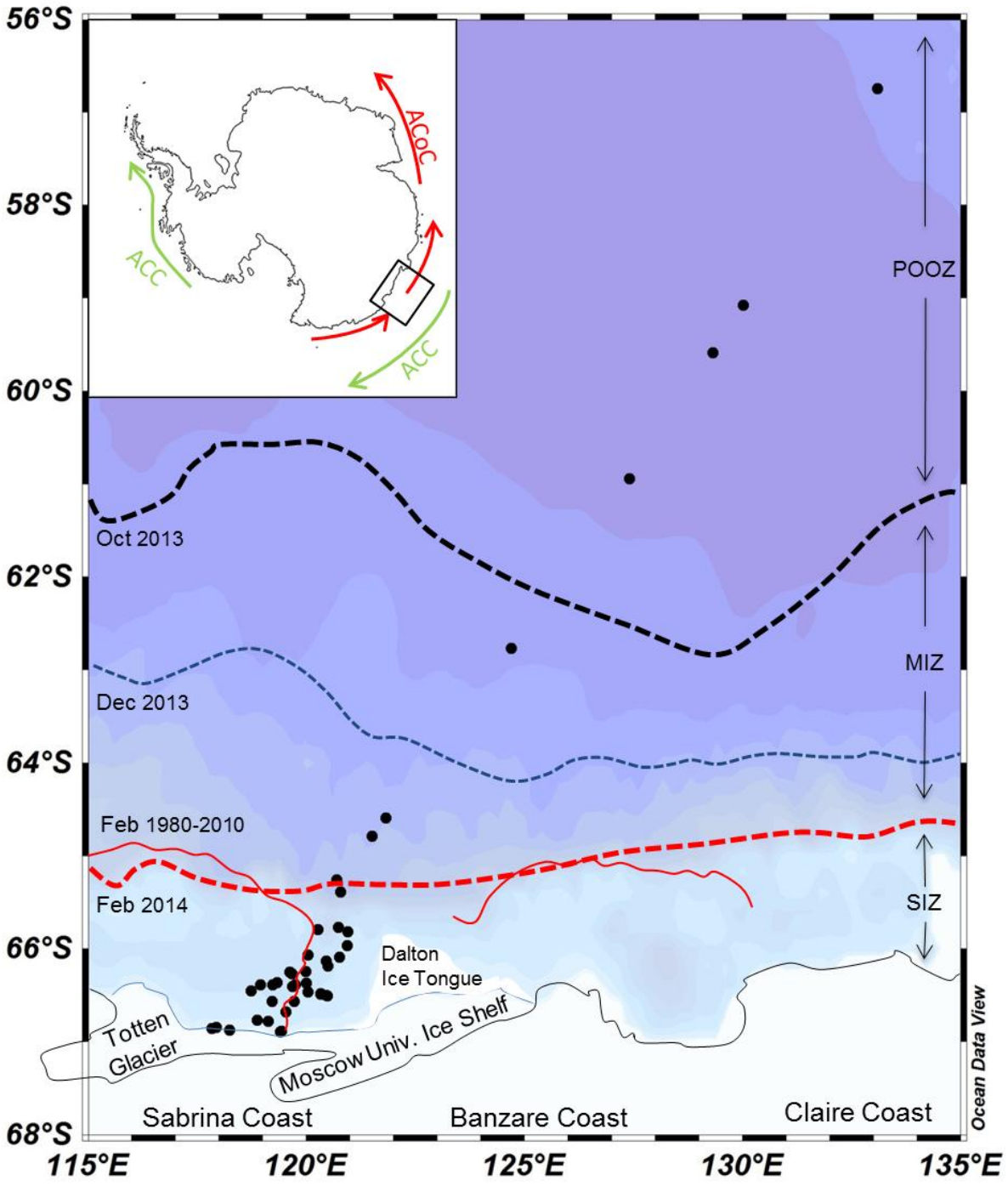


Figure 3

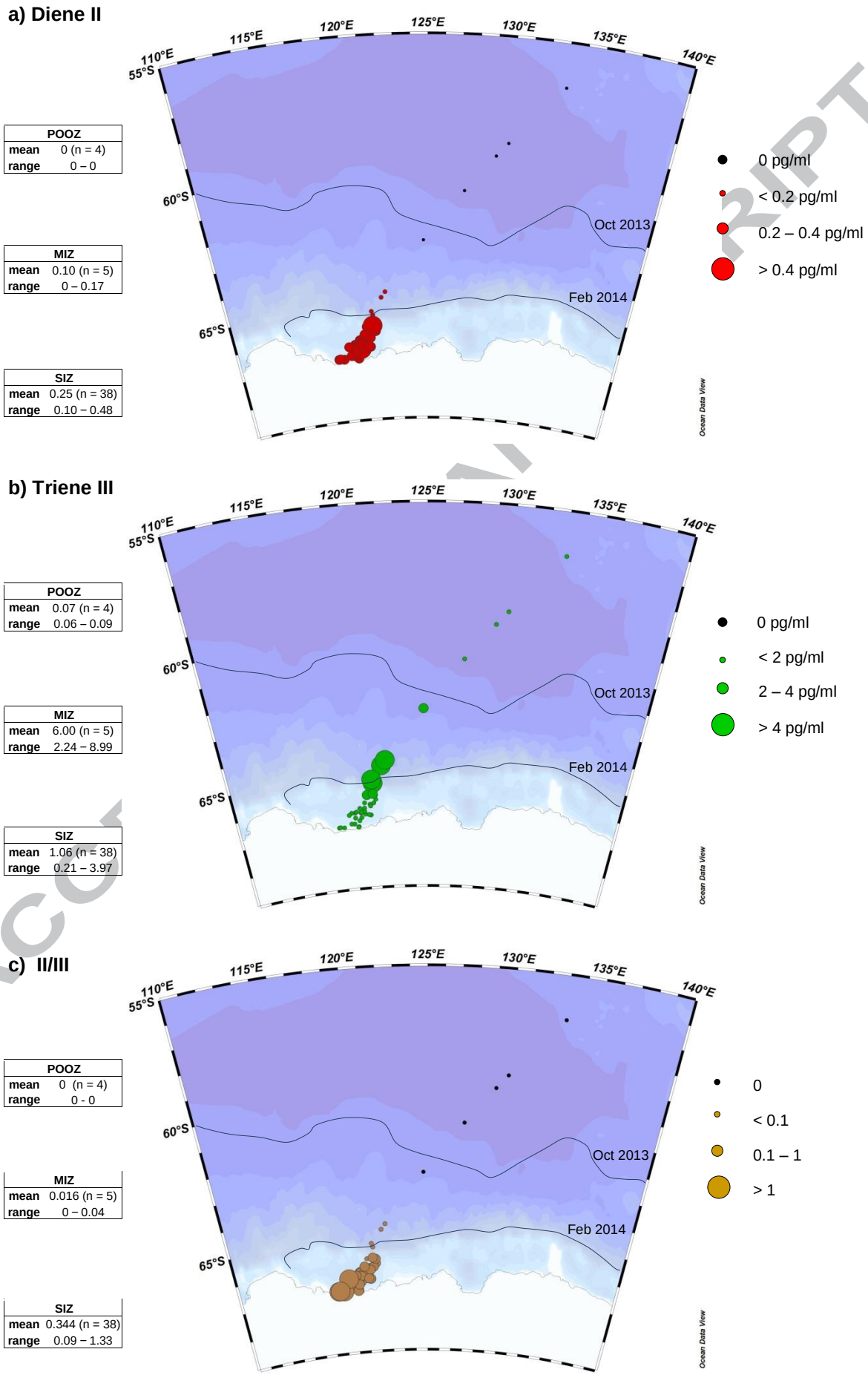


Figure 4

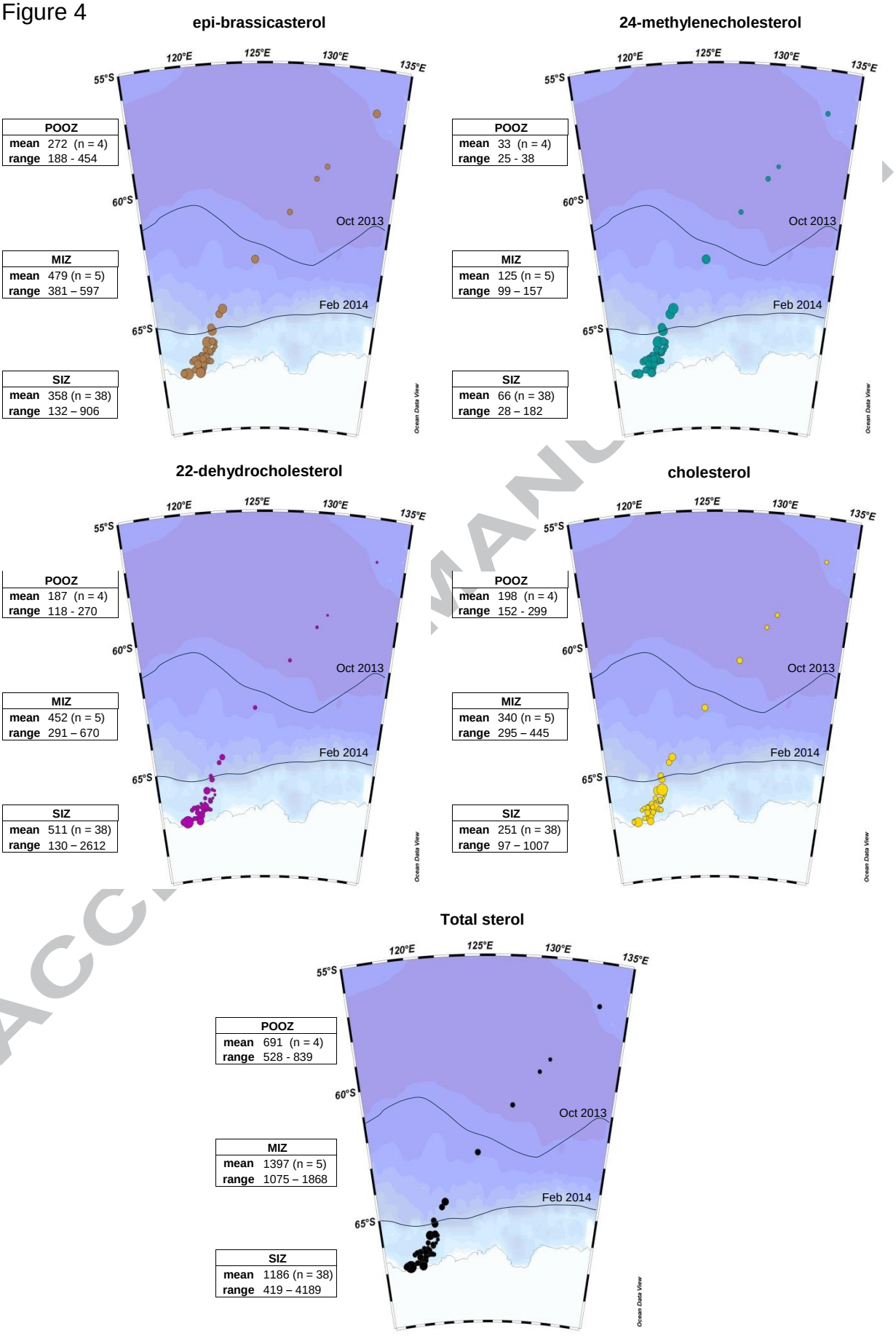
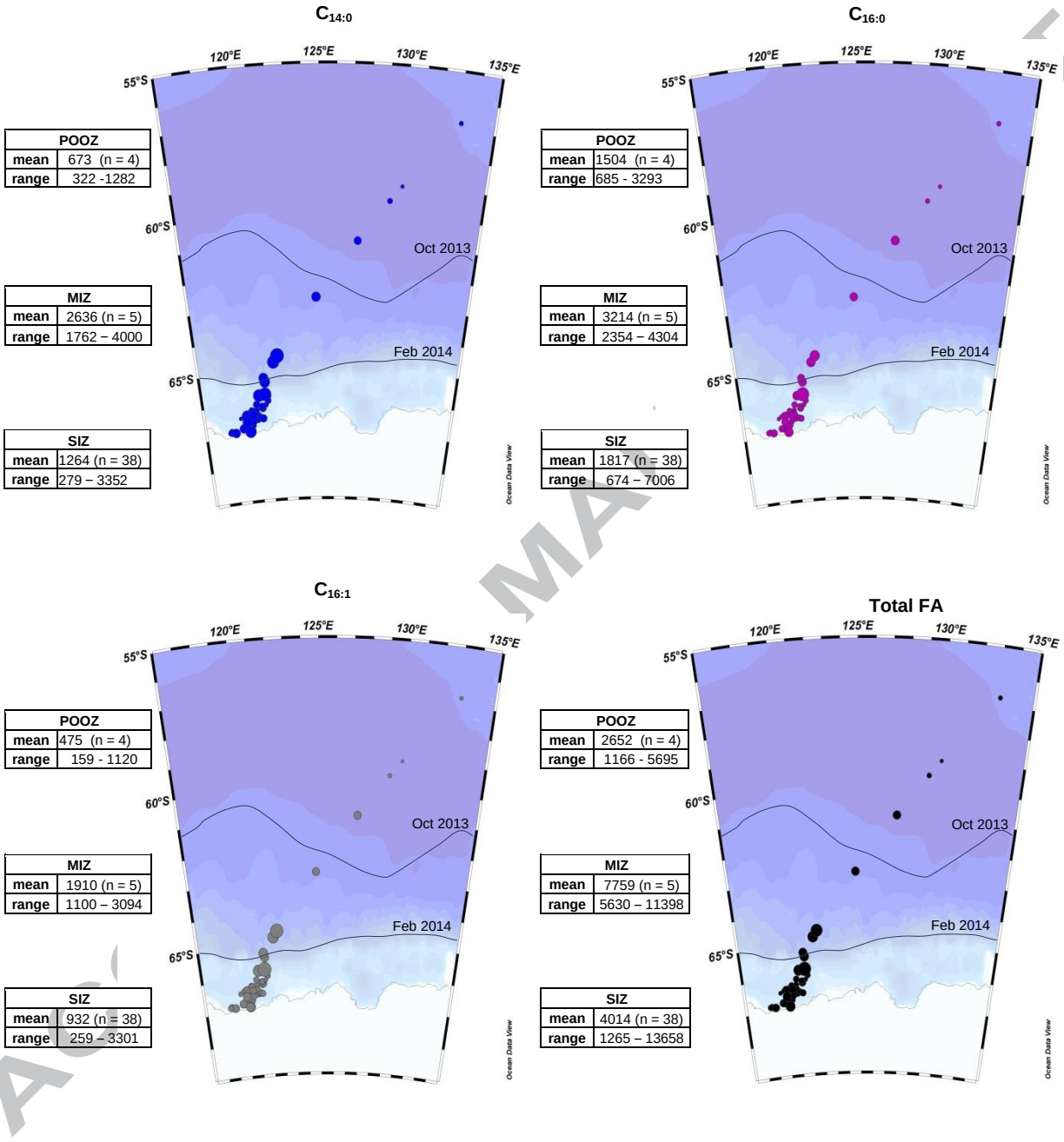


Figure 5

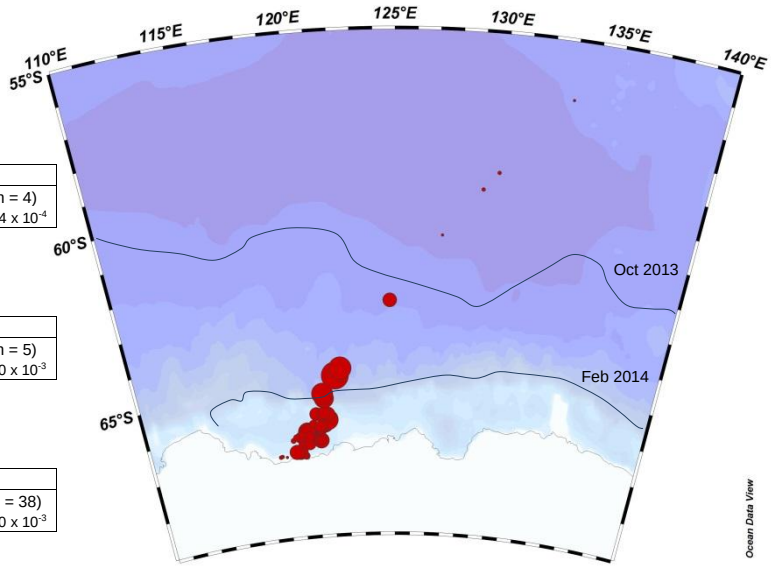


a) **HBI III / Total sterol**

POOZ	
mean	1.1×10^{-4} (n = 4)
range	$7.0 \times 10^{-5} – 1.4 \times 10^{-4}$

MIZ	
mean	4.3×10^{-3} (n = 5)
range	$1.8 \times 10^{-3} – 7.0 \times 10^{-3}$

SIZ	
mean	1.2×10^{-3} (n = 38)
range	$6.9 \times 10^{-5} – 4.0 \times 10^{-3}$

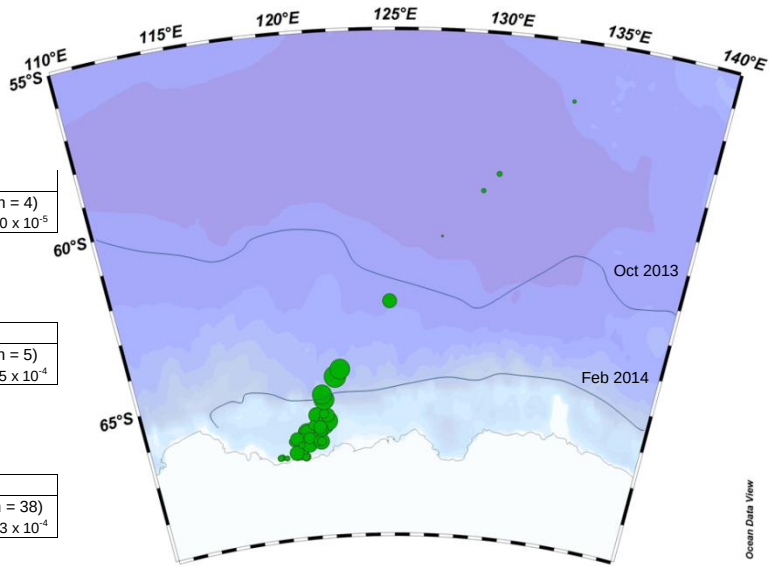


b) **HBI III / Total FA**

POOZ	
mean	3.7×10^{-5} (n = 4)
range	$1.0 \times 10^{-5} – 6.0 \times 10^{-5}$

MIZ	
mean	7.5×10^{-4} (n = 5)
range	$4.0 \times 10^{-4} – 9.5 \times 10^{-4}$

SIZ	
mean	2.9×10^{-4} (n = 38)
range	$6.0 \times 10^{-5} – 7.3 \times 10^{-4}$



c) **Total FA / Total sterol**

POOZ	
mean	3.6 (n = 4)
range	2.2 – 6.8

MIZ	
mean	5.6 (n = 5)
range	4.3 – 7.3

SIZ	
mean	3.8 (n = 38)
range	1.2 – 8.1

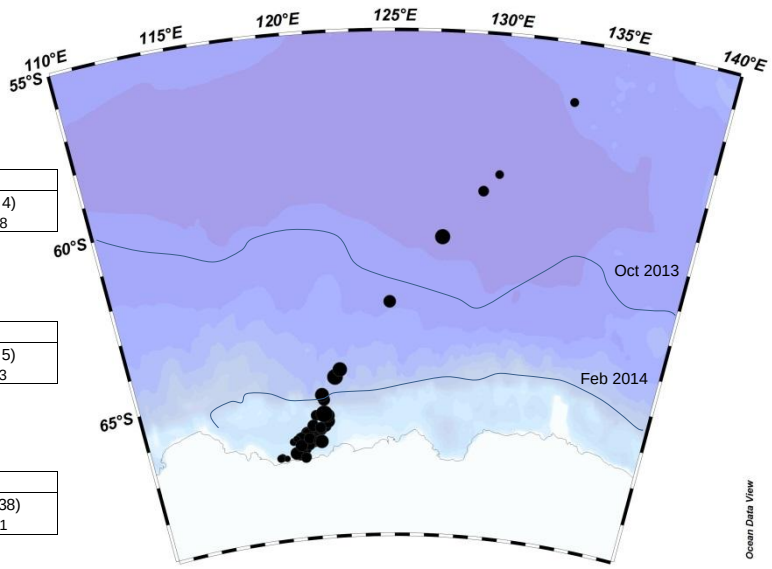


Figure 7

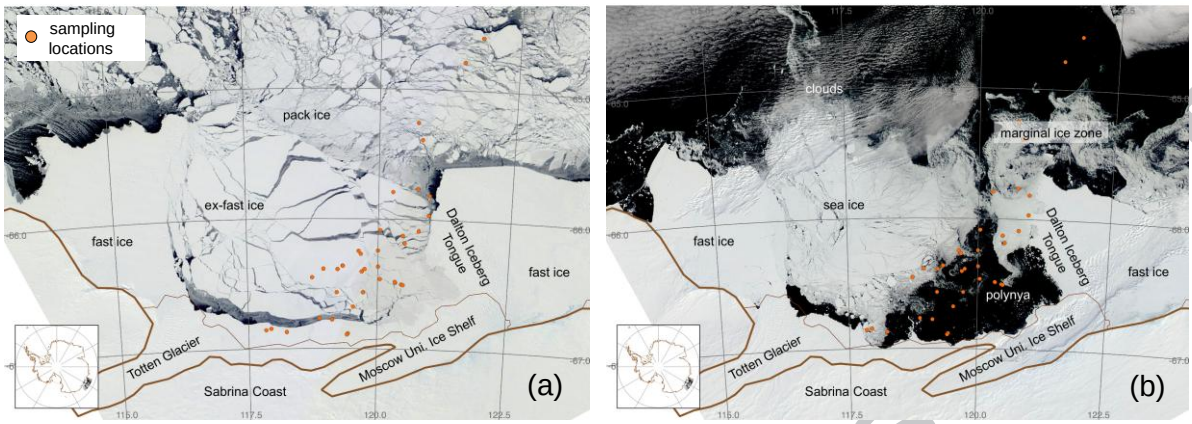


Table 1

	Diene II	Triene III	epi-brassicasterol	24-methylenecholesterol	22-dehydrocholesterol	cholesterol	$C_{14:0}$ FA	$C_{16:0}$ FA
Diene II								
Triene III	-0.028							
epi-brassicasterol	-0.005	0.223						
24-methylenecholesterol	0.042	**0.651**	**0.808**					
22-dehydrocholesterol	0.111	-0.024	**0.820**	**0.543**				
cholesterol	0.238	**0291**	**0.575**	**0.557**	**0.490**			
$C_{14:0}$ FA	0.094	**0.706**	**0.587**	**0.785**	**0.309**	**0.676**		
$C_{16:0}$ FA	0.100	**0.526**	**0.452**	**0.588**	0.218	**0.848**	**0.885**	
$C_{16:1}$ FA	0.170	**0.687**	**0.521**	**0.746**	0.268	**0.775**	**0.949**	**0.920**

p = 0.05; n = 47

Highlights

•Highly branched isoprenoid (HBI) alkenes measured in Antarctic surface waters.

•HBI diene identified in surface waters from regions of seasonal sea ice cover

•HBI triene found in waters from all regions but enhanced within the marginal ice zone

•Sterol and fatty acid distributions less sensitive to sea ice cover than HBI alkenes

•HBI distributions provide new insights for biomarker-based paleo sea ice reconstruction