

1 **Highly branched isoprenoids for Southern Ocean sea ice**  
2 **reconstructions: a pilot study from the Western Antarctic**  
3 **Peninsula**

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12 **Abstract.** Organic geochemical and micropaleontological analyses of surface sediments collected in the southern  
13 Drake Passage and the Bransfield Strait, Antarctic Peninsula, enable a proxy-based reconstruction of recent sea  
14 ice conditions in this climate sensitive area. We study the distribution of the sea ice biomarker IPSO<sub>25</sub>, and  
15 biomarkers of open marine environments such as more unsaturated highly branched isoprenoid alkenes and  
16 phytosterols. Comparison of the sedimentary distribution of these biomarker lipids with sea ice data obtained from  
17 satellite observations and diatom-based sea ice estimates provide for an evaluation of the suitability of these  
18 biomarkers to reflect recent sea surface conditions. The distribution of IPSO<sub>25</sub> supports earlier suggestions that the  
19 source diatom seems to be common in near-coastal environments characterized by an annually recurring sea ice  
20 cover, while the distribution of the other biomarkers is highly variable. Offsets between sea ice estimates deduced  
21 from the abundance of biomarkers and satellite-based sea ice data are attributed to the different time intervals  
22 recorded within the sediments and the instrumental records from the study area, which experienced rapid  
23 environmental changes during the past 100 years. To distinguish areas characterized by permanently ice-free  
24 conditions, seasonal sea ice cover and extended sea ice cover, we apply the concept of the PIP<sub>25</sub> index from the  
25 Arctic Ocean on our data and introduce the term PIPSO<sub>25</sub> as a potential sea ice proxy. While the trends in PIPSO<sub>25</sub>  
26 are generally consistent with satellite sea ice data and winter sea ice concentrations estimated by diatom transfer  
27 functions, more studies on the environmental significance of IPSO<sub>25</sub> as a Southern Ocean sea ice proxy are needed  
28 before this biomarker can be applied for semi-quantitative sea ice reconstructions.

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Key Words: biomarker, IPSO<sub>25</sub>, sea ice, Bransfield Strait, satellite observation

### 1 Introduction

In the last century, the Western Antarctic Peninsula (WAP) has undergone a rapid warming of the atmosphere of  $3.7 \pm 1^\circ \text{C}$ , which exceeds several times the average global warming (Pachauri et al., 2014; Vaughan et al., 2003). Simultaneously, a reduction in sea ice coverage (Parkinson and Cavalieri, 2012), a shortening of the sea ice season (Parkinson, 2002) and a decreasing sea ice extent of ~4-10 % per decade (Liu et al., 2004) are recorded in the adjacent Bellingshausen Sea. The loss of seasonal sea ice and increased melt water fluxes impact the formation of deep and intermediate waters, the ocean-atmosphere-exchange of gases and heat, the primary production and higher trophic levels (Arrigo et al., 1997; Mendes et al., 2013; Morrison et al., 2015; Orsi et al., 2002; Rintoul, 2007). Since the start of satellite-based sea ice observations, however, a slight increase in total Antarctic sea ice extent has been documented, which contrasts the significant decrease of sea ice in Western Antarctica, especially around the WAP (Hobbs et al., 2016).

For an improved understanding of the oceanic and atmospheric feedback mechanisms associated with the observed changes in sea ice coverage, reconstructions of past sea ice conditions in climate sensitive areas such as the WAP are of increasing importance. A common approach for sea ice reconstructions in the Southern Ocean is based on the investigation of sea ice associated diatom assemblages preserved in marine sediments (Bárcena et al., 1998; Gersonde and Zielinski, 2000; Heroy et al., 2008; Leventer, 1998; Minzoni et al., 2015). By means of transfer functions, this approach can provide quantitative estimates of a paleo sea ice coverage (Crosta et al., 1998; Esper and Gersonde, 2014a). The application of diatoms for paleoenvironmental studies, however, can be limited by the selective dissolution of biogenic opal frustules (Burckle and Cooke, 1983; Esper and Gersonde, 2014b) in the photic zone (Ragueneau et al., 2000) and in surface sediments (Leventer, 1998). As an alternative or additional approach to diatom studies, Massé et al. (2011) proposed the use of a specific biomarker lipid – a diunsaturated highly branched isoprenoid alkene (HBI C<sub>25:2</sub>, Fig. 1) – for Southern Ocean sea ice reconstructions. The HBI diene was first described by Nichols et al. (1988) from sea ice diatoms. <sup>13</sup>C isotopic analyses of the HBI diene suggest a sea ice origin for this molecule (Sinninghe Damsté et al., 2007; Massé et al., 2011) and this is further corroborated by the identification of the sea ice diatom *Berkeleya adeliensis* as a producer of this HBI diene (Belt et al., 2016). *Berkeleya adeliensis* is associated with Antarctic landfast ice and the underlying so-called platelet ice (Riaux-Gobin and Poulin, 2004). In a survey of surface sediments collected from proximal sites around Antarctica, Belt et al. (2016) note a widespread sedimentary occurrence of the HBI diene and – by analogy with the Arctic HBI

1 monoene termed IP<sub>25</sub> (Belt et al., 2007) – proposed the term IPSO<sub>25</sub> (Ice Proxy for the Southern Ocean with 25  
2 carbon atoms) as a new name for this biomarker.

3 In previous studies, an HBI triene (HBI C<sub>25:3</sub>; Fig. 1) found in polar and sub-polar phytoplankton samples (Massé  
4 et al., 2011) has been considered alongside IPSO<sub>25</sub> and the ratio of IPSO<sub>25</sub> to this HBI triene hence has been  
5 interpreted as a measure for the relative contribution of organic matter derived from sea ice algae versus open  
6 water phytoplankton (Massé et al., 2011; Collins et al., 2013; Etourneau et al., 2013; Barbara et al., 2013, 2016).  
7 Collins et al. (2013) further suggested that the HBI triene might reflect phytoplankton productivity in marginal ice  
8 zones (MIZ) and, based on the observation of elevated HBI triene concentrations in East Antarctic MIZ surface  
9 waters, this has been strengthened by Smik et al. (2016a). Known source organisms of HBI trienes (Fig. 1 shows  
10 molecular structures of both the E- and Z-isomer) are, for example, *Rhizosolenia* and *Pleurosigma* diatom species  
11 (Belt et al., 2000, 2017). In the subpolar North Atlantic, the HBI Z-triene has been used to further modify the so-  
12 called PIP<sub>25</sub> index (Smik et al., 2016b) - an approach for semi-quantitative sea ice estimates. Initially, PIP<sub>25</sub> was  
13 based on the employment of phytoplankton-derived sterols, such as brassicasterol (24-methylcholesta-5,22E-dien-  
14 3β-ol) and dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol) (Kanazawa et al., 1971; Volkman, 2003), to  
15 serve as open-water counterparts, while IP<sub>25</sub> reflects the occurrence of a former sea ice cover (Belt et al., 2007;  
16 Müller et al., 2009, 2011). Consideration of these different types of biomarkers helps to discriminate between ice-  
17 free and permanently ice-covered ocean conditions, both resulting in a lack of IP<sub>25</sub> and IPSO<sub>25</sub>, respectively (for  
18 further details see Belt, 2018; Belt and Müller, 2013). Uncertainties in the source-specificity of brassicasterol  
19 (Volkman, 1986) and its identification in Arctic sea ice samples, however, require caution when pairing this sterol  
20 with a sea ice biomarker lipid for Arctic sea ice reconstructions (Belt et al., 2013). In this context, we note that  
21 Belt et al. (2018) reported that brassicasterol is not evident in the IPSO<sub>25</sub> producing sea ice diatom *Berkeleya*  
22 *adeliensis*. While the applicability of HBIs (and sterols) to reconstruct past sea ice conditions has been thoroughly  
23 investigated in the Arctic Ocean (Belt, 2018; Stein et al., 2012; Xiao et al., 2015), only two studies document the  
24 distribution of HBIs in Southern Ocean surface sediments (Belt et al., 2016; Massé et al., 2011). The circum-  
25 Antarctic data set published by Belt et al. (2016), however, does neither report HBI triene nor sterol abundances.  
26 Significantly more studies so far focused on the use of IPSO<sub>25</sub> and the HBI Z-triene for paleo sea ice  
27 reconstructions and these records are commonly compared to micropaleontological diatom analyses (e.g., Barbara  
28 et al., 2013; Collins et al., 2013; Denis et al., 2010).

29 Here, we provide a first overview of the distribution of IPSO<sub>25</sub>, HBI trienes, brassicasterol and dinosterol in surface  
30 sediments from the permanently ice-free ocean in the Drake Passage towards the seasonal sea ice inhabited area  
31 of the Bransfield Strait at the northern WAP. Sea ice estimates based on biomarkers are compared to sea ice

1 concentrations derived from diatom transfer functions and satellite-derived data on the recent sea ice conditions in  
2 the study area. We further introduce and discuss the so-called PIPSO<sub>25</sub> index (phytoplankton-IPSO<sub>25</sub> index),  
3 which, following the PIP<sub>25</sub> approach in the Arctic Ocean (Müller et al., 2011), may serve as a further indicator of  
4 past Southern Ocean sea ice cover.

## 1    2    **Oceanographic setting**

2    The study area includes the southern Drake Passage and the Bransfield Strait located between the South Shetland  
3    Islands and the northern tip of the WAP (Fig. 2a and b). The oceanographic setting in the Drake Passage is  
4    dominated by the Antarctic Circumpolar Current (ACC) and several oceanic fronts showing large geostrophic  
5    water mass flows and subduction and upwelling of water masses (Orsi et al., 1995). The Antarctic Polar Front  
6    (APF) divides relatively warm subantarctic waters from the cold and salty Antarctic waters, while the southern  
7    Antarctic Circumpolar Current Front (SACCF) often associates with the maximum sea ice extent (Kim and Orsi,  
8    2014). The current system in the Bransfield Strait is relatively complex and the mixture of water masses is not yet  
9    well understood (Moffat and Meredith, 2018; Sangrà et al., 2011). A branch of the ACC enters the Bransfield  
10    Strait in the west as the Bransfield Current, carrying transitional waters under the influence of the Bellingshausen  
11    Sea (Transitional Bellingshausen Sea Water, TBW). The TBW is characterized by a well-stratified, fresh and  
12    warm water mass with summer sea surface temperatures (SST) above 0° C. Below the shallow TBW, a narrow  
13    tongue of circumpolar deep water (CDW) flows along the slope of the South Shetland Islands (Sangrà et al., 2011).  
14    In the eastern part, transitional water from the Weddell Sea (Transitional Weddell Sea Water, TWW) enters the  
15    Bransfield Strait through the Antarctic Sound and from the Antarctic Peninsula (AP). This water mass corresponds  
16    to the Antarctic Coastal Current (Collares et al., 2018; Thompson et al., 2009). The TWW is significantly colder  
17    (summer SST < 0° C) and saltier due to extended sea ice formation in the Weddell Sea Gyre. The two water masses  
18    are separated at the sea surface by the Peninsula Front characterized by a TBW anticyclonic eddy system (Sangrà  
19    et al., 2011). While the TWW occupies the deep water column of the Bransfield Strait (Sangrà et al., 2011), it joins  
20    the surface TBW in the southwestern Bransfield Strait (Collares et al., 2018).

21    Due to high concentrations of dissolved iron on the shelf (Klunder et al., 2014), the area around the WAP is  
22    characterized by a high primary production with high vertical export fluxes during early summer associated with  
23    the formation of fast sinking mineral aggregates and fecal pellets (Kim et al., 2004; Wefer et al., 1988). The  
24    Peninsula Front divides the Bransfield Strait into two biogeographic regimes of high chlorophyll and diatom  
25    abundance in the TBW and low chlorophyll values and a pre-dominance of nanoplankton in the TWW (Gonçalves-  
26    Araujo et al., 2015), which is also reflected in the geochemistry of surface sediments (Cárdenas et al., 2018).

### 1 3 Materials and Methods

#### 2 3.1 Sediment Samples and radiocarbon dating

3 In total, 26 surface sediment samples obtained by multicorers and box corers during the RV *Polarstern* cruise  
4 PS97 (Lamy, 2016) were analyzed (Fig. 2, Table 1). All samples were stored frozen and in glass vials. The  
5 composition of the sediments ranges from foraminiferal mud in the Drake Passage to diatomaceous mud with  
6 varying amounts of ice rafted debris in the Bransfield Strait (Lamy, 2016).

7 <sup>14</sup>C radiocarbon dating of two samples from the PS97 cruise and one from the *Polarstern* cruise ANT-VI/2  
8 (Fütterer, 1988) was conducted using the mini carbon dating system (MICADAS) at the Alfred Wegener Institute  
9 (AWI) in Bremerhaven, Germany, following the method of Wacker et al. (2010). The <sup>14</sup>C ages were calibrated to  
10 calendar years before present (cal BP) using the Calib 7.1 software (Stuiver et al., 2019) with an estimated reservoir  
11 age of 1178 years, derived from the six closest reference points listed in the Marine Reservoir Correction Database  
12 ([www.calib.org](http://www.calib.org)).

#### 14 3.2 Organic geochemical analyses

15 For biomarker analyses, sediments were freeze-dried and homogenized using an agate mortar. After freeze-drying,  
16 samples were stored frozen to avoid degradation. The extraction, purification and quantification of HBIs and  
17 sterols follow the analytical protocol applied by the international community of researchers performing HBI and  
18 sterol-based sea ice reconstructions (Belt et al., 2013, 2014; Stein et al., 2012). Prior to extraction, internal  
19 standards 7-hexylnonadecane (7-HND) and 5 $\alpha$ -androstan-3 $\beta$ -ol were added to the sediments. For the ultrasonic  
20 extraction (15 min), a mixture of CH<sub>2</sub>Cl<sub>2</sub>:MeOH (v/v 2:1; 6 ml) was added to the sediment. After centrifugation  
21 (2500 rpm for 1 min), the organic solvent layer was decanted. The ultrasonic extraction step was repeated twice.  
22 From the combined total organic extract, apolar hydrocarbons were separated via open column chromatography  
23 (SiO<sub>2</sub>) using hexane (5 ml). Sterols were eluted with ethylacetate:hexane (v/v 20:80; 8 ml). HBIs were analyzed  
24 using an Agilent 7890B gas chromatography (30 m DB 1MS column, 0.25 mm diameter, 0.250  $\mu$ m film thickness,  
25 oven temperature 60° C for 3 min, rise to 325° C within 23 min, holding 325° C for 16 min) coupled to an Agilent  
26 5977B mass spectrometer (MSD, 70 eV constant ionization potential, ion source temperature 230° C). Sterols  
27 were first silylated (200  $\mu$ l BSTFA; 60° C; 2 hours; Belt et al., 2013; Brault and Simoneit, 1988; Fahl and Stein,  
28 2012) and then analyzed on the same instrument using a different oven temperature program (60° C for 2 min, rise  
29 to 150° C within 6 min, rise to 325° C within 56 min 40 sec). As recommended by Belt (2018), the identification  
30 of IPSO<sub>25</sub> and HBI trienes is based on comparison of their mass spectra with published mass spectra (Belt, 2018;  
31 Belt et al., 2000; see supplementary material S1). Regarding the potential sulfurization of IPSO<sub>25</sub>, we examined

1 the GC-MS chromatogram and mass spectra of each sample for the occurrence of the HBI C<sub>25</sub> sulfide (Sinninghe  
2 Damsté et al., 2007). The C<sub>25</sub> HBI thiane was absent in all samples. For the quantification, manually integrated  
3 peak areas of the molecular ions of the HBIs in relation to the fragment ion m/z 266 of 7-HND were used.  
4 Instrumental response factors are determined by means of an external standard sediment from the Lancaster Sound,  
5 Canada. The HBI concentrations in this sediment are known and a set of calibration series was applied to determine  
6 the different response factors of the HBI molecular ions (m/z 346; m/z 348) and the fragment ion of 7-HND (m/z  
7 266) (supplement S2; Belt, 2018; Fahl and Stein, 2012). The identification of sterols was based on comparison of  
8 their retention times and mass spectra with those of reference compounds run on the same instrument. Comparison  
9 of peak areas of individual analytes and the internal standard was used for sterol quantification. The error  
10 determined by duplicate GC-MS measurements was below 0.7 %. The detection limit for HBIs and sterols was  
11 0.5 ng/g sediment. Absolute concentrations of HBIs and sterols were normalized to total organic carbon contents  
12 (for TOC data see Cárdenas et al., 2018).

13 The herein presented phytoplankton-IPSO<sub>25</sub> index (PIPSO<sub>25</sub>) is calculated using the same formula as for the PIP<sub>25</sub>  
14 index following Müller et al. (2011):

$$15 \quad PIPSO_{25} = \frac{IPSO_{25}}{IPSO_{25} + (c \times \text{phytoplankton marker})} \quad (1)$$

16 The balance factor c (c = mean IPSO<sub>25</sub> / mean phytoplankton biomarker) is applied to account for the high offsets  
17 in the magnitude of IPSO<sub>25</sub> and sterol concentrations (see Belt and Müller, 2013; Müller et al., 2011; Smik et al.,  
18 2016b for details and a discussion of the c-factor). Since the concentrations of IPSO<sub>25</sub> and both HBI trienes are in  
19 the same range, the c-factor has been set to 1 (following Smik et al., 2016b). For the calculation of the sterol-based  
20 PIPSO<sub>25</sub> index using brassicasterol and dinosterol the applied c-factor is 0.0048 and 0.0137, respectively.

21 Stable carbon isotope composition of IPSO<sub>25</sub>, requiring a minimum of 50 ng carbon, was successfully determined  
22 on five samples using GC-irm-MS. The ThermoFisher Scientific Trace GC was equipped with a 30 m Restek Rxi-  
23 5 ms column (0.25 mm diameter, 0.25 µm film thickness) and coupled to a Finnigan MAT 252 isotope ratio mass  
24 spectrometer via a modified GC/C interface. Combustion of compounds was done under continuous flow in  
25 ceramic tubes filled with Ni wires at 1000° C under an oxygen trickle flow. The same GC program as for the HBI  
26 identification was used. The calibration was done by comparison to a CO<sub>2</sub> reference gas. The values of δ<sup>13</sup>C are  
27 expressed in per mill (‰) against Vienna PeeDee Belemnite (VPDB) and the mean standard deviation was <0.9  
28 ‰. An external standard mixture was measured every six runs, achieving a long-term mean standard deviation of  
29 0.2‰ and an average accuracy of <0.1 ‰. Stable isotopic composition of neither HBI trienes nor sterols could be  
30 determined due to coeluting compounds.

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### 3.3 Diatoms

Details of the standard technique of diatom sample preparation were developed in the micropaleontological laboratory at the Alfred Wegener Institute (AWI) in Bremerhaven, Germany. The preparation included a treatment of the sediment samples with hydrogen peroxide and concentrated hydrochloric acid to remove organic and calcareous remains. After washing the samples several times with purified water, the water was removed and the diatoms were embedded on permanent mounts for counting (see detailed description by Gersonde and Zielinski, 2000). The respective diatom counting was carried out according to Schrader and Gersonde (1978). On average, 400 to 600 diatom valves were counted in each slide using a Zeiss Axioplan 2 at x1000 magnification. In general preservation state of the diatom assemblages was moderate to good in the Bransfield Strait and decreased towards the Drake Passage where it is moderate to poor.

Diatoms were identified to species or species group level and if possible to forma or variety level. The taxonomy follows primarily Hasle and Syvertsen (1996), Zielinski and Gersonde (1997), and Armand and Zielinski (2001). Following Zielinski and Gersonde (1997) and Zielinski et al. (1998) we combined some taxa to groups:

The *Thalassionema nitzschioides* group combines *T. nitzschioides* var. *lanceolata* and *T. nitzschioides* var. *capitulata*, two varieties with gradual transition of features between them and no significantly different ecological response. The species *Fragilariopsis curta* and *Fragilariopsis cylindrus* were combined as *F. curta* group taking into account their similar relationship to sea ice and temperature (Armand et al., 2005; Zielinski and Gersonde, 1997). Furthermore, the *Thalassiosira gracilis* group comprises *T. gracilis* var. *gracilis* and *T. gracilis* var. *expecta* because the characteristic patterns in these varieties are often transitional, which hampers distinct identification.

Although the two varieties *Eucampia antarctica* var. *recta* and *E. antarctica* var. *antarctica* display different biogeographical distribution (Fryxell and Prasad, 1990), they were combined to the *E. antarctica* group. This group was not included in the transfer function (TF) as it shows no relationship to either sea ice or temperature variation (Esper and Gersonde, 2014a, b). Besides the *E. antarctica* group, we also discarded diatoms assembled as *Chaetoceros* spp. group from the TF-based re-constructions, following Zielinski et al. (1998) and Esper and Gersonde (2014a). This group combines mainly resting spores of a diatom genus with a ubiquitous distribution pattern that cannot be identified to species level due to the lack of morphological features during light microscopic inspection. Therefore, different ecological demands of individual taxa cannot be distinguished.

For estimating winter sea ice (WSI) concentrations we applied the marine diatom TF MAT-D274/28/4an, comprising 274 reference samples from surface sediments in the western Indian, the Atlantic and the Pacific sectors of the Southern Ocean, with 28 diatom taxa and taxa groups, and an average of 4 analogs (Esper and



1 Gersonde, 2014a). The WSI estimates refer to September sea-ice concentrations averaged over a time period from  
2 1981 to 2010 at each surface sediment site (National Oceanic and Atmospheric Administration, NOAA; Reynolds  
3 et al., 2002, 2007). The reference data set is suitable for our approach as it uses a 1° by 1° grid, representing a  
4 higher resolution than previously used and results in a root mean squared error of prediction (RMSEP) of 5.52%  
5 (Esper and Gersonde, 2014a). We defined 15% concentration as threshold for maximum sea-ice expansion  
6 following the approach of Zwally et al. (2002) for the presence or absence of sea ice, and 40% concentration  
7 representing the average sea-ice edge (Gersonde et al., 2005; Gloersen et al., 1993). MAT calculations were carried  
8 out with the statistical computing software R (R Core Team, 2012) using the additional packages Vegan (Oksanen  
9 et al., 2012) and Analogue (Simpson and Oksanen, 2012). Further enhancement of the sea-ice reconstruction was  
10 obtained by consideration of the abundance pattern of the diatom sea-ice indicators allowing for qualitative  
11 estimate of sea-ice occurrence, as proposed by Gersonde and Zielinski (Gersonde and Zielinski, 2000).

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### 13 **3.4 Sea ice data**

14 The mean monthly satellite sea ice concentration was derived from Nimbus-7 SMMR and DMSP SSM/I-SSMIS  
15 passive microwave data and downloaded from the National Snow and Ice Data Center (NSIDC; Cavalieri et al.,  
16 1996). The sea ice concentration is expressed to range from 0 to 100 %, with concentrations below 15 %  
17 suggesting the minor occurrence of sea ice. Accordingly, the sea ice extent is defined as the ocean area with a sea  
18 ice cover of at least 15 %.

19 An interval from 1980 to 2015 was used to generate an average sea ice distribution for each season; spring (SON),  
20 summer (DJF), autumn (MAM) and winter (JJA) (Table 2) and the data is considered to reflect the modern mean  
21 state of sea ice coverage around the WAP. The high standard deviation in the seasonal sea ice concentrations (up  
22 to 26 % in winter; Table 2) in the vicinity of the WAP is attributed to the distinct intra- and interannual variability  
23 in sea ice coverage. In this regard, Kim et al. (2005) already related interannual changes in particle flux to annual  
24 changes in sea ice cover in the Bransfield Strait. We here suggest that by considering mean sea ice concentrations  
25 determined for an observational period of 35 years, reflects a good estimate of average sea ice conditions and  
26 facilitates the comparison with sedimentary archives.

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## 4 Results and Discussion

In the following we present and discuss the sedimentary concentrations of IPSO<sub>25</sub>, HBI trienes and phytosterols regarding their spatial distribution patterns in relation to the environmental conditions and oceanographic features in the study area. We especially focus on the applicability of these biomarkers for reconstructing sea ice conditions and integrate information derived from satellite observations and diatom-based sea ice estimations. We further discuss the possible approach of a sea ice index PIPSO<sub>25</sub> by analogy with the Arctic sea ice index PIP<sub>25</sub> (Müller et al., 2011).

### 4.1 Biomarker distributions in surface sediments

#### *Distribution of IPSO<sub>25</sub>*

The sea ice biomarker IPSO<sub>25</sub> was detected in 14 samples, with concentrations ranging between 0.37 and 17.81 µg g<sup>-1</sup> TOC (Table 1). The distribution of IPSO<sub>25</sub> in the study area shows a clear northwest-southeast gradient (Fig. 3a) with concentrations increasing from the continental slope and around the South Shetland Islands towards the continental shelf. Maximum IPSO<sub>25</sub> concentrations are observed at stations under TWW influence with distinctly cold summer SSTs in the Bransfield Strait. According to Belt et al. (2016), deposition of IPSO<sub>25</sub> is highest in areas covered by landfast sea ice and platelet ice during early spring and summer. Platelet ice is formed under supercooling ocean conditions in the vicinity of ice-shelves and subsequently may be incorporated into drifting sea ice (Gough et al., 2012; Hoppmann et al., 2015). We note that, for example, core sites PS97/068, PS97/069, PS97/072, and PS97/073 in the central and eastern Bransfield Strait are located too distal to be covered by fast ice and suggest that peak IPSO<sub>25</sub> concentrations at these sites may refer to the frequent drift and melt of sea ice exported from the Weddell Sea into the Bransfield Strait. The vertical export of biogenic material from sea ice towards the seafloor may be accelerated significantly by the formation of organic-mineral aggregates, fecal pellets or by (cryogenic) gypsum ballasting, which promotes a rapid burial and sedimentation of organic matter in polar settings (De La Rocha and Passow, 2007; Wefer et al., 1988; Wollenburg et al., 2018). A recent study from Schmidt et al. (2018) shows that the occurrence of IPSO<sub>25</sub> in suspended matter and pelagic grazers (krill) is closely linked to the position of the sea ice edge. Lateral subsurface advection of organic matter (including biomarkers) through the TWW, however, may also contribute to elevated IPSO<sub>25</sub> concentrations at these sites. IPSO<sub>25</sub> was not detected in sediments from the permanently ice-free areas in the Drake Passage.

The δ<sup>13</sup>C values of IPSO<sub>25</sub> are between -10.3 ‰ and -14.7 ‰ which is the commonly observed range for IPSO<sub>25</sub> in surface sediments, sea ice derived organic matter, and in Antarctic krill stomachs (Belt et al., 2016; Massé et al., 2011; Schmidt et al., 2018). These values contrast the low δ<sup>13</sup>C values of marine phytoplankton lipids in

1 Antarctic sediments (-38 ‰ to -41 ‰ after Massé et al., 2011) and support the sea ice origin of IPSO<sub>25</sub> in the study  
2 area.

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#### 4 *Distribution of HBI trienes*

5 The HBI Z-triene was present in all 26 samples (0.33-26.86 µg g<sup>-1</sup> TOC) and the HBI E-triene was found in 24  
6 samples (0.15-13.87 µg g<sup>-1</sup> TOC) (Table 1). Highest concentrations of both HBI trienes are found in the eastern  
7 Drake Passage and along the continental slope, where IPSO<sub>25</sub> is absent, while their concentrations in the Bransfield  
8 Strait are generally low (Fig. 3b and c) suggesting unfavorable environmental conditions for their producers (e.g.,  
9 cooler SSTs, sea ice cover, grazing pressure) for their source diatoms. Contrary to the finding of elevated HBI Z-  
10 triene concentrations in surface waters along an ice-edge (Smik et al., 2016a) and earlier suggestions that this  
11 biomarker may be used as a proxy for MIZ conditions (Belt et al., 2015; Collins et al., 2013; Schmidt et al., 2018),  
12 we observe highest concentrations of the HBI Z- and E-triene at the permanently ice-free northernmost stations  
13 PS97/083 and PS97/084 in the eastern Drake Passage. These core sites are located in close vicinity to the Polar  
14 Front (Fig. 2) and we assume that the productivity of HBI triene source diatoms may benefit from mixing and  
15 upwelling of warm and cold water masses in this area (Moore and Abbott, 2002). Sediments collected south of the  
16 Polar Front and along the Hero Fracture Zone in the western Drake Passage (Fig. 2) contain moderate and very  
17 low concentrations of HBI trienes, respectively. The Hero Fracture Zone is mainly barren of fine-grained  
18 sediments and dominated by sands (Lamy, 2016), which may point to intensive winnowing by ocean currents  
19 impacting the deposition and burial of organic matter. Moderate concentrations of HBI trienes at the continental  
20 slope along the WAP (PS97/053, PS97/074, PS97/077) and in the Bransfield Strait likely refer to primary  
21 production associated with the retreating sea ice margin during spring and summer. This indicates seasonally ice-  
22 free waters in high production coastal areas influenced by upwelling (Gonçalves-Araujo et al., 2015) and feeding  
23 of the local food web (Schmidt et al., 2018). The similarity in the distribution of the HBI Z- and the E-triene in  
24 our surface sediments – the latter of which so far is not often considered for Southern Ocean paleoenvironmental  
25 studies – supports the assumption of a common diatom source for these HBIs (Belt et al., 2000, 2017).

26 We consider that degradation of biomarker lipids may affect their distribution within surface sediments. While  
27 laboratory studies on HBIs in solution point to a low reactivity of IPSO<sub>25</sub> towards auto- and photooxidative  
28 degradation (Rontani et al., 2014, 2011), a more recent investigation into Antarctic surface sediments shows that  
29 IPSO<sub>25</sub> may potentially be affected by partial autoxidative and bacterial degradation but oxidation products are  
30 found in only minor proportions (Rontani et al., 2019a). Since HBI trienes exhibit a generally higher sensitivity to  
31 degradation than the C<sub>25</sub> HBI diene (Rontani et al., 2014, 2019b) - and this is supported by a recent observation

1 of increasing IPSO<sub>25</sub>/HBI triene ratios with increasing water depths in a polynya system off Eastern Antarctica  
2 (Rontani et al., 2019b) – their lower concentrations in the Bransfield Strait have to be considered with care. Vice  
3 versa, regarding maximum HBI triene concentrations and the absence of IPSO<sub>25</sub> in Drake Passage sediments, we  
4 conclude that the absence of the latter in these samples can be linked to the lack of sea ice (and not to the  
5 degradation of IPSO<sub>25</sub> as HBI trienes would have been removed first).

#### 6 7 *Distribution of sterols*

8 Brassicasterol is present in all samples with concentrations ranging from 3.39 to 5017.44  $\mu\text{g g}^{-1}$  TOC, while  
9 dinosterol was detected in 22 samples (0.0002-1983.75  $\mu\text{g g}^{-1}$  TOC). It is noticeable that the concentrations of  
10 sterols exceed the concentrations of IPSO<sub>25</sub> and HBI trienes by more than two orders of magnitude. We observe  
11 higher concentrations of brassicasterol and dinosterol in the eastern part of the Drake Passage supporting an open  
12 marine source for these sterols. Surprisingly, elevated concentrations of brassicasterol are also found at stations  
13 PS97/048-1 and 049-2 in the Hero Fracture Zone, which may argue against a winnowing signal leading to lower  
14 accumulation of organic matter. We can only speculate if transport and deposition of reworked sediment  
15 containing brassicasterol via iceberg rafting could explain these higher values. In contrast to the observation made  
16 for HBI trienes, high sterol concentrations are found in the eastern and central Bransfield Strait (Fig. 3d and e).  
17 Previously, elevated concentrations of steroidal components including brassicasterol and dinosterol in sediment  
18 cores from the Bransfield Strait have been interpreted to reflect a high productivity and significant inputs from  
19 diatoms and dinoflagellates (Brault and Simoneit, 1988). In a more recent overview, also Cárdenas et al. (2018)  
20 report peak concentrations of pigments, sterols and total organic carbon in the Bransfield Strait, which they relate  
21 to large seasonal phytoplankton blooms and higher accumulation rates. Dinosterol and, in particular, brassicasterol  
22 are known to have different source organisms including diatoms, dinoflagellates, cryptophytes, prymnesiophycean  
23 algae and cyanobacteria (Volkman, 1986) and we assume that this diversity accounts for the higher concentration  
24 of these lipids in Bransfield Strait sediments, while concentrations of HBI trienes, mainly derived from diatoms,  
25 are significantly lower. Regarding the potential input of brassicasterol from cryptophytes (Gladu et al., 1990; Goad  
26 et al., 1983), changes in the dominance of this phytoplankton group over diatoms have been reported for our study  
27 area and have been associated with a shallowing of the mixed layer and lower salinity due to intensified glacial  
28 ice-melting along the WAP (Mendes et al., 2013).

29 Similar to the observations made for HBIs, selective degradation may also affect the concentration of phytosterols  
30 within surface sediments. With respect to the preservation potential of terrigenous and marine derived sterols,  
31 Rontani et al. (2012) note an only weak effect of biotic and abiotic degradation of brassicasterol in Arctic Ocean

1 shelf sediments – if this is also true for Southern Ocean shelf areas needs to be determined. In general, further  
2 investigations into degradation processes affecting both HBIs and phytosterols within (the same) sediment samples  
3 would address an important knowledge gap regarding in-situ biochemical modifications of the biomarker signal.  
4

#### 5 **4.2 Comparison of satellite-derived modern sea ice conditions and biomarker data**

6 The spring and winter sea ice concentrations are shown in Figure 4a and b. Winter sea ice is estimated to not  
7 extend north of 61° S (Fig. 4b) and varies between 1 % and 50 % in the study area, while sea ice is reduced to less  
8 than 20 % in spring (Fig. 4a, Table 2). Sea ice concentrations of up to 50 % are common in winter between the  
9 South Shetland Islands and north of the Antarctic Sound where the influence of TWW is highest. Permanent sea  
10 ice cover is uncommon in the Bransfield Strait and around the WAP and this area is mainly characterized by a  
11 high sea ice seasonality, drift ice from the Weddell Sea (Collares et al., 2018) and a seasonally fluctuating sea ice  
12 margin.

13 Comparisons of IPSO<sub>25</sub> and winter sea ice concentrations derived from satellite data reveal a positive correlation  
14 ( $r^2 = 0.53$ ). The strongest relationship is observed in the eastern Bransfield Strait where the influence of TWW is  
15 high. Correlations with spring sea ice ( $r^2 = 0.27$ ) and other seasons are weak. As photosynthesis is not possible  
16 and a release of sea ice diatoms from melting sea ice is highly reduced during the Antarctic winter, the observation  
17 of a stronger correlation between recent winter sea ice concentrations and IPSO<sub>25</sub> is unexpected. We hence suggest  
18 that this offset may be related to the fact that the sediment samples integrate a longer time interval than is covered  
19 by satellite observations. Radiocarbon dating of selected samples that contain calcareous material reveals an age  
20 of 100 years BP in the vicinity of the South Shetland Islands (station PS97/059-2) and 142 years BP at the Antarctic  
21 Sound (station PS1546-2, Table 3). A significantly older age was determined for a sample of *N. pachyderma* from  
22 station PS97/044-1 (4830 years BP) which likely denotes the winnowing and/or very low sedimentation rates in  
23 the Drake Passage. Bioturbation effects and uncertainties in reservoir ages potentially mask the ages of the near-  
24 coastal samples. Nevertheless, since also other published ages of surface sediments within the Bransfield Strait  
25 (Barbara et al., 2013; Barnard et al., 2014; Etourneau et al., 2013; Heroy et al., 2008) are in the range of 0-270  
26 years, we consider that our surface samples likely reflect the paleoenvironmental conditions that prevailed during  
27 the last two centuries (and not just the last 35 years covered by satellite observations). In the context of the rapid  
28 warming during the last century (Vaughan et al., 2003) and the decrease of sea ice at the WAP (King, 2014; King  
29 and Harangozo, 1998), we suggest that the biomarker data of the surface sediments relate to a spring sea ice cover,  
30 which must have been enhanced compared to the recent (past 35 years) spring sea ice recorded via remote sensing.  
31 Presumably, the average spring sea ice conditions over the past 200 years might have been similar to the modern

1 (past 35 years) winter conditions, which would explain the stronger correlation between IPSO<sub>25</sub> and winter sea ice  
2 concentrations. The absence of IPSO<sub>25</sub> at stations PS97/052 and PS97/053, off the continental slope, is in conflict  
3 with the satellite data depicting an average winter sea ice cover of 23 %. Earlier documentations that the IPSO<sub>25</sub>  
4 producing sea ice diatom *Berkeleya adeliensis* favors land-fast ice communities in East Antarctica and platelet ice  
5 occurring mainly in near-coastal areas (Belt et al., 2016; Riaux-Gobin and Poulin, 2004) could explain this  
6 mismatch between biomarker and satellite data, which further strengthens the hypothesis that the application of  
7 IPSO<sub>25</sub> seems to be confined to continental shelf or near-coastal and meltwater affected environments (Belt, 2018;  
8 Belt et al., 2016). Alternatively, strong ocean currents (i.e. the ACC) could have impacted the deposition of IPSO<sub>25</sub>  
9 in this region.

10 Although the distribution pattern of HBI trienes reveals generally higher concentrations in ice-free environments,  
11 we note only very weak negative correlations with satellite sea ice data ( $r^2 < 0.1$ ). This may relate to the strong  
12 spatial variability in HBI triene concentrations within the Drake Passage and the different time periods represented  
13 by the satellite and sediment data. Similar to the HBI trienes, also the sterols do not show any significant  
14 relationship to the satellite sea ice concentrations. High abundances of brassicasterol and dinosterol are observed  
15 in both ice free as well as in seasonally ice-covered regions, which points to a broad environmental adaptation of  
16 the source organisms. We hence consider that other environmental parameters than sea ice (e.g., nutrient  
17 availability, water temperature and/or grazing pressure) exert a major control on the productivity of HBI triene  
18 and sterol producers in the study area.

19

#### 20 **4.3 Comparison of biomarker distributions and diatom-based sea ice estimates**

21 The diatoms preserved in sediments from the study area (Table 4) can be associated with open ocean and sea ice  
22 conditions (Fig. 5a-d). North of the South Shetland Islands, the strong influence of the ACC is reflected in the high  
23 abundance of open ocean diatom species such as *Fragilariopsis kerguelensis* and *Thalassiosira lentiginosa* (Esper  
24 et al., 2010). The two diatom species *Fragilariopsis curta* and *Fragilariopsis cylindrus* – known to not produce  
25 HBIs (Belt et al., 2016; Sinninghe Damsté et al., 2004) - mark the vicinity to sea ice (Buffen et al., 2007; Pike et  
26 al., 2008) and indicate fast and melting ice, a stable sea ice margin and stratification due to melting processes and  
27 the occurrence of seasonal sea ice. These observations are in accordance with previous diatom studies revealing a  
28 dominance of *Fragilariopsis kerguelensis* in the permanently open-ocean zone in the Drake Passage and an  
29 assemblage shift to more cold water adapted and sea ice-associated species in the seasonal sea ice zone of the  
30 Bransfield Strait (Cárdenas et al., 2018).

1 The high abundance of these sea ice diatoms in our samples is in good agreement with high and moderate IPSO<sub>25</sub>  
2 concentrations in the Bransfield Strait and around the South Shetland Islands, respectively. The only HBI source  
3 diatom identified is the HBI Z-triene producing *Rhizosolenia hebetata* (Belt et al., 2017), which is present in four  
4 samples in relatively small amounts which do not show a relation to the measured HBI Z-triene concentrations  
5 (Table 1 and 4). The source diatom of IPSO<sub>25</sub> *Berkeleya adeliensis* was not observed (or preserved) in the samples,  
6 and we suggest that additional, hitherto unknown, producers for IPSO<sub>25</sub> as well as for the HBI trienes may exist.  
7 We applied the transfer function of Esper and Gersonde (2014a) with four analogs (4an, Table 4) to our samples  
8 to estimate winter sea ice concentrations (WSI; Figure 5e). The diatom approach shows a clear trend of high winter  
9 sea ice concentrations in the range of 78-91 % in the Bransfield Strait and low sea ice concentrations (between 6-  
10 39 %) north of the continental slope. The fact that diatom data propose sea ice in the Drake Passage may result  
11 from the high ages of surface sediments but also from drift, resuspension and sedimentation of diatom remains.  
12 Because of the absence of IPSO<sub>25</sub> in the Drake Passage the correlation of its concentrations with WSI is only weak  
13 ( $r^2 = 0.29$ ).

14

#### 15 **4.4 Testing a semi-quantitative sea ice approach for the Southern Ocean: PIPSO<sub>25</sub>**

16 Following the PIP<sub>25</sub>-approach applied in the Arctic Ocean (Müller et al., 2011; Belt and Müller, 2013; Xiao et al.,  
17 2015), we used IPSO<sub>25</sub>, HBI triene and sterol data to calculate the PIPSO<sub>25</sub> index. The main concept of combining  
18 the sea ice proxy with an indicator of an ice-free ocean environment (i.e. a phytoplankton biomarker; Müller et al.,  
19 2011), aims at a more detailed assessment of the sea ice conditions. By reducing the light penetration through the  
20 ice, a thick and perennial sea ice cover limits the productivity of bottom sea ice algae (Hancke et al., 2018), which  
21 results in the absence of both sea ice and pelagic phytoplankton biomarker lipids in the underlying sediments. Vice  
22 versa, sediments from permanently ice-free ocean areas only lack the sea ice biomarker but contain variable  
23 concentrations of phytoplankton biomarkers (Müller et al., 2011). The co-occurrence of both biomarkers in a  
24 sediment sample suggests seasonal sea ice coverage promoting algal production indicative of sea ice as well as  
25 open ocean environments (Müller et al., 2011). Consideration of a phytoplankton biomarker alongside the sea ice  
26 proxy hence helps to avoid an underestimation of the past sea ice cover deduced from the absence of the sea ice  
27 proxy, which, in fact, may also be due to a permanent sea ice cover (Belt, 2018, 2019; Belt and Müller, 2013).  
28 Depending on the biomarker reflecting pelagic (open ocean) conditions, we here define P<sub>Z</sub>IPSO<sub>25</sub> (using the HBI  
29 Z-triene), P<sub>E</sub>IPSO<sub>25</sub> (using the HBI E-triene), P<sub>B</sub>IPSO<sub>25</sub> (using brassicasterol), and P<sub>D</sub>IPSO<sub>25</sub> (using dinosterol).  
30 The PIPSO<sub>25</sub> values are 0 in the Drake Passage and increase to intermediate values at the South Shetland Islands  
31 and the continental slope and reach highest values in the Bransfield Strait (Fig. 6a-d). Minimum PIPSO<sub>25</sub> values

1 are supposed to refer to a predominantly ice-free oceanic environment in the Drake Passage, while moderate  
2 PIPSO<sub>25</sub> values mark the transition towards a marginal sea ice coverage at the continental slope and around the  
3 South Shetland Islands. Elevated PIPSO<sub>25</sub> values in samples from the northeastern Bransfield Strait suggest an  
4 increased sea ice cover (probably sustained through the drift of sea ice originating in the Weddell Sea). This pattern  
5 reflects the oceanographic conditions of a permanently ice-free ocean north of the South Shetland Islands and a  
6 seasonal sea ice zone at the WAP influenced by the Weddell Sea as described by Cárdenas et al. (2018). Both HBI  
7 triene-based PIPSO<sub>25</sub> indices show constantly high values at the coast of the WAP of >0.7 (P<sub>Z</sub>IPSO<sub>25</sub>) and >0.8  
8 (P<sub>E</sub>IPSO<sub>25</sub>), respectively, and in the southern Bransfield Strait paralleling the southwest-northeast oriented  
9 Peninsula Front described by Sangrà et al. (2011). This front is reported to act as a barrier for phytoplankton  
10 communities (Gonçalves-Araujo et al., 2015) and is associated with the encounter between TWW carrying  
11 Weddell Sea sea ice through the Antarctic Sound and the TBW. The high PIPSO<sub>25</sub> values suggesting an extended  
12 sea ice cover west of the Peninsula Front (station PS97/054 and PS97/056) result from minimum concentrations  
13 of pelagic biomarkers and moderate concentrations of IPSO<sub>25</sub>. PIPSO<sub>25</sub> values based on the HBI E-triene are about  
14 0.2 higher compared to P<sub>Z</sub>IPSO<sub>25</sub>, due to the generally lower concentrations of the HBI E-triene (Table 1).

15 The sterol-based PIPSO<sub>25</sub> values display a generally similar pattern as P<sub>Z</sub>IPSO<sub>25</sub> and P<sub>E</sub>IPSO<sub>25</sub>, respectively, and  
16 we note a high comparability between the P<sub>E</sub>IPSO<sub>25</sub> and P<sub>B</sub>IPSO<sub>25</sub> values ( $r^2 = 0.73$ ). Some differences, however,  
17 are observed in the southwestern part of the Bransfield Strait (station PS97/056) where P<sub>B</sub>IPSO<sub>25</sub> indicates a lower  
18 sea ice cover and in the central Bransfield Strait (stations PS97/068 and PS97/069) where P<sub>B</sub>IPSO<sub>25</sub> and P<sub>D</sub>IPSO<sub>25</sub>  
19 point to only MIZ conditions. Regarding the modern sea ice conditions, the HBI triene-based PIPSO<sub>25</sub> indices  
20 hence seem to reflect the oceanographic conditions within the Bransfield Strait more satisfactorily. It has to be  
21 noted that the brassicasterol- or dinosterol-based PIPSO<sub>25</sub> index links environmental information derived from  
22 biomarker lipids belonging to different compound classes (i.e. HBIs and sterols), which have fundamentally  
23 different chemical properties. This requires special attention as, for example, selective degradation of one of the  
24 compounds may affect the sedimentary concentration of the respective lipids (Rontani et al., 2018). Previous  
25 studies linking HBI and sterol-based sea ice reconstructions with satellite-derived or, with respect to downcore  
26 paleo studies, paleoclimatic data, however, demonstrate that the climatic/environmental conditions controlling the  
27 production of HBIs and sterols seem to exceed the influence of a potential preferential degradation of these  
28 biomarkers within the sediments (e.g., Berben et al., 2014; Cabedo-Sanz et al., 2013; Müller et al., 2009, 2012;  
29 Müller and Stein, 2014; Stein et al., 2017; Xiao et al., 2015). A comparison of PIP<sub>25</sub> records determined using  
30 brassicasterol and the HBI Z-triene for three sediment cores from the Arctic realm covering the past up to 14.000  
31 years BP (Belt et al., 2015) reveals very similar trends for both versions of the PIP<sub>25</sub> index in each core, which



1 may point to, at least, a similar degree of degradation of HBI trienes and sterols through time. More such studies  
2 are needed to evaluate the preservation potential of HBIs and sterols in Southern Ocean sediments, especially for  
3 down core paleo studies.

4 Since brassicasterol and dinosterol are highly abundant in both seasonally ice-covered Bransfield Strait sediments  
5 as well as in permanently ice-free Drake Passage sediments, their use as an indicator of fully open-marine  
6 conditions in the study area is questionable. Elevated concentrations of both sterols in the Bransfield Strait could  
7 either point to an additional input of these lipids from melting sea ice (Belt et al., 2013) or a better adaptation of  
8 some of their source organisms to cooler and/or ice-affected ocean environments. Production and accumulation of  
9 these lipids in (late) summer (i.e. after the sea ice season) has to be considered as well. This observation highlights  
10 the need for a better understanding of the source organisms and the mechanisms involved in the synthesis of these  
11 sterols. Similarly, more research is needed on the production of IPSO<sub>25</sub> in Southern Ocean sea ice environments.  
12 The source diatom *Berkeleya adeliensis* seems to be restricted to a very unique ice environment. Previous studies  
13 documenting the lack of IPSO<sub>25</sub> in distal though winter sea ice covered areas (e.g., Belt et al., 2016) emphasize  
14 this limitation and it has been suggested that IPSO<sub>25</sub> may be more indicative of the type of sea ice rather than sea  
15 ice extent (Belt, 2019), which needs to be considered when targeting at more quantitative sea ice reconstructions  
16 using this biomarker.

#### 17 18 *Comparison of PIPSO<sub>25</sub> with satellite sea ice data and diatom sea ice estimations*

19 The contour lines in Figure 6a-d show the observed extent of 15 %, 30 %, 40 % and 50 % winter sea ice compared  
20 to the PIPSO<sub>25</sub> values. In the northeastern part of the study area, the HBI triene based PIPSO<sub>25</sub> indices align well  
21 with the contour lines of winter sea ice concentrations and depict the gradient from the marginally ice-covered  
22 southern Drake Passage towards the intensively ice-covered Weddell Sea. In the southwestern part of the  
23 Bransfield Strait, all PIPSO<sub>25</sub> indices suggest a higher sea ice cover than it is reflected in the satellite data. This  
24 may be explained by the transport (and melt) of drift ice through the TWW, joining the TBW at the southwestern  
25 Peninsula Front and/or a higher sea ice cover in this area prior to the remote sensing observational period (and  
26 prior to the recent WAP warming).

27 Correlations of PIPSO<sub>25</sub> values with satellite-derived sea ice concentrations (for spring, summer, autumn and  
28 winter) contrast earlier observations made for the PIP<sub>25</sub> index in the Arctic Ocean, where the closest linear  
29 relationship is found mainly with the spring sea ice coverage (i.e. the blooming season of sea ice algae; Müller et  
30 al., 2011; Xiao et al., 2015). We observe a remarkably low correlation between PIPSO<sub>25</sub> values and spring sea ice  
31 concentrations of less than 20 % with a coefficient of determination  $r^2 = 0.37$  for P<sub>Z</sub>IPSO<sub>25</sub>,  $r^2 = 0.50$  for P<sub>E</sub>IPSO<sub>25</sub>

1 (Fig. 7a),  $r^2 = 0.31$  for  $P_B\text{IPSO}_{25}$ , and  $r^2 = 0.34$  for  $P_D\text{IPSO}_{25}$  (Fig. 7b). The highest correlation is observed between  
2 winter sea ice concentrations and  $P_E\text{IPSO}_{25}$  ( $r^2 = 0.72$ ), and  $P_Z\text{IPSO}_{25}$  ( $r^2 = 0.65$ , Fig. 7c) with a weaker correlation  
3 for the sterol-based  $\text{PIPSO}_{25}$  values ( $P_B\text{IPSO}_{25}$ :  $r^2 = 0.52$ ;  $P_D\text{IPSO}_{25}$ :  $r^2 = 0.44$ , Fig. 7d). As discussed above, we  
4 attribute this seemingly conflicting result of a better agreement between biomarker data and winter (instead of  
5 spring) sea ice conditions to the offset in the time intervals reflected in satellite and sediment data. For the  
6 application of the  $\text{PIPSO}_{25}$  approach, more aspects concerning the physical environmental conditions controlling  
7 the formation of platelet ice, which, at least at this state of research, is regarded as a main source of  $\text{IPSO}_{25}$  (Belt  
8 et al., 2016) need to be considered. The formation and accumulation of platelet ice in supercooled waters below  
9 landfast sea ice or underneath an ice-shelf (e.g., Gough et al., 2012; Hoppmann et al., 2015) seem to limit the  
10 spatial occurrence of  $\text{IPSO}_{25}$  and hence the applicability of  $\text{PIPSO}_{25}$  to coastal environments. However, transport  
11 of supercooled waters away from the coast may lead to platelet ice formation (and colonization of *Berkeleya*  
12 *adeliensis*) in more distal areas (Hoppmann et al., 2015) and also the drift of sea ice (including the underlying  
13 platelet ice) may impact the distribution of  $\text{IPSO}_{25}$  in Southern Ocean sediments and these processes require further  
14 investigations. Even though  $\text{PIPSO}_{25}$  values show a stronger relationship to satellite sea ice concentrations than  
15  $\text{IPSO}_{25}$  concentrations more insight into the production and sedimentation of the involved biomarker lipids is  
16 needed to develop such a semi-quantitative approach.

17 With regard to the spatially and temporally variable sea ice extent, Esper and Gersonde (2014a) studied the  
18 response of diatom species to changes in environmental conditions and their response to the non-linear behavior  
19 of sea ice dynamics (Zwally et al., 2002). In contrast to ice free areas or areas of permanent sea ice cover, areas  
20 characterized by the transition from consolidated to unconsolidated sea ice show rapid changes in satellite derived  
21 sea ice concentrations (ranging from 90 % to 15 %) and exhibit a large variability in species composition. To  
22 reflect this curve in sea ice we hence chose a cubic polynomial regression (polynomial of third degree) to determine  
23 the relation between  $\text{PIPSO}_{25}$  values and satellite data depicting sea ice concentrations of more than 20 %. A  
24 slightly sigmoid-shaped regression line of winter sea ice concentrations and  $\text{PIPSO}_{25}$  values depicts the non-  
25 linearity of sea ice cover in different sea ice regimes.

26 A positive correlation is found between WSI concentrations derived from diatoms and the  $\text{PIPSO}_{25}$  indices based  
27 on HBI trienes ( $P_Z\text{IPSO}_{25}$  with  $r^2 = 0.76$ ;  $P_E\text{IPSO}_{25}$  with  $r^2 = 0.77$ , Fig. 8a). The correlations of sterol-based  $\text{PIPSO}_{25}$   
28 values with WSI are slightly lower but in the same range ( $P_B\text{IPSO}_{25}$  with  $r^2 = 0.74$ ;  $P_D\text{IPSO}_{25}$  with  $r^2 = 0.69$ , Fig.  
29 8b). A slightly weaker correlation is noted for diatom- and satellite-based winter sea ice concentrations ( $r^2 = 0.63$ ;  
30 Fig. 8c). Overall, the diatom approach indicates higher sea ice concentrations than the satellite data with an offset  
31 of up to 65 %. This may be due to different sources of satellite reference data used for the transfer function or also

1 due to the fact that the sediment samples integrate a longer time period with a higher sea ice cover than the satellite  
2 data (see discussion in section 4.2). Regarding future sea ice reconstructions based on IPSO<sub>25</sub> and other  
3 biomarkers, we note that the simultaneous study of diatom assemblages provides valuable information on the sea  
4 surface conditions and may help to avoid misleading interpretation of the biomarker data (Belt, 2019). Vice versa,  
5 while diatom-based transfer functions mainly refer to winter sea ice concentrations, the IPSO<sub>25</sub> (and PIPSO<sub>25</sub>)  
6 signal holds critical information on coastal spring/summer sea ice conditions, which are often crucial for ice-shelf  
7 (melting) processes. Pairing the micropaleontological and the biomarker approach hence provides for a more  
8 comprehensive reconstruction of Southern Ocean sea ice conditions.

## 1   **5   Conclusions**

2   The distribution of the sea ice biomarker IPSO<sub>25</sub>, related HBI trienes and phytosterols as well as diatoms in a suite  
3   of surface sediments from the southern Drake Passage and the WAP reflects recent sea surface water characteristics  
4   reasonably well. While highest HBI triene concentrations are observed in the permanently open ocean zone of the  
5   Drake Passage, they are significantly reduced in the seasonally ice-covered Bransfield Strait. This pattern is  
6   reversed for the sea ice proxy IPSO<sub>25</sub> and in accordance with previous surface sediment analyses revealing a  
7   preferential occurrence of this biomarker in near-coastal environments. The distribution of phytosterols points to  
8   a broader environmental significance of brassicasterol and dinosterol in terms of ocean temperature and sea ice  
9   tolerance, and/or nutrient availability. Following the PIP<sub>25</sub> approach established for Arctic Ocean sea ice  
10   reconstructions, the herein proposed sea ice index PIPSO<sub>25</sub> indicates seasonal sea ice cover along the coast of the  
11   WAP and in the Bransfield Strait, whereas mainly ice-free conditions prevail in the Drake Passage. In general, this  
12   pattern is consistent with satellite-derived sea ice data and diatom-based sea ice estimates and we note that the  
13   PIPSO<sub>25</sub> index seems a potential approach towards semi-quantitative sea ice reconstructions in the Southern  
14   Ocean. The recent rapid warming in the study area, however, affects the comparability of proxy and satellite data.  
15   The fact that the surface sediments integrate a significantly longer time interval than the remote sensing data  
16   thwarts attempts to calibrate PIPSO<sub>25</sub> values against observed sea ice concentrations. Additional data from other  
17   circum-Antarctic coastal (and distal) environments and investigations into potential calibration methods are  
18   needed to further develop this approach. Importantly, more information is needed on the mechanisms of IPSO<sub>25</sub>  
19   and HBI triene synthesis, transport and preservation within sediments. Despite a generally good agreement  
20   between PIPSO<sub>25</sub>-, diatom- and satellite-based sea ice distributions, we note that the basically different sea ice  
21   patterns and sea ice varieties in the Southern Ocean and accordingly different mechanisms controlling the IPSO<sub>25</sub>  
22   signal need to be considered carefully, when adapting a (not yet fully validated) semi-quantitative approach  
23   initially developed for the Arctic Ocean.

24

1 **Data Availability**

2 All data can be found in this paper and will be available at the open access repository [www.pangaea.de](http://www.pangaea.de)  
3 (<https://doi.pangaea.de/10.1594/PANGAEA.897165>).

4  
5 **Author contributions**

6 The study was conceived by MV and JM. Data collections and experimental investigations were done by MV  
7 together with OE (diatoms), GM (radiocarbon dating), CH (satellite data), and ES (isotope data). MV wrote the  
8 manuscript and did the visualizations. KF provided technical support. JM supervised the study. All authors  
9 contributed to the interpretation and discussion of the results and the conclusion of this study.

10

11 **Competing interests**

12 None of the authors has a conflict of interest.

13

14 **Acknowledgement**

15 We thank the captain, crew and chief scientist Frank Lamy of RV Polarstern cruise PS97, and the following  
16 supporters: Mandy Kiel and Denise Diekstatt (technicians), Lester Lembke-Jene (biology, dating), Liz Bonk and  
17 Hendrik Grotheer (from MICADAS), Max Mues (sample preparation), Nicoletta Ruggieri (lab support), Walter  
18 Luttmmer (lab support). Simon Belt is acknowledged for providing the 7-HND internal standard for HBI  
19 quantification. We also acknowledge the two anonymous reviewers and the editor for their constructive and  
20 detailed comments. Financial support was provided through the Helmholtz Research grant VH-NG-1101.

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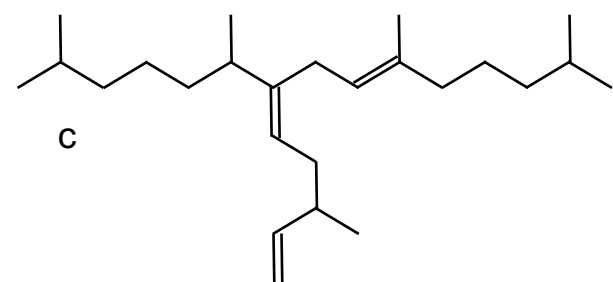
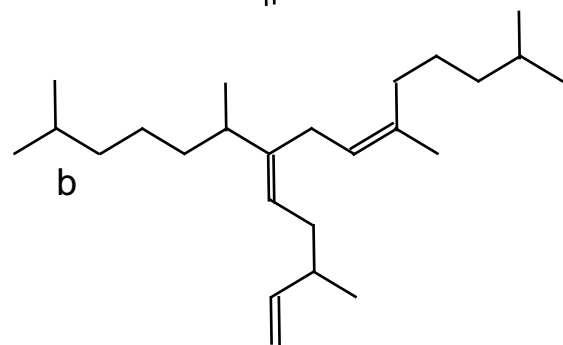
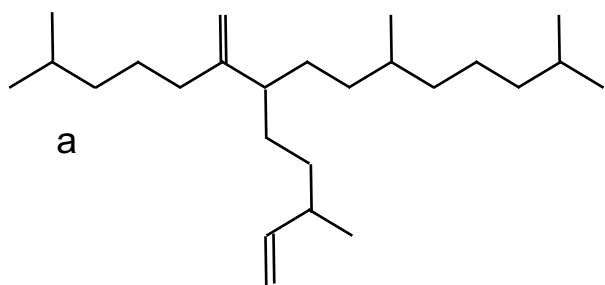
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1 **Figures**

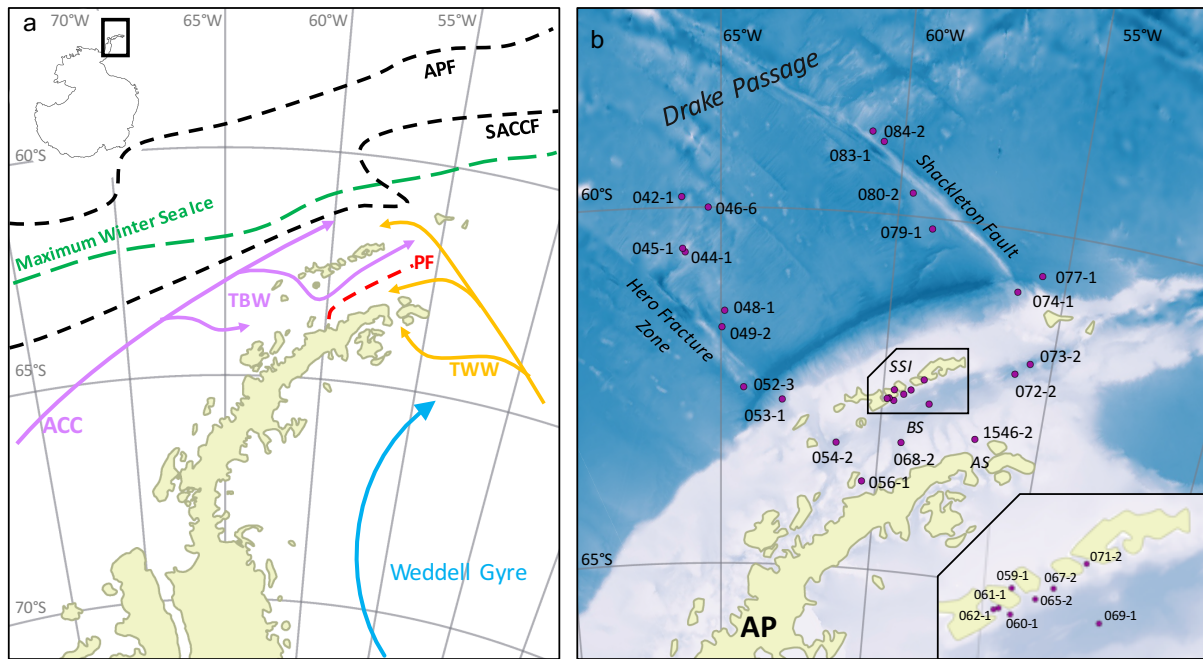


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3 **Figure 1: The molecular structures of a) IPSO<sub>25</sub>, b) the HBI Z-triene, and c) the HBI E-triene.**

4

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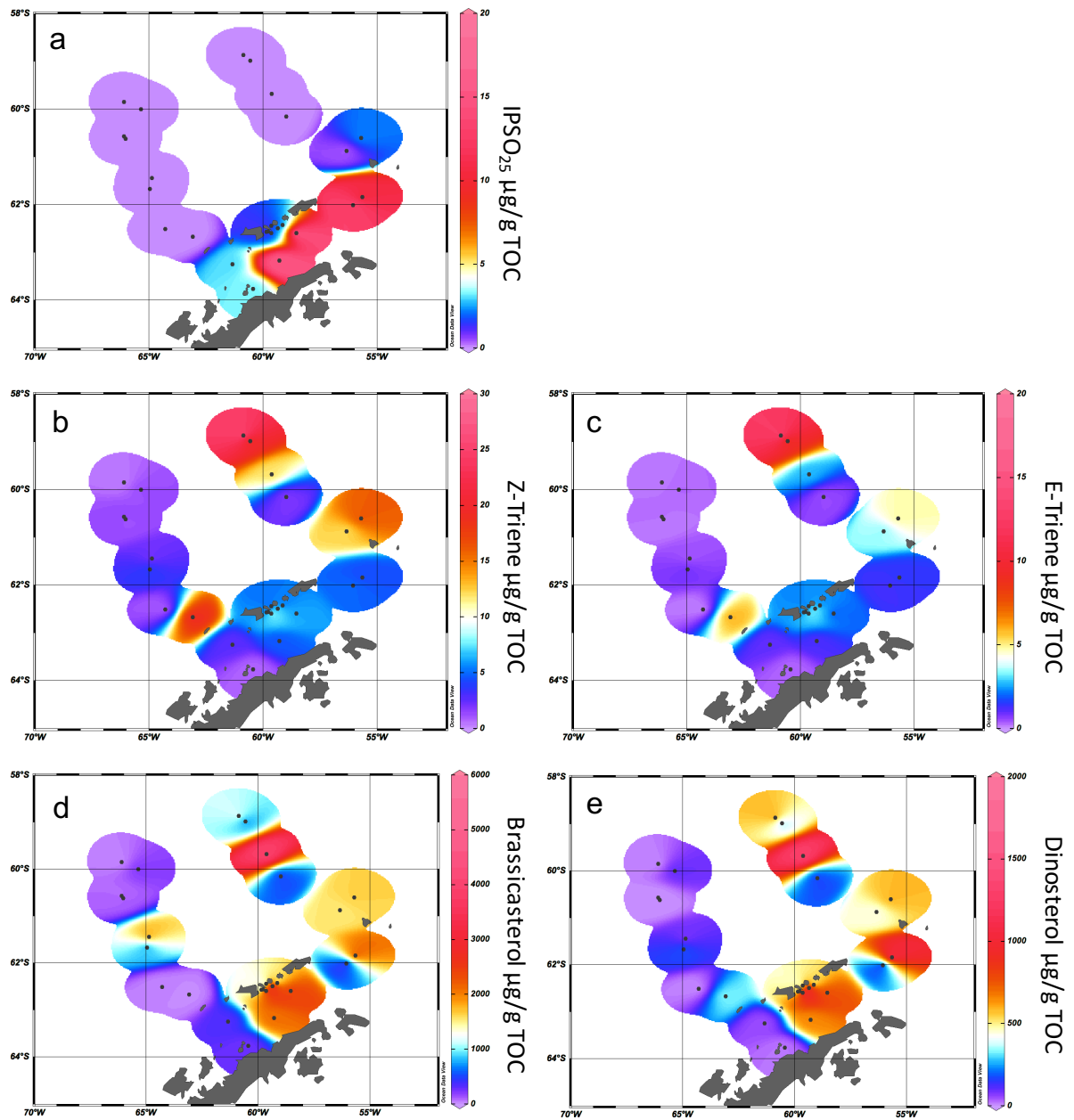
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3 **Figure 2: a) Oceanographic setting of the study area (modified after Hofmann et al., 1996; Sangrà et al., 2011) with**  
4 **ACC = Antarctic Circumpolar Current, TBW = Transitional Bellingshausen Water, TWW = Transitional Weddell**  
5 **Water, APF = Antarctic Polar Front, SACCF = Southern Antarctic Circumpolar Current Front, and PF = Peninsula**  
6 **Front, and the maximum winter sea ice extent (after Cárdenas et al., 2018). b) The bathymetric map of the study area**  
7 **with locations of all stations; AP = Antarctic Peninsula, AS = Antarctic Sound, BS = Bransfield Strait, and SSI = South**  
8 **Shetland Islands. A detailed station map at the South Shetland Islands is integrated.**

9 **The overview maps were done with QGIS 3.0 from 2018 and the bathymetry was taken from GEBCO\_14 from 2015.**

10

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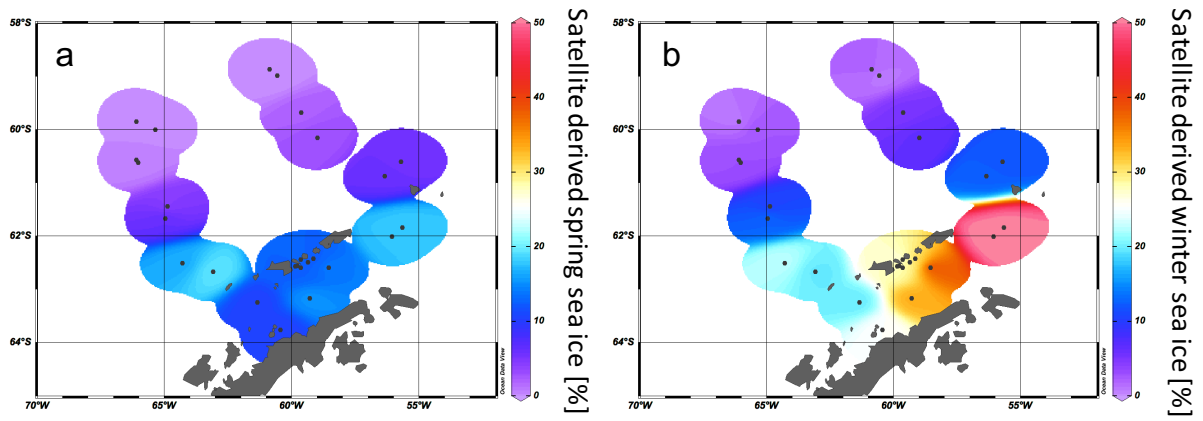


2

3 **Figure 3: Distribution of a) IPSO<sub>25</sub>, b) HBI Z-triene, c) HBI E-triene, d) brassicasterol, and e) dinosterol concentrations**  
4 **normalized to TOC. All distribution plots were made with Ocean Data View 4.7.10 (2017).**

5

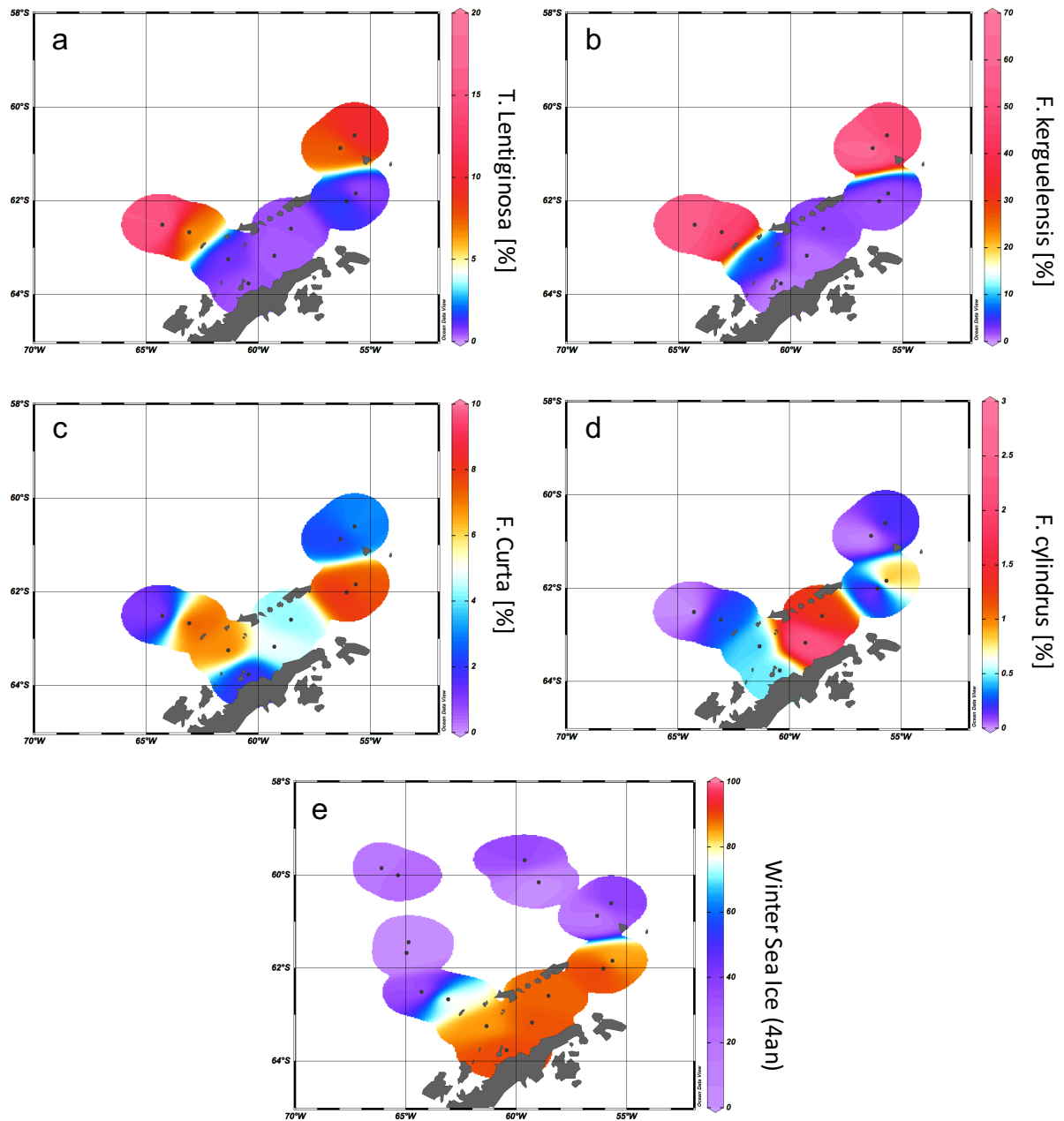
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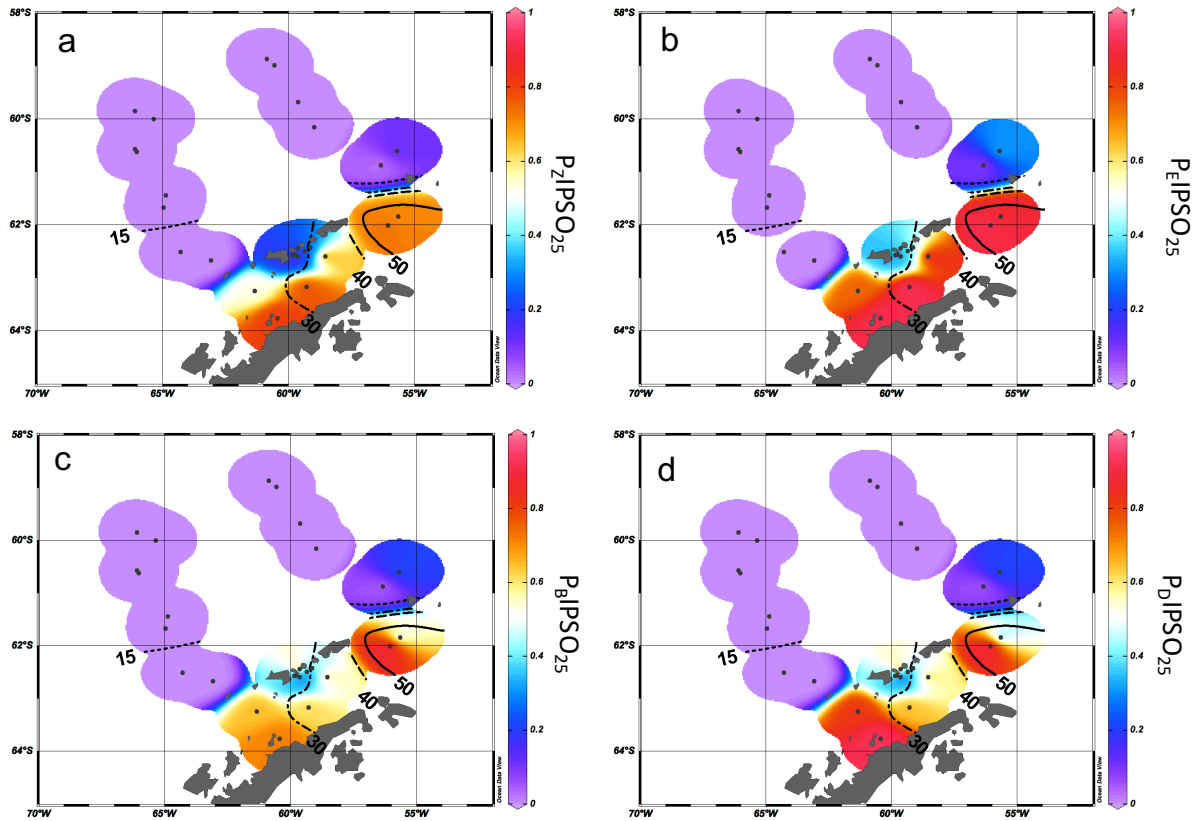
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3 **Figure 4: The satellite derived mean sea ice concentrations at each sampling station for a) spring and b) winter.**

4



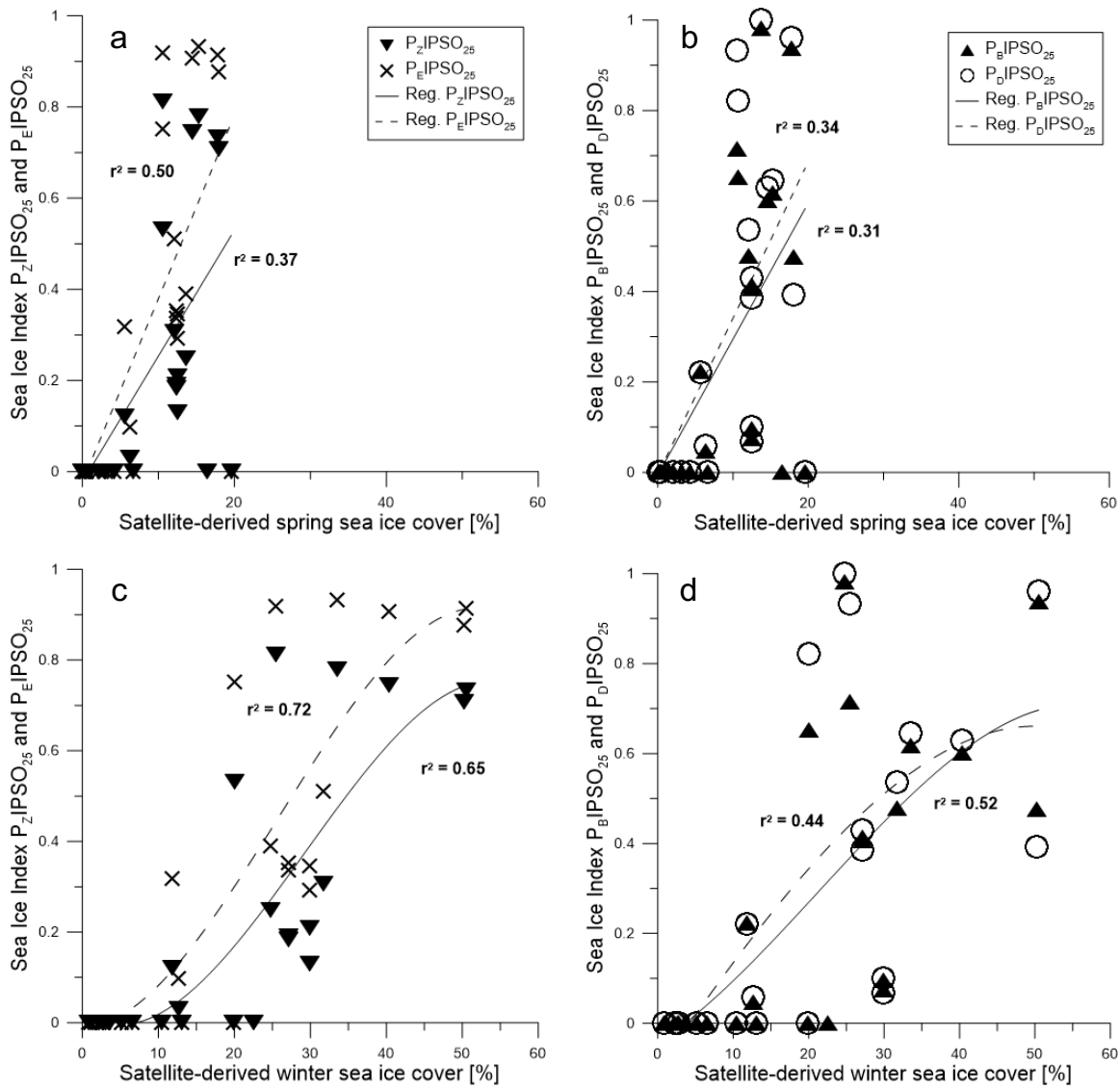
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 2 **Figure 5: Distribution of the diatoms a) *T. lentiginosa*, b) *F. kerguelensis*, c) *F. curta*, and d) *F. cylindrus* in the study**  
 3 **area (percentage per sample). The winter sea ice concentrations from the application of transfer function of Esper and**  
 4 **Gersonde (2014a) are shown in e).**  
 5



1  
 2 **Figure 6: Distribution of a)  $P_ZIPSO_{25}$ , b)  $P_EIPSO_{25}$ , c)  $P_BIPSO_{25}$ , and d)  $P_DIPSO_{25}$  values in the study area. The extent**  
 3 **of 15 %, 30 %, 40 % and 50 % satellite sea ice concentrations during winter is added as contour lines (see also Figure**  
 4 **4b).**

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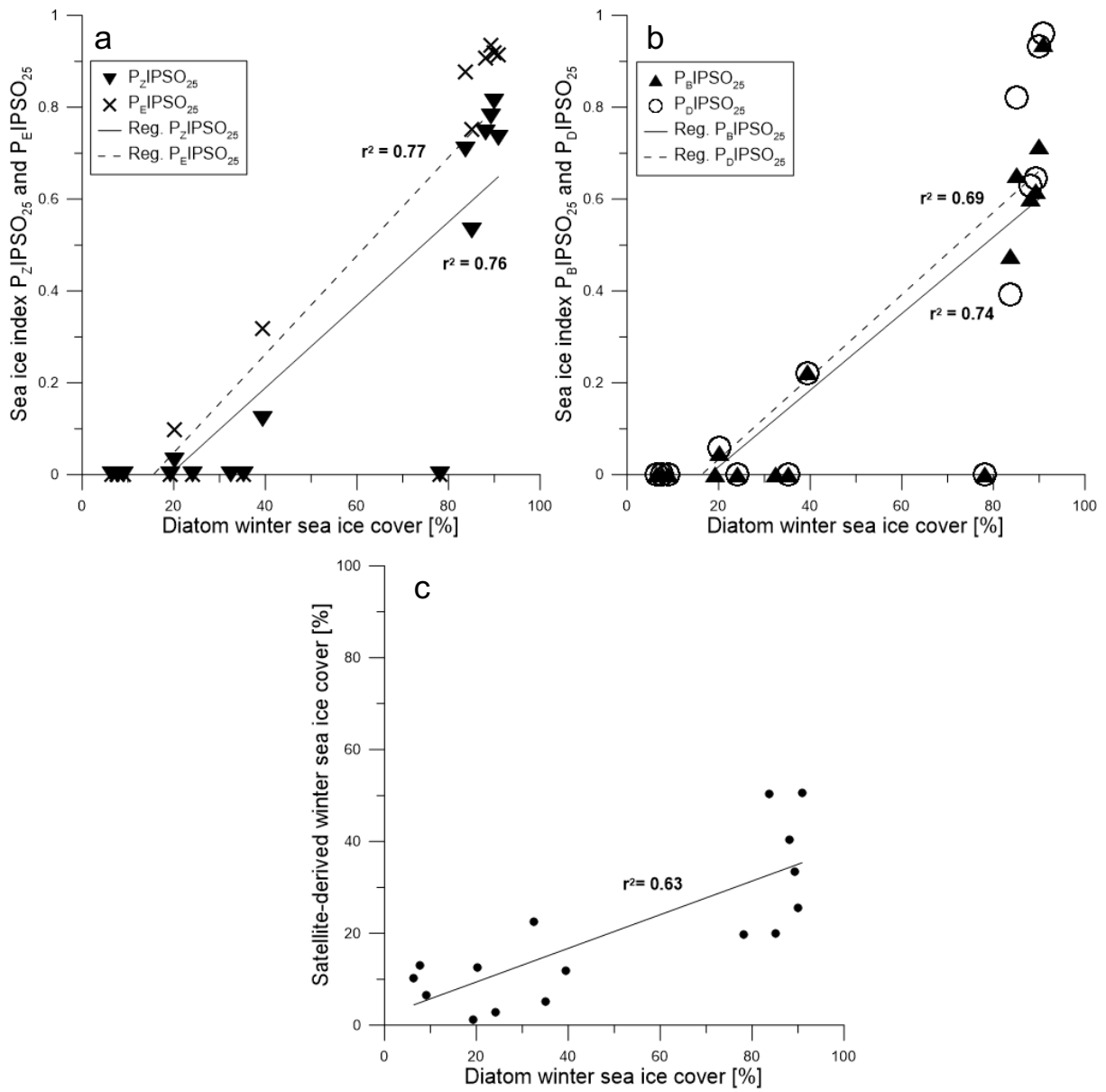
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2 **Figure 7: Scatter plots of satellite spring sea ice concentrations and a)  $P_Z$ IPSO<sub>25</sub> (triangles, solid regression line) and**  
3  **$P_E$ IPSO<sub>25</sub> (crosses, dashed regression line) and b)  $P_B$ IPSO<sub>25</sub> (triangles, solid regression line) and  $P_D$ IPSO<sub>25</sub> (circles,**  
4 **dashed regression line). Scatter plots of satellite winter sea ice concentrations with c)  $P_Z$ IPSO<sub>25</sub> (triangles, solid**  
5 **regression line) and  $P_E$ IPSO<sub>25</sub> (crosses, dashed regression line) and d)  $P_B$ IPSO<sub>25</sub> (black triangles, solid regression line)**  
6 **and  $P_D$ IPSO<sub>25</sub> (circles, dashed regression line). All scatter plots were done with Grapher™ 13.**

7

1



2

3 **Figure 8: Scatter plots of a)  $P_Z$ IPSO<sub>25</sub> (triangles, solid regression line) and  $P_E$ IPSO<sub>25</sub> (crosses, dashed regression line)**  
4 **and b)  $P_B$ IPSO<sub>25</sub> (triangles, solid regression line) and  $P_D$ IPSO<sub>25</sub> (circles, dashed regression line) against diatom derived**  
5 **winter sea ice concentrations. c) Scatter plot of diatom transfer function winter sea ice concentrations and satellite**  
6 **winter sea ice concentrations.**



7 **Tables**

8 **Table 1: Coordinates of sample stations with water depth, concentrations of IPSO<sub>25</sub>, HBI Z- and E-trienes, brassicasterol and dinosterol normalized to TOC,  $\delta^{13}\text{C}$  values for IPSO<sub>25</sub>, and**  
9 **values of sea ice indices PIPSO<sub>25</sub> based on the HBI Z- and E-trienes, brassicasterol and dinosterol. Concentrations below the detection limit are expressed as 0. The PIPSO<sub>25</sub> could not be**  
10 **calculated where IPSO<sub>25</sub> and the phytoplankton marker is absent (blank fields).**

Station	Water			HBI Z-Triene	HBI E-Triene	Brassicasterol	Dinosterol	$\delta^{13}\text{C}$ of					
	Lon	Lat	Depth	IPSO <sub>25</sub> /TOC	/TOC	/TOC	/TOC	/TOC	IPSO <sub>25</sub>	P <sub>2</sub> IPSO <sub>25</sub>	P <sub>E</sub> IPSO <sub>25</sub>	P <sub>B</sub> IPSO <sub>25</sub>	P <sub>D</sub> IPSO <sub>25</sub>
	[dE]	[dN]	[m]	[ $\mu\text{g/g TOC}$ ]	[ $\mu\text{g/g TOC}$ ]	[ $\mu\text{g/g TOC}$ ]	[ $\mu\text{g/g TOC}$ ]	[ $\mu\text{g/g TOC}$ ]	[‰]				
PS97/042-1	-66.10	-59.85	4172	0	0.333	0.152	12.997	0		0.000	0.000	0.000	
PS97/044-1	-66.03	-60.62	1203	0	1.080	0	143.688	0		0.000		0.000	
PS97/045-1	-66.10	-60.57	2292	0	1.531	0.386	36.902	0		0.000	0.000	0.000	
PS97/046-6	-65.36	-60.00	2803	0	1.359	0.291	214.634	101.809		0.000	0.000	0.000	0.000
PS97/048-1	-64.89	-61.44	3455	0	2.085	0.375	1859.609	73.532		0.000	0.000	0.000	0.000
PS97/049-2	-64.97	-61.67	3752	0	3.924	0.851	719.155	178.446		0.000	0.000	0.000	0.000
PS97/052-3	-64.30	-62.51	2890	0	0.679	0	26.554	0		0.000		0.000	
PS97/053-1	-63.10	-62.67	2021	0	19.350	5.948	13.356	332.868		0.000	0.000	0.000	0.000
PS97/054-2	-61.35	-63.24	1283	3.033	2.675	1.000	337.686	48.579	-14.741	0.531	0.752	0.652	0.820
PS97/056-1	-60.45	-63.76	633	3.232	0.752	0.290	268.190	17.158	-10.3 ± 0.9	0.811	0.918	0.716	0.932
PS97/059-1	-59.66	-62.44	354	0.835	2.523	1.305	3.386	0.0002		0.249	0.390	0.981	0.999
PS97/060-1	-59.65	-62.59	462	1.934	12.937	4.693	5017.437	1983.750		0.130	0.292	0.074	0.066
PS97/061-1	-59.80	-62.56	467	1.018	4.341	1.870	302.356	119.512		0.190	0.352	0.413	0.383
PS97/062-1	-59.86	-62.57	477	0.907	4.044	1.787	276.372	88.272		0.183	0.337	0.407	0.428
PS97/065-2	-59.36	-62.49	480	2.416	9.184	4.549	4788.292	1587.309		0.208	0.347	0.095	0.100
PS97/067-2	-59.15	-62.42	793	1.785	4.038	1.710	406.567	113.728		0.307	0.511	0.478	0.533
PS97/068-2	-59.30	-63.17	794	16.206	4.558	1.152	2096.690	653.977	-14.1 ± 0.6	0.780	0.934	0.617	0.643

PS97/069-1	-58.55	-62.59	1642	17.814	6.115	1.824	2472.025	774.345	-12.6 ± 0.4	0.744	0.907	0.601	0.626
PS97/072-2	-56.07	-62.01	1992	13.689	4.997	1.277	192.625	40.686	-13.6 ± 0.3	0.733	0.915	0.937	0.961
PS97/073-2	-55.66	-61.84	2624	10.369	4.283	1.451	2388.458	1180.752		0.708	0.877	0.476	0.390
PS97/074-1	-56.35	-60.87	1831	0.371	12.075	3.409	1539.629	438.073		0.030	0.098	0.048	0.058
PS97/077-1	-55.71	-60.60	3587	2.267	16.356	4.874	1647.616	589.731		0.122	0.317	0.223	0.219
PS97/079-1	-59.00	-60.15	3539	0	1.893	0.510	479.917	154.400		0.000	0.000	0.000	0.000
PS97/080-2	-59.64	-59.68	3113	0	12.021	2.705	4019.003	1329.129		0.000	0.000	0.000	0.000
PS97/083-1	-60.57	-58.99	3756	0	18.256	8.280	686.502	308.610		0.000	0.000	0.000	0.000
PS97/084-2	-60.88	-58.87	3617	0	26.857	13.871	1245.652	648.474		0.000	0.000	0.000	0.000

12 **Table 2: Seasonal sea ice concentrations from satellite observations for spring, summer, autumn and winter with**  
 13 **standard deviations.**

	Sea Ice	Sea Ice	Sea Ice	Sea Ice	Sea Ice	Sea Ice	Sea Ice	Sea Ice
	Spring	Spring StDev	Summer	Summer	Autumn	Autumn	Winter	Winter
Station	Spring [%]	[%]	[%]	StDev [%]	[%]	StDev [%]	Winter [%]	StDev [%]
PS97/042-1	0.04	0.19	0.00	0.00	0.01	0.05	1.14	5.00
PS97/044-1	0.92	3.25	0.02	0.23	0.00	0.00	3.67	9.38
PS97/045-1	0.52	2.08	0.01	0.08	0.00	0.04	2.65	7.81
PS97/046-6	0.29	1.35	0.00	0.00	0.00	0.00	2.84	8.55
PS97/048-1	4.22	8.52	0.00	0.00	0.00	0.00	10.36	18.17
PS97/049-2	6.65	11.85	0.00	0.00	0.00	0.04	13.02	19.91
PS97/052-3	16.48	21.62	0.40	2.95	0.04	0.31	22.59	24.94
PS97/053-1	19.59	23.59	0.29	2.45	0.04	0.35	19.86	24.13
PS97/054-2	10.62	15.18	0.44	0.79	0.76	2.62	20.06	20.72
PS97/056-1	10.55	16.21	4.73	3.25	2.77	4.44	25.47	23.02
PS97/059-1	13.67	16.13	4.23	2.25	5.03	5.48	24.77	20.33
PS97/060-1	12.53	16.84	1.87	2.15	5.43	9.24	29.93	22.05
PS97/061-1	12.43	16.18	1.86	2.07	4.15	7.30	27.14	21.31
PS97/062-1	12.43	16.18	1.86	2.07	4.15	7.30	27.14	21.31
PS97/065-2	12.53	16.84	1.87	2.15	5.43	9.24	29.93	22.05
PS97/067-2	12.08	17.22	0.82	1.88	5.60	10.10	31.74	22.69
PS97/068-2	15.30	19.35	4.89	3.40	6.44	10.45	33.49	23.13
PS97/069-1	14.51	19.85	0.40	2.34	7.83	13.78	40.41	24.27
PS97/072-2	17.74	22.74	1.46	5.38	16.69	20.35	50.49	25.09
PS97/073-2	17.99	23.28	1.81	6.14	16.43	19.85	50.29	26.01
PS97/074-1	6.30	13.65	0.02	0.12	0.55	2.29	12.65	19.30
PS97/077-1	5.60	12.20	0.04	0.13	0.77	2.99	11.83	17.81
PS97/079-1	3.10	8.91	0.03	0.27	0.01	0.12	6.50	15.49
PS97/080-2	2.08	7.52	0.01	0.08	0.00	0.04	5.14	14.17
PS97/083-1	0.03	0.23	0.00	0.00	0.00	0.04	0.87	4.27
PS97/084-2	0.40	2.21	0.00	0.00	0.00	0.04	2.23	9.59

15 **Table 3: Details of the radiocarbon dates and calibrated ages.**

Sample Name	AWI-No.	Material	F <sup>14</sup> C ± error	Conventional <sup>14</sup> C age [a]	Calibrated age (cal BP) [a]
PS97/044-1	1657.1.1	N. pachyderma	0.5076	5447 ± 111	4830
PS97/059-2	1434.1.1	calcareous	0.8507	1299 ± 49	100
PS1546-2	1602.1.1	Moll.-Echinod	0.8456	1347 ± 64	142

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Table 4: Estimations of winter sea ice (WSI) derived from diatom species and the distribution of main diatom species in each sample.

Station	Diatoms	A. tabularis [%]	E. antarctica [%]	F. vanheurckii [%]	F. kerguelensis [%]	F. obliquecostata [%]	F. sublinearis [%]	F. curta [%]	F. cylindrus [%]	N. directa [%]	O. weißflogii [%]	P. lineola-turgid.-gr. [%]	R. alata [%]	R. hebetata fo. semispina [%]	S. microtrias [%]	T. lentiginosa [%]	T. oliverana [%]	Thalassiosira MT 3 [%]	P. pseudodenticulata [%]	Stephanopyxis sp. [%]
	WSI																			
	(4an) [%]																			
PS97/042-1	19.2	0	0	0	0.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PS97/046-6	24.2	0	0	0	0.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PS97/048-1	6.4	0	0	0	0.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PS97/049-2	7.7	0	0	0	0.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PS97/052-3	32.4	1.4	4.3	0	60.3	0.2	0	0.9	0	0	0.5	0	0	0	0	16.2	0.5	0	0	0
PS97/053-1	78.1	0.4	1.2	0	48.5	0.1	0.1	7.4	0.3	0	0.4	0	0.3	0	0.1	6.5	0	0	0	0
PS97/054-2	85.2	0	0.4	0	6.2	0	0	6.9	0.4	0.2	2.7	0.2	0.2	0.2	0.4	0.9	0	0.2	0	0.4
PS97/056-1	89.9	0	0	0	0.5	0.3	0	1.9	0.5	0.3	0.5	0	0	0	0.5	0.5	0	0.0	0.5	0.3
PS97/068-2	89.2	0	0	0	0.7	0.3	0.6	4.9	2.4	0.1	0.5	0.1	0	0	0.4	0.4	0	0.4	0.2	0
PS97/069-1	88.2	0	0.2	0.4	2.1	0.2	0.4	4.3	1.3	0	0.6	0.2	0	0	0.2	0.4	0	0.2	0	0
PS97/072-2	90.9	0	0.2	1.1	1.7	0.6	0.9	8.1	0	0	5.7	0.2	0.2	0	0	1.7	0	0.9	0.9	0
PS97/073-2	83.7	0	0.2	0.2	1.8	0	0.4	7.4	1.0	0	1.0	0	1.6	0.8	0	0.4	0	2.1	0.6	0
PS97/074-1	20.1	0.4	0.6	0	63.1	0	0	2.3	0	0	0.2	0	0.0	0.2	0	7.4	0.4	0	0.2	0
PS97/077-1	39.4	0.6	3.3	0	49.1	0.8	0	3.1	0.2	0	0.2	0	0.0	1.3	0	10.0	0.2	0	0	0

PS97/079-1	9.1	0	0	0	0.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PS97/080-2	35.1	0	0	0	0.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0