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Reconstruction of paleo sea ice and climate dynamics based on highly branched isoprenoids at the Western Antarctic Peninsula

Maria-Elena Vorrath

HELMHOLTZ

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"… we have to speak clearly, no matter how uncomfortable that may be.
…
Our civilization is being sacrificed for the opportunity of a very small number of people to continue making enormous amounts of money.
Our biosphere is being sacrificed so that rich people in countries like mine can live in luxury. It is the sufferings of the many which pay for the luxuries of the few.
…
You say you love your children above all else, and yet you are stealing their future in front of their very eyes.
…
We have run out of excuses and we are running out of time."

– Greta Thunberg at COP24, 12.12.2018, Katowice, Poland –

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Die vorliegende Arbeit ist die inhaltlich gekürzte Fassung einer Dissertation, die am Fachbereich Geowissenschaften in der Sektion Marine Geologie des Alfred-Wegener-Instituts Helmholtz-Zentrum für Polar- und Meeresforschung entstand und im Mai 2020 dem Fachbereich Geowissenschaften der Universität Bremen vorgelegt wurde. Da bei dieser kumulativen Dissertation die dritte Publikation noch aussteht wurde sie aus der Arbeit entfernt und die Daten unter ein Moratorium gestellt.

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ABSTRACT

In context of rapid environmental change, the investigation of vulnerable parts of the global climate system is the focus of recent research. The assessment of global interactions between a changing climate and Antarctic sea ice, especially at the rapidly warming Western Antarctic Peninsula (WAP), aims to improve climate and ice sheet modelling for future projections. For this, the reconstruction of past sea ice distribution provides crucial information to enhance the capability of climate models. The goal of this thesis is the evaluation of the novel organic sea ice biomarker $IPSO_{25}$ (ice proxy for the Southern Ocean with 25 carbon atoms) and its application as a new tool for past sea ice reconstructions analogously to its counterpart IP_{25} in the Arctic Ocean. This organic biomarker is a source specific organic compound from sea ice algae and associated with Antarctic spring sea ice. Information about the significance and limitations of this sea ice biomarker is still sparse and shall be revealed by using surface and downcore marine sediments. Comparisons to independent data such as biomarkers for open marine conditions, diatom assemblages, satellites data, ice core and marine sediment records improve the precise assessment of $IPSO_{25}$.

The distribution and evaluation of $IPSO_{25}$ with recent sea ice data is the topic of the first study (Part I). The multiproxy investigation of surface sediment samples from the Drake Passage and the WAP reveals a good agreement of $IPSO_{25}$ with ecological diatom data and satellite sea ice observations. The implementation of a sea ice index from combined open marine and sea ice biomarkers – $PIPSO_{25}$ – implies that this tool is promising for paleo sea ice studies. The following two investigations (Part II and III) cover the last 200 a and 17 ka BP, respectively, based on three short and one long sediment records, and highlight the regional significance of $IPSO_{25}$. Evaluation of the relation to sea salt sodium, methanesulfonic acid, numerical model output and reconstructed atmospheric circulation patterns (El Niño Southern Oscillation, Southern Annular Mode and Southern Westerly Winds) reveals that $IPSO_{25}$ and $PIPSO_{25}$ more likely indicate seasonal and dynamic sea ice changes than sea ice quantities. The development of past sea ice during the deglaciation and the Holocene at the WAP shows a significant change in sea ice seasonality in agreement with past investigations. The influence of the El Niño Southern Oscillation, the Southern Annular Mode and the Southern Westerly Winds is evident in sea ice biomarker production pattern due to high variability and the latitudinal position of westerly winds at the WAP.

This thesis provides new reference data for paleo sea ice studies and provides a first research approach in further application of $IPSO_{25}$, $PIPSO_{25}$ and paleo sea ice investigations in Antarctica and the Southern Ocean.

ZUSAMMENFASSUNG

Zur Abschätzung zukünftiger Veränderungen in Polargebieten stehen die Wechselwirkungen zwischen einzelnen Klimakomponenten im Zusammenhang mit der globalen Erwärmung im Mittelpunkt der jüngsten Forschung. Die Rekonstruktion der Meereisbedeckung in der Antarktis, und insbesondere an der sich sehr schnell erwärmenden Westantarktischen Halbinsel, zielt darauf ab, die Modelle von Klima- und Eisschildveränderungen zu verbessern. Das Ziel dieser Dissertation ist die Evaluierung und Anwendung eines neuartigen organischen Biomarkers für Meereis, IPSO$_{25}$ (**I**ce **P**roxy für den **S**üdlichen **O**zean mit **25** C-Atomen), um ihn für Meereisrekonstruktionen analog zu seinem Pendant der Arktis, dem Meereisbiomarker IP$_{25}$, anzuwenden. Der Ursprung des organischen Biomarkers sind Eisalgen, deren Wachstum mit Antarktischem Frühlingsmeereis assoziiert wird. Aussagen über den Informationsgehalt und mögliche Grenzen dieses Proxys sind bisher kaum vorhanden und sollen in dieser Arbeit durch die Untersuchung von marinen Sedimenten der Oberfläche und in der Tiefe offengelegt werden. Der Abgleich mit weiteren Biomarkern, mit fossilierten Diatomeen, Satelliten- und Eiskerndaten und mit vergleichbaren älteren Studien sollen die präzise Bewertung von IPSO$_{25}$ unterstützen und dessen Anwendung ermöglichen.

Die erste Studie (Part I) behandelt die räumliche Verteilung von IPSO$_{25}$ in rezenten Oberflächensedimenten und zielt auf eine Evaluierung des Biomarkers als Anzeiger für Antarktisches Meereis ab. Der Abgleich von mehreren Meereis- und Klimaanzeigern aus der Drake Passage und von der Westantarktischen Halbinsel zeigt gute Übereinstimmungen mit IPSO$_{25}$ und deutet darauf hin, dass dieser sich in den Daten von Diatomeen als auch in Satellitenaufzeichnungen wiederspiegelt. Die Anwendung eines Meereisindex in Analogie zu seinem Arktischen Pendant (eine Kombination aus Biomarkern stellvertretend für den eisfreien und eisbedeckten Ozean) als PIPSO$_{25}$ (Phytoplankton-IPSO$_{25}$) ist vielversprechend. Die folgenden zwei Paläostudien (Part II und III) über einen Zeitraum von 200 und 17.000 Jahren basieren auf drei kurzen und einem langen Sedimentkern und zeigen deutlich die regionale Aussagekraft des Biomarkers. Beim Vergleich mit Meersalz- und biologischen Aerosolen (Natrium und Methansulfonsäure), mit den Ergebnissen numerischer Modelle, mit rekonstruierten atmosphärischen Zirkulationsmustern (El Niño, die Antarktische Zirkulation und die südlichen Westwinde) und mit Meereisstudien von benachbarten Sedimentkernen zeigt sich, dass IPSO$_{25}$ und PIPSO$_{25}$ verstärkt die Saisonalität und Dynamik von Meereis statt der Meereismenge überliefern. Im Übergang von der letzten Eiszeit und während des Holozäns zeigen sich signifikante Veränderungen der Meereisbedeckung und -saisonalität, die bereits aus vorherigen Studien bekannt sind. Der Einfluss der El Niño Variabilität, der Antarktischen Zirkulation und von den südlichen Westwinden, wirkt sich auf die Produktionsmuster des Meereisbiomarkers aus und spiegelt sich in den klimatischen Wechseln des untersuchten Zeitraumes wieder.

Diese Dissertation liefert neben einem neuen Referenzdatensatz für Paläomeereisuntersuchen auch einen Fortschritt in der Erforschung des Biomarkers IPSO$_{25}$ und dessen Meereisindex PIPSO$_{25}$ und ermöglicht so zukünftige Paläoklima- und Meereisstudien in der Antarktis und dem Südozean.

1. INTRODUCTION

1.1. Why we should study the eternal ice

The Swedish chemist Svante Arrhenius was the first who calculated the increase of Earth´s surface temperature caused by the greenhouse effect under rising atmospheric carbon dioxide (CO_2). In his opinion, mankind would benefit from burning fossil fuels and changing the global climate so “*we may hope to enjoy ages with more equable and better climates*” (Arrhenius, 1908). Today, facing a global warming of approximately +1.0°C above preindustrial levels and advanced environmental degradation (IPCC, 2018) we know that we push the natural system towards its limits where critical thresholds of the earth system, i.e. climate tipping points may be crossed in the coming decades leading to non-linear, fast and irreversible changes (Lenton et al., 2008). These changes could drastically diminish the ability of the earth system to support vital ecosystems that sustain human nutrition, health and livelihood, and have already become one of the biggest threats of humanity according to the World Economic Forum (2020). Yet, changes in the environment are omnipresent in everyday´s life, for example as the rise of sea level, droughts, floods, heat waves, wild fires and most prominent in the warming of polar regions (IPCC, 2019). Since the decline of Arctic sea ice, thawing of permafrost soil, atmospheric warming, and disturbance of circulation pattern in the northern hemisphere can be directly linked to anthropogenically forced global warming, changes in the Antarctic have long been overseen and not attributed to a human influence. But recent studies show: the eternal ice might be less permanent than we thought.

The urgency to study the changes in Antarctica is based on the potential of its ice sheet being the main future contributor to a global sea level rise of up to 1.0 m within the 21st century (Oppenheimer et al., 2019) leading to dramatic economic and geopolitical consequences for coastal metropoles around the globe (FitzGerald et al., 2008). Still, the observations of fast retreating Antarctic ice shelves, accelerated flow of ice sheets towards the ocean and rapid ocean warming are contradicted by an increase of sea ice extent in the Southern Ocean (Cheng et al., 2020; Meredith et al., 2019). Until now, climate models fail to reproduce observed sea ice changes in Antarctica, and their capability to project future ice sheet and sea ice development in the context of global warming is weak (Bracegirdle et al., 2019; Meredith et al., 2019). To enhance the understanding of sea ice in the global climate system and the interplay within the ice-ocean-atmosphere system, reconstructions of past climate and sea ice dynamics are an effective tool. Therefore, this study aims at the establishment and application of a novel paleo record for sea ice reconstructions in Antarctica which could improve climate models and projections in the future.

1.2. Antarctic sea ice

Southern Ocean sea ice is highly dynamic with seasonal variations of 85% with respect to sea ice extent between seasonal minimum in March and maximum in September (Figure 1.1). Over the last 40 years, since the start of satellite observations, its extent has increased by about 70,000 km^{-2} yr^{-1} or 1.5% per decade (Eayrs et al., 2019), while the development of sea ice thickness is poorly constrained during this period (Williams et al., 2015). Due to the high inter-seasonal dynamic and the annual sea ice formation and melt, multi-year sea ice is rare and an average sea ice thickness of about 1 m is common (National Snow and Ice Data Center, NSIDC Homepage, accessed April 2020). A record low sea ice extent in 2016/17 may be due to natural variability (Schlosser et al., 2018) while the interannual variability was found to increase since satellite observations begun, especially in response to air temperatures rise (Hobbs et al., 2016; Turner et al., 2019). Many regions and seasons contribute to the total Antarctic sea ice extent and opposite trends can be observed in different sectors of the Southern Ocean (Holland, 2014). Strong positive sea ice trends in several regions and strong negative trends in other regions make it difficult to find a clear relationship of environmental drivers for sea ice growth and fate in the Southern Ocean (Stroeve et al., 2016).

The impacts of Antarctic sea ice on the environment are manifold (Figure 1.2). The white surface of sea ice and its snow cover lead to a high albedo effect where about 50% to 70% of the incoming solar radiation is reflected leading to low atmospheric temperatures, while the albedo effect of the darker sea surface reflects only about 6% of the incoming radiation (NSIDC Homepage, accessed April 2020). Where sea ice is present the ocean surface is decoupled from the atmosphere, so the exchange of gases and heat is blocked. This causes the trap of heat in the ocean and cools down the surface air, it decreases air moisture due to diminished evaporation of the sea surface and slows down wind-induced surface mixing (Thomas, 2017). The freezing point of sea water with a salinity of 34 is at -1.86°C, which is also the point of maximum density of sea water. When sea ice forms, sea water above the freezing point starts to experience thermohaline convection, so colder water sinks down and is replaced by warmer waters at the surface, which causes a mixing and cooling of the ocean surface layer (Thomas, 2017). Sea ice growth starts from single ice crystals, often in the shape of needles or platelets, that aggregate to frazil ice (or pancake ice under wind stress) and layers of sea ice are added one after another to the bottom of sea ice. Most of inorganic dissolved ions (e.g. sea salt) are excluded from the ice crystal lattice, so brine solution drains in the underlying sea water (Petrich and Eicken, 2016) and only small amounts of sea water remain trapped in a labyrinth of channels. As a result, cold, salty, and dense water

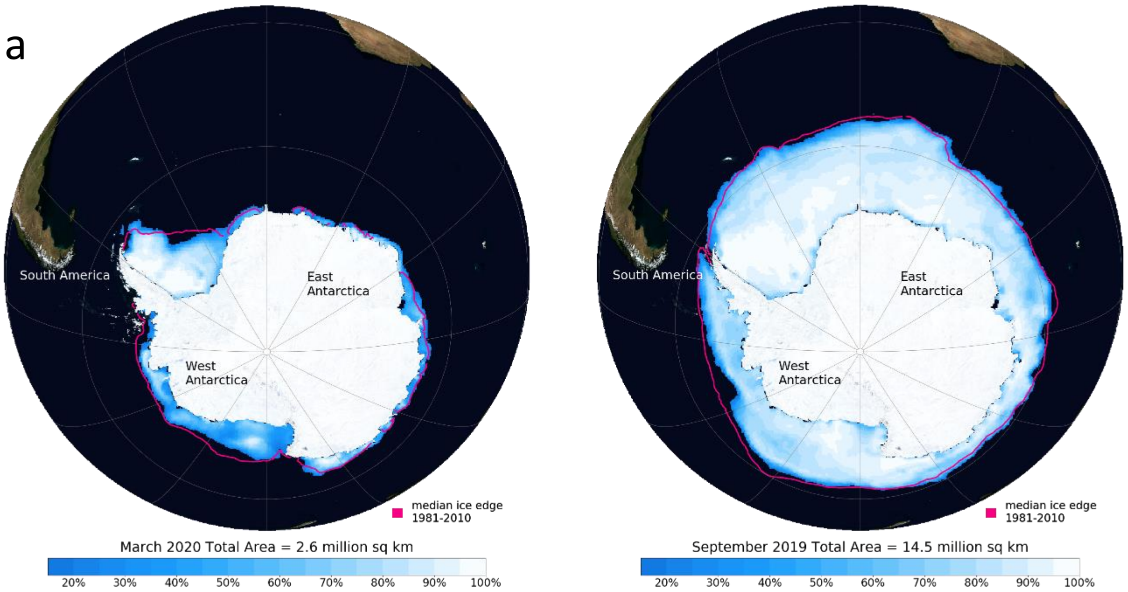

Figure 1.1 Recent Antarctic sea ice concentrations during a) the sea ice minimum in March 2020 and b) the sea ice maximum in September 2019 representative for the seasonal variability in the Southern Ocean. The pink lines present the median ice edge between 1981 and 2010 for each month. Maps are from the National Snow and Ice Data Center (NSIDC Homepage, accessed April 2020).

masses form and act as a barrier for warm ocean currents to enter the shelf area at the continental margin of Antarctica. This prevents basal melting of the ice shelves with implications for the ice sheet stability especially in West Antarctica (Cook et al., 2016; Hellmer et al., 2012). Further, the dense water contributes to the formation of Antarctic Bottom Water and is an important driver of the global thermohaline circulation (Nicholls et al., 2009). Not only sea ice formation but also the melting of sea ice releases less dense, fresher water and support ocean stratification during spring and summer (Arrigo et al., 1997; Klinck, 1998). The formation of leads by break-up of floating ice can be initiated by divergence or shear stress and is an important gateway for latent heat and moist exchange (Marcq and Weiss, 2012). The fate of sea ice via melting in spring and summer is mainly driven by ocean heat transfer and takes place along margins and at the sea ice bottom (Thomas, 2017).

At the sea ice bottom a dense network of brine filled channels and pores build a unique habitat for marine species and influence the chemical composition of biogenic matter formed under these conditions (Thomas and Dieckmann, 2002). In case of high primary production, the brine composition shifts to a remarkable reduction of total inorganic carbon, depletion of CO_2, higher pH values and higher oxygen concentrations (Thomas and Dieckmann, 2002). Photosynthesis in the semi-enclosed channels lead to the consumption of ^{12}C stable isotopes and an enrichment of ^{13}C stable isotopes (Sinninghe Damsté et al., 2007) expressed in heavy $\delta^{13}C$ isotope signatures of up to -8‰ for sea-ice derived organic matter (Arrigo et al., 2003; Gibson et al., 1999).

Photosynthesis and marine primary production are depleted under sea ice because of the lack of ocean mixing, depletion of nutrients and reduced light penetration, especially with snow cover (Arrigo, 2014). Nevertheless, sea ice provides a habitat for settling and hiding for many microorganisms and metazoans (Garrison, 1991), large vertebrates (Ainley and DeMaster, 1990) and sea ice algae (Arrigo, 2014). Sea ice algae are

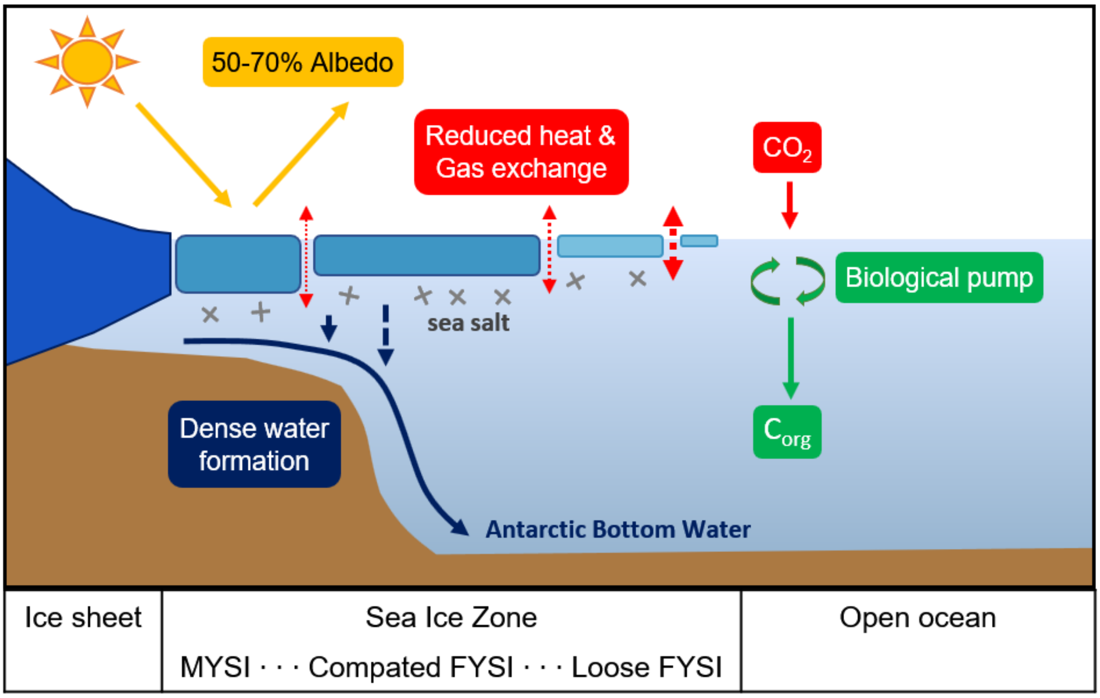

Figure 1.2 Scheme of the impacts of sea ice in the Southern Ocean and Antarctica. Only a small part is multi-year sea ice (MYSI) while the majority is first-year sea ice which can be compacted (sea ice concentrations above 40%) or lose (sea ice concentrations below 40%). Figure after Crosta (2009).

responsible for the typical brown colour at the bottom of sea ice floes and their growth sustains the rich marine sea ice community (Lizotte, 2001). Although their microbial mass is generally low due to the depletion of nutrients in the brine channels (Arrigo and Thomas, 2004), carbon fixation is enhanced with the presence of sea ice due to higher primary production (Schofield et al., 2018). The thickness and snow cover of sea ice is crucial for algae growth, responding with initial growth to the onset of irradiance in early spring (Hancke et al., 2018). At the same time wind-induced upwelling occurs at the sea ice edges (Alexander and Niebauer, 1981) and melting sea ice releases nutrients and fuels algae growth in both, sea ice and ice-free waters (Vernet et al., 2008). For this reason, high sea-ice related primary production occurs mainly at the sea ice edge where it is a crucial factor for enhanced fixation of CO_2 from the atmosphere and transformation into organic carbon (C_{org}) that is transported to the ocean floor via sinking particles (Berger and Wefer, 1990; DeLaRocha and Passow, 2007; Wefer et al., 1988)(Figure 1.2). This so-called biological carbon pump drives the long-term sequestration of CO_2 in the Southern Ocean and is an important mechanism affecting atmospheric CO_2 concentrations (Falkowski et al., 1998). The primary production within sea ice is restricted due to its physical properties and contributes only a small fraction to the production of the Southern Ocean. Still, it is estimated that the marginal ice zone and continental shelf make up 12% of the total annual production (Arrigo et al., 1998).

Within sea ice, the most habitable and biologically productive zone is the bottom within the lowest 5 cm to 10 cm due to connection to seawater nutrients and mild temperatures (compared to the upper sea ice)(Arrigo, 2014). The microbial community in sea ice consists of archaea, bacteria and eukaryota, the latter most prominent through single-celled microalgae which form the base of the marine food web in this area (Arrigo and Thomas, 2004). The most common microalgae are sea ice diatoms with 30 to 170 different species. Because sea ice deforms during aging and requires robust diatom frustules it is mainly inhabited by small pennate sea ice diatoms like *Fragilariopsis curta* (Arrigo and Thomas, 2004; Hamm et al., 2003), but also large species such as *Amphiprora*, *Pinnularia* and *Pleurosigma* are common (Riaux-Gobin et al., 2003; Smetacek et al., 1992). The growth of sea ice algae is also responsible for the production of dimethylsulphide which is the main source of marine derived sulphates in Antarctica and acts as a cloud nuclei changing the radiation budget due to cloud formation (Arrigo and Thomas, 2004; Trevena and Jones, 2006). Due to sea ice melt in spring and summer, sea ice algae are released and small amounts are deposited on the ocean floor via downward particle flux.

Since the start of satellite observations of Antarctic sea ice in 1979 changes in its distribution and seasonality have been recorded (Hobbs et al., 2016). For example, sea ice concentrations in austral summer show an increase of up to 20% across East Antarctica (here March 2020, Figure 1.3a), while there is a decline of sea ice concentrations of 20% in West Antarctica leading to large sea-ice free areas during summer and shorter sea ice seasons (Parkinson, 2002). In winter, the differences are smaller (here September 2019, Figure 1.3b). These different trends affect the physical and ecological properties that interact with sea ice and sea ice formation. Since the flow of the West Antarctic Ice Sheet accelerated and melting rates increased over the last decades (Meredith et al., 2019), it has been suggested that the ocean is the main driver of ice sheet retreat and that basal melting of the ice shelves due to warm water intrusion of the deep ocean is connected to the loss of sea ice in West Antarctica (e.g. Hellmer et al., 2013; Hillenbrand et al., 2017). Higher temperatures and in particular the thinning of sea ice lead to a possible intensification of algae growth with increased grazing and nutrient cycling (Melnikov, 2009). A general loss of sea ice is suggested to reduce its related algae communities and the decrease of krill which is crucial for the marine food web of higher trophic levels (Flores et al., 2012; Nicol et al., 2008).

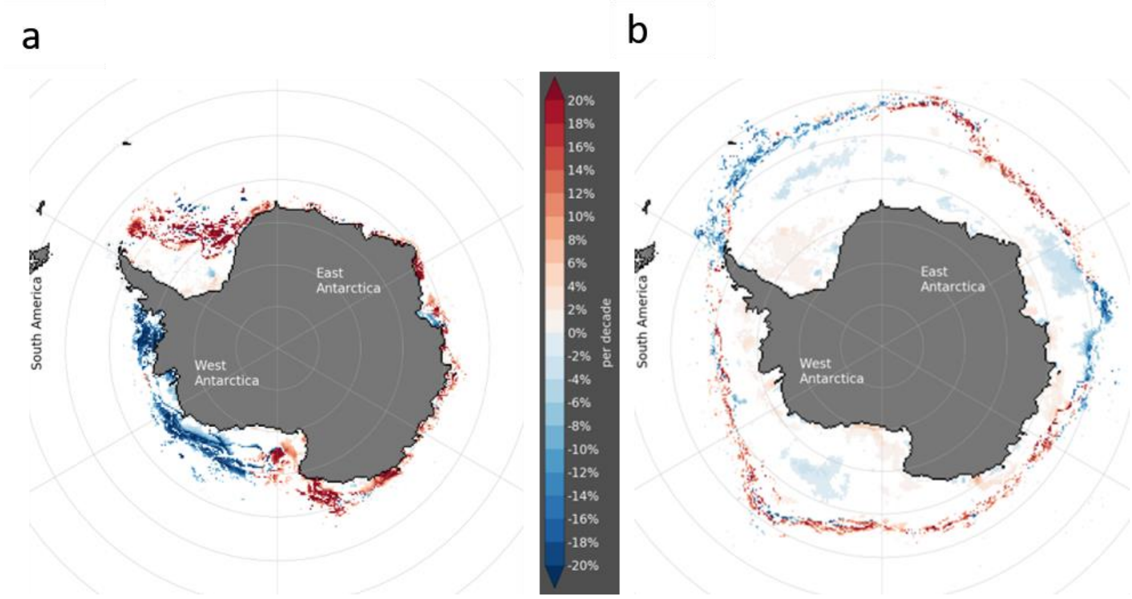

Figure 1.3 Maps of sea ice concentration trends for a) March 2020 and b) September 2019 where blue areas stand for a decrease and red areas for an increase of sea ice. Maps are from the National Snow and Ice Data Center (https://nsidc.org, accessed April 2020).

1.3. Sea ice reconstruction

Sea ice reconstructions in Antarctica

In the course of global warming, projections of Arctic sea ice point to a significant decline and potentially sea ice free summers within the next decades, while projections of future Antarctic sea ice show a wide range of trends and uncertainties and confidence levels of model outputs are still very low (Meredith et al., 2019). As the direct observation of sea ice is limited to the satellite era, climate-archive based reconstructions of past sea ice target the questions of drivers and implications within the global climate system during different climate periods and transitions (De Vernal et al., 2013). To understand the past boundary conditions for sea ice variability is a key to translate these findings to modern day interaction of ocean, atmosphere and ice. It is still unclear how different kinds of forcing from atmosphere, ocean heat flux or thermal isolation affect long-term sea ice variability (Armand et al., 2016). Without this knowledge modelling of past and future climate interactions in response of sea ice is strongly limited. Further, the global impact of Antarctic sea ice variability is still unclear, nor, how Antarctic sea ice will change under global warming.

Antarctic past sea ice estimations from ice cores are based on their chemical and isotopic composition, revealing differences in e.g. temperature driven fractionation of stable isotopes, the precipitation of sea salt and marine aerosols and snow accumulation (Thomas et al., 2019). Sea salt aerosols origin from sea spray by breaking waves and are often used in the form of sea salt sodium ($ssNa^+$) fluxes (e.g. EPICA Community Members et al., 2004; WAIS Divide Project Members et al., 2015). The longest records from the 800,000 year ice core from EPICA Dome C shows a response of sea salt fluxes in relation to the last eight glacial cycles and is referred to Southern Ocean sea ice extent (Wolff et al., 2006). Other, shorter records, resolve regional sea ice dynamics in relation to climate modulations much better, e.g. the EPICA Dronning Maud Land ice core that is related to Weddell Sea ice (Rahaman et al., 2016) or the WAIS Divide ice core that represents sea ice in the Ross and Amundsen Sea (WAIS Divide Project Members et al., 2013). Currently, the longest sea ice record based on the organic aerosol methanesulfonic acid (MSA) is an ice core dating back to 1702 (Thomas and Abram, 2016). MSA is an oxidation product of dimethylsulfide originating from diatoms and is referred to the break-up of sea ice in spring and related to high algae production. Stable isotopes ($\delta^{18}O$ and δD) depend on temperature, evaporation and precipitation and are more likely to represent climate conditions (Jouzel et al., 1987). Nevertheless, the deuterium excess ($d = \delta D - 8 * \delta^{18}O$) was related to sea ice area in addition to MSA and sea salt aerosols (Sinclair et al., 2014). Snow accumulation may reflect increased air moisture and evaporation from open ocean surfaces and correlates negatively with sea ice extent e.g. at the Antarctic Peninsula (Porter et al., 2016; Thomas and Bracegirdle, 2015). Sea ice reconstructions from ice cores depend on knowledge of past wind patterns and meteorological conditions that control the catchment area of the ice core. Records must always considered to display regional changes and not absolute sea ice cover. Also, regional difference in the interpretation of ice core records may occur. For example, MSA is suggested to be an indicator for summer sea ice mainly in the ocean of West Antarctica (Criscitiello et al., 2013; Rhodes et al., 2009; Sinclair et al., 2014), while it is representative for winter sea ice in East Antarctica (Foster et al., 2006) and the Southern Indian Ocean (Xiao et al., 2015a).

Marine sediments contain information of paleo sea ice in form of fossilised diatoms, sedimentological composition, and biogeochemical records. The most commonly used proxies are diatoms and their ecological community composition that allows estimations about primary production, environmental conditions and the qualitative estimation of past seasonal sea ice extent (Crosta, 2009). In a statistical examination the quantities of different diatom species are applied to estimate the probability of winter sea ice (Esper and Gersonde, 2014a) and summer sea surface temperatures (Esper and Gersonde, 2014b). Fossilised diatom frustules are found all around Antarctica which make them very useful for inter-comparison studies and allow sea ice reconstructions for the whole Southern Ocean (Gersonde et al., 2005). Nevertheless, during the process of sinking, deposition and fossilisation frustules from sea ice algae are affected by dissolution of biogenic opal (Burckle and Cooke, 1983; Esper and Gersonde, 2014b; Leventer, 1998; Ragueneau et al., 2000) leaving a gap in the scope of their interpretation.

The sedimentological approach for sea ice reconstructions is mainly based on the presence of drop stones, ice rafted debris (IRD) and lithogenic particles transported from icebergs or with free-floating ice which broke up from fast ice after incorporating sediment loads from the coast (Rothwell and Croudace, 2015, and references therein). Also, the composition of stable carbon isotopes ($\delta^{13}C$) of calcium carbonate (from foraminifera, corals and shells) allows conclusions on the presence of sea ice. This is based on the fact that sea ice derived organic matter has significant higher $\delta^{13}C$ isotope signatures due to the limited gas exchange within the brine channels (Gibson et al., 1999; Sinninghe Damsté et al., 2007; Tortell et al., 2013).

Biomarker-based sea ice reconstructions: the novel sea ice proxy IPSO$_{25}$

A comprehensive approach for past sea ice reconstructions provide the use of biomarkers: biosynthesized, chemically persistent molecules, produced by species living under certain environmental conditions, that leave a characteristic biogeochemical signature in marine sediments (Eglinton and Eglinton, 2008; Volkman, 2006). First described by Nichols et al. (1988), an unique source-specific lipid, a highly branched

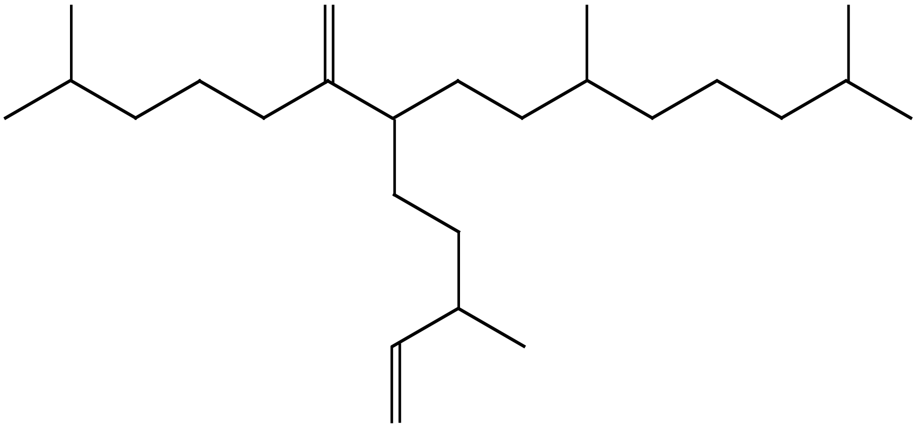

Figure 1.4 The chemical structure of $IPSO_{25}$ (systematic name 2,10,14-Trimethyl-6-enyl-7-(3-methylpent-1-enyl)pentadecene) with two double bonds at $C_{7\text{-}8}$ and $C_{23\text{-}24}$ (after Belt et al., 2000; Johns et al., 1999).

isoprenoid alkene (HBI) with 25 carbon atoms, is used as a biomarker and a proxy for the presence of sea ice. In Antarctica the diunsaturated HBI (also expressed as $C_{25:2}$) remains from Antarctic sea-ice associated (sympagic) algae and was first assessed by Massé et al. (2011) as a possible proxy for past sea ice conditions (Figure 1.4). The expression $IPSO_{25}$, ice proxy for the Southern Ocean, was introduced for the HBI diene (Belt et al., 2016) in analogy to the Arctic sea ice proxy IP_{25} (Belt et al., 2007). The sea ice origin of $IPSO_{25}$ is identified by its heavy isotopic composition characteristic of sea ice derived organic matter, showing common $\delta^{13}C$ signatures between -5.7‰ and -8.5‰ in sea ice and -18‰ in sediments (Massé et al., 2011). $IPSO_{25}$ is referred to the diatom species *Berkeleya adeliensis* (Belt et al., 2016), a species found commonly widespread in Antarctic sea ice but rare in fossil assemblages. Although *B. adeliensis* is not highly abundant in present sea ice diatom communities, it is yet the only identified $IPSO_{25}$ producer (Belt et al., 2016) and the present distribution of this diatom species in near-coastal land fast sea and platelet ice (Riaux-Gobin and Poulin, 2004) corresponds to their sedimentary abundance (a summary of both *B. adeliensis* and $IPSO_{25}$ occurring in the same region can be found in Belt et al., 2016). As the growth of sea ice diatoms is mainly restricted to sunlight availability, growth starts with the end of the polar night and the onset of spring. With sea ice melt in late spring and summer, sea ice diatoms are released and transported to the ocean floor and deposited via downward particle flux (Kim et al., 2005). Therefore, $IPSO_{25}$ is supposed to possibly indicate spring sea ice distribution but due to the small number of studies, it is suggested to rather be a qualitative indicator for e.g. sea ice extent or seasonality (Belt, 2019). During sinking in the water column, $IPSO_{25}$ is supposed to be affected by photo-degradation, induced by visible light in the upper water column (Rontani et al., 2011) but so far this effect was not found to be significant. Although it is likely that $IPSO_{25}$ is affected by partial autoxidative and bacterial degradation in surface sediments (Rontani et al., 2019a) and within the sediment (Rontani et al., 2014), it is known to sustain up to 60,000 years in marine sediments (Collins et al., 2013).

So far, $IPSO_{25}$ has been studied in Antarctic sea ice, diatoms, the water column and marine sediments for identification, distribution and degradation of the biomarker and further in a small number of sea ice reconstruction studies (see Table 1.1). Past sea ice reconstructions were mainly conducted at the Antarctic Peninsula, in the Scotia Sea and in the Ross Sea in the west, and in the Pacific and Indian sector in East Antarctica. Except for one study that covers 60,000 years (Collins et al., 2013), the majority of sea ice reconstructions covers for the last 11,000 years or shorter time periods. The interpretation of sea ice cover and seasons is examined by the concentration or anomaly of $IPSO_{25}$ in the sediment cores. Biomarkers such as the triunsaturated HBI ($C_{25:3}$ or HBI triene) produced by e.g. *Rhizosolenia* and *Pleurosigma* diatom species (Belt et al., 2000, 2017) are commonly used as an indicator for open marine conditions like the marginal sea ice zone (Collins et al., 2013) or permanently open ocean zone (Massé et al., 2011; Smik et al., 2016a). Both, $IPSO_{25}$ and HBI triene, are either used in direct comparison or as a ratio. With this procedure the presence of sea ice as well as estimations of seasonal characteristics and amplitudes could be determined in combination with other proxy data (e.g. specific diatom assemblages). The comparison of concentration pattern of $IPSO_{25}$ and the open ocean biomarker can be interpreted as indicators for seasonal variability (Collins et al., 2013). The ratio of $IPSO_{25}$ and open marine biomarker points out the dominance of either sea ice or ice-free environmental conditions (e.g. Barbara et al., 2016; Etourneau et al., 2013). It has been discussed that downcore records of both sea ice and open marine biomarkers may show patterns that correlate positively or negatively to teach other, depending on different environmental conditions (Müller et al., 2011; Navarro-Rodriguez et al., 2013; Xiao et al., 2013). Biomarker production is not linearly related to sea ice: sea ice edges with thin, translucent ice or high sea ice dynamics with sufficient nutrient supply allow producers of both IP_{25} and phytoplankton biomarker to bloom, while their concentrations under extensive sea ice conditions is lower. Therefore, similar patterns of sea ice and open marine biomarkers are seen as a marker of rapid seasonal changes, whereas opposite patterns represent changing positions of sea ice margins (Belt, 2018).

Table 1.1 Overview of past studies on $IPSO_{25}$ regarding the sample material and study focus.

Sample material	Study focus	References
Sea Ice	- Identification - Distribution	Belt et al., 2016 Johns et al., 1999 Massé et al., 2011 Nichols et al., 1993, 1988, 1989 Smik et al., 2016a
Water column	- Identification - Distribution - Degradation	Cripps and Clarke, 1998 Rontani et al., 2019b Schmidt et al., 2018
Diatoms	- Identification - Distribution - Laboratory cultures	Belt et al., 2017 Johns et al., 1999 Massé et al., 2011 Smik et al., 2016a
Surface sediments	- Identification - Distribution	Belt et al., 2016 Johns et al., 1999 Massé et al., 2011 Rontani et al., 2019a Smik, 2016
Short sediment cores	- Distribution - Analytical methods - Degradation	Belt and Cabedo-Sanz, 2015 Cabedo-Sanz et al., 2016 Massé et al., 2011 Rontani et al., 2018a, 2018b Sinninghe Damsté et al., 2007 Venkatesan, 1988
Long sediment cores	- Sea ice reconstructions - Reconstruction of ice shelf and climatic development	Barbara et al., 2010, 2013, 2016 Campagne et al., 2015, 2016 Collins et al., 2013 Denis et al., 2010 Etourneau et al., 2013 Matsumoto et al., 1992

1.4. The Western Antarctic Peninsula

The Antarctic Peninsula (AP) is the northernmost spur of the Antarctic continent and approximately 1000 km away from South America. The opening of the Drake Passage through sea floor spreading initialized the transition to the modern configuration of the Antarctic continent by the separation of South America and the Antarctic Peninsula. The opening of the Southern Ocean gateways began in the Eocene, 50 Ma, continued with the spreading of the West Scotia Ridge (water depth >2000 m) and finally established in the Miocene around 20 Ma (Livermore et al., 2005). Today, the geology of the AP is dominated by volcanic and magmatic formations from the Mesozoic and Cenozoic with the South Shetland Islands as an (mostly inactive) volcanic island arc and the Bransfield Strait as a backarc basin (Figure 1.5 left)(Barker et al., 2003; Haase et al., 2012). On both sides of the AP the continental shelf is between 200 km and 300 km wide. The Bransfield Basin is located between the AP and the South Shetland Islands, next to the steep continental slope, and sedimentation in the Bransfield Basin is frequently disturbed by sediment discharge from the continental margin and turbidites with various volcanic, magmatic and glacial debris (Barker et al., 2003; Haase et al., 2012). The opening of deeper ocean gateways in the Drake Passage between 34 Ma and 30 Ma correlates with δ^{18}O Southern Ocean isotope records (Scher and Martin, 2006). The establishment of the Antarctic Circumpolar Current (ACC) (Figure 1.5 right) led to the thermal isolation of the Antarctic continent, promoted southern hemisphere glaciation and the formation of the Antarctic Ice Sheet (Kennett, 1977). The abrupt cooling at the Eocene-Oligocene boundary is supposed to be related to a higher Southern Ocean upwelling and turnover that led to enhanced carbon sequestration in the ocean and a decrease in atmospheric CO_2 (Pearson and Palmer, 2000; Scher and Martin, 2006). Several tectonic events such as the opening of the deep-sea passage between Australia and Indonesia were connected to the progressing glaciation of Antarctica and ice sheet formation in the Miocene (approximately between 14 Ma and 11 Ma) and the global cooling after 5 Ma with significant Antarctic ice sheet extension (Kennett, 1977). Since the onset of the Cenozoic glaciation the extent of the Antarctic ice sheet is controlled by the oscillating global glacial-interglacial cycles, driven by orbital forcing (DeConto et al., 2008). With the end of the Last Glacial Maximum (LGM, about 20 ka ago, Clark et al., 2009) the Antarctic Peninsula ice sheet (APIS) retreated significantly from 18 ka to 10 ka nearly to its present configuration (Bentley et al., 2014).

Diatom-based studies by Gersonde et al. (2005) suggest a latitudinal northward migration of winter sea ice extent by 3° to 4° degree in the Drake Passage during the last glacial period, but due to a lack of sufficient data of siliceous microfossils these results are quite uncertain. Further, the dissolution of siliceous microfossils and absence of microfossil records under perennial sea ice limits the ability of diatom studies for summer sea ice reconstructions. Applications of coupled climate models revealed a huge disagreement to climate proxies and poorly reproduced seasonal sea ice cycles during

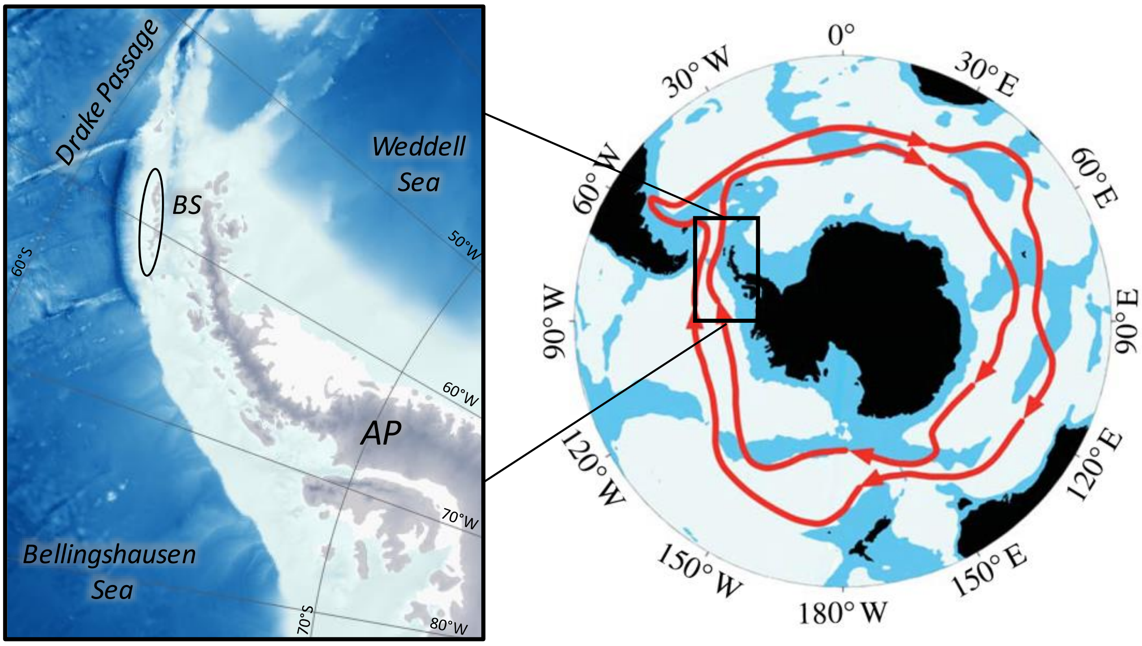

Figure 1.5 Left: bathymetric features at the Antarctic Peninsula (AP) between the Bellingshausen Sea and the Weddell Sea. The Bransfield Strait (BS) is located between the Antarctic mainland the South Shetland Islands (black elipse). Map done with QGIS 3.0 (2018), bathymetry taken from GEBCO_14 (2015). Right: the modern configuration of the Antarctic Circumpolar Current (ACC) (red arrows) in the Southern Ocean (Thompson, 2008).

the LGM and recent times. For example, the northward boundary of LGM winter sea ice was estimated near the Antarctic mainland (63° S) or near South America (55° S) by different models, respectively (Roche et al., 2012).

The ice sheet retreat after the LGM is often investigated through glacial sediment records (e.g. Heroy and Anderson, 2007) and shows a rapid warming that is interrupted by a cold excursion, called the Antarctic Cold Reversal from 14.7 ka to 13.0 ka BP (e.g. Mulvaney et al., 2012; Pedro et al., 2016). The development of Holocene climate and sea ice at the western and eastern AP was examined in numerous studies from marine and lake sediments (several summaries in Allen et al., 2010; Ingólfsson et al., 2003; Minzoni et al., 2015; Taylor and Sjunneskog, 2002). The Antarctic Peninsula Climate Synthesis by Minzoni et al. (2015) (Figure 1.6 left) summarizes the major findings from terrestrial and marine records and displayed the warm Holocene Climatic Optimum clearly at all study sites. Holocene sea ice reconstructions reveal certain differences in timing and intensity of sea ice cover between the west and east side of the AP (Figure 1.6 right) but also on smaller local scales. The Western Antarctic Peninsula (WAP) experienced higher ocean temperatures and reduced sea ice conditions during the deglacial and Early Holocene, while conditions were opposite at the Eastern Antarctic Peninsula (EAP). The Middle Holocene Climatic Optimum led to high seasonal amplitudes with moderate and/or increasing sea ice cover on both sides, while the Late Holocene is clearly colder and favourable for extended sea ice cover in the whole region (Allen et al., 2010; Barbara et al., 2016; Etourneau et al., 2013; Heroy et al., 2008; Minzoni et al., 2015; Shevenell et al., 2011; Taylor and Sjunneskog, 2002).

The Southern Westerly Winds (SWWs) form a wind belt around the Antarctic continent. When the winds are strong, the core of the wind belt contracts, shifts southward and enhanced upwelling of deep warm waters brings heat to the WAP shelf (Lamy et al., 2010; Pike et al., 2013). In case of weak SWWs this mechanism is reduced. Due to a strong coupling of atmosphere and ocean, large-scale atmospheric circulation pattern, such as the Southern Annular Mode (SAM) and the El Niño Southern Oscillation (ENSO) seem to influence not just ocean temperature but also sea ice distribution and seasonality (Liu et al., 2004; Stammerjohn et al., 2008a). At the WAP, a high variability of ENSO is suggested to contribute to an amplification of seasonal contrasts and fast changing interannual sea ice cover (Etourneau et al., 2013) which is similar to EAP sea ice and climate variability but not fully constrained yet (Barbara et al., 2016). Further, the state of SAM describes the north-southward movement of the westerly wind belt and causes different sea ice trends in the Pacific and Atlantic sector of the Southern Ocean and drives the upwelling of warm upper circumpolar deep waters (Stammerjohn et al., 2008b; Yuan, 2004). Because of the sparse high-resolution sea ice reconstructions at both sides of the AP, the exact interplay of atmospheric circulation patterns with sea ice cover is only constrained for the era of satellite observations. For the WAP, a tendency to cold and ice-rich ocean was found during an El Niño event simultaneous to a negative state of SAM. In contrast, warm, ice-reduced conditions were evident when La Niña events occurred together with a positive SAM (Stammerjohn et al., 2008b).

Today, the AP is a region extremely exposed to modern global warming (Vaughan et al., 2003) with distinct differences between the warmer western and colder eastern side (Siegert et al., 2019). Further, heavy retreat of West Antarctic Peninsula glaciers (Cook et al., 2005), the disappearance of almost all perennial sea ice (Stammerjohn et al., 2008a), near-surface ocean temperature rise of +1° C (Meredith and King, 2005) and the decline of e.g. Adélie penguin populations (Ducklow et al., 2007) are observed. Therefore, a detailed assessment of past sea ice development is helpful for the determination of future implications of global climate and the ice sheet at the AP and West Antarctica.

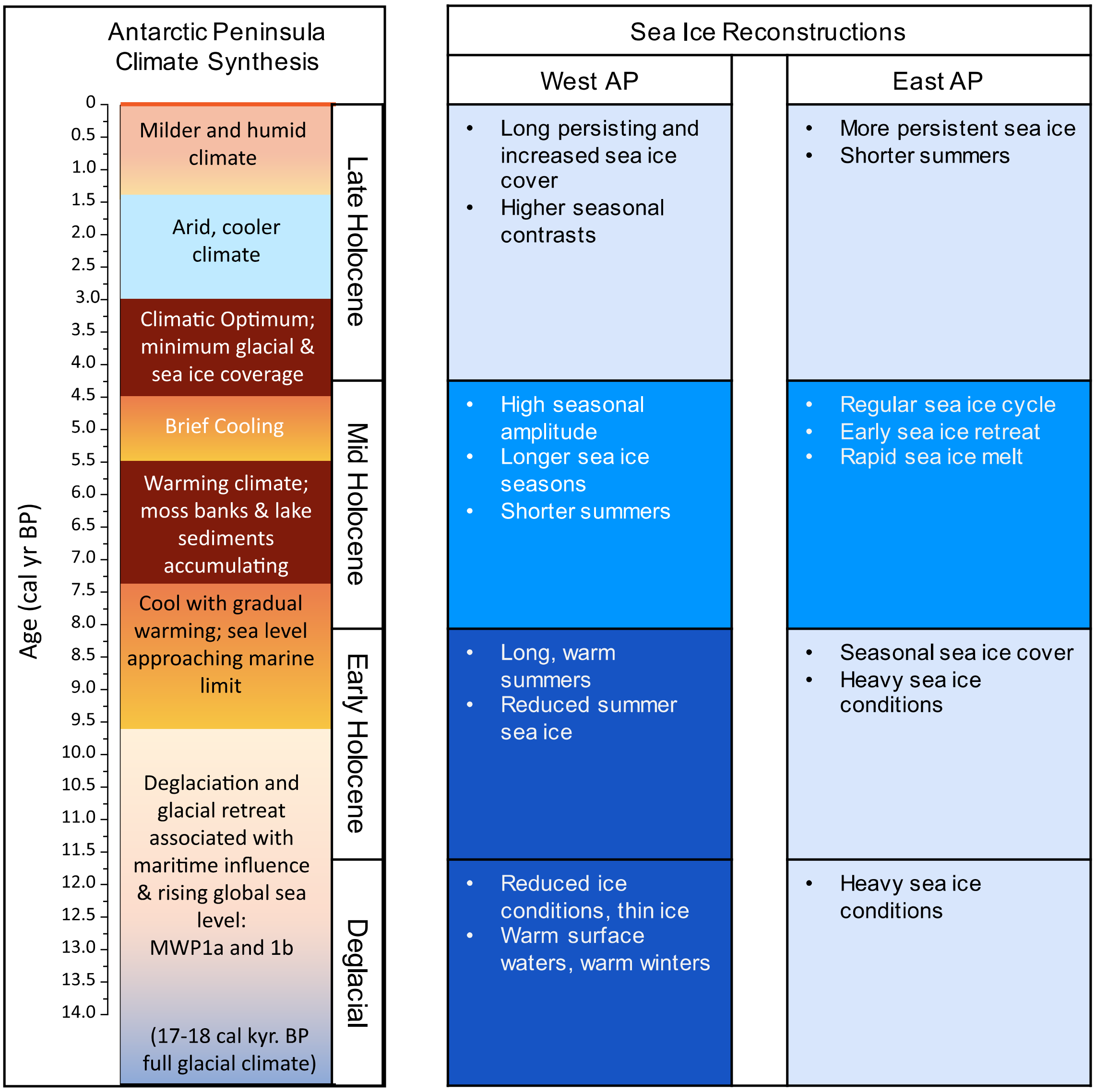

Figure 1.6 Left: the Antarctic Peninsula Climate Synthesis by Minzoni et al. (2015) (after Ingólfsson et al., 2003) summarizes the climatic history derived from marine and lake sediments since the end of the Last Glacial Maximum. Right: a broad summary of sea ice reconstructions at the west AP (Allen et al., 2010; Etourneau et al., 2013; Heroy et al., 2008; Shevenell et al., 2011; Taylor and Sjunneskog, 2002) and the east AP (Barbara et al., 2016; Minzoni et al., 2015), the background colours refer to dark blue = open waters and low sea ice concentrations, light blue = higher sea ice concentrations.

2. OBJECTIVES OF THIS THESIS

The primary goal of this thesis is the assessment of the organic biomarker $IPSO_{25}$ for paleo sea ice and climate reconstructions in Antarctica. The specific objectives are the evaluation of $IPSO_{25}$ itself and the assessment of its application as a new biomarker-based sea ice index according to the concept of PIP_{25} in the Arctic. Since $IPSO_{25}$ is only applied in a few numbers of sea ice studies and its specific characteristics were not studied yet, relevant basic information about this proxy is still missing. For example, there is only one study on how $IPSO_{25}$ water samples correspond to the sea ice extent in East Antarctica (Smik et al., 2016a) and none for West Antarctica. A number of studies were done to reveal the significance of $IPSO_{25}$ in comparison with qualitative sea ice reconstructions from diatom assemblages (Barbara et al., 2010, 2013, 2016; Campagne et al., 2015, 2016; Collins et al., 2013; Denis et al., 2010; Etourneau et al., 2013) but a comparison to sea ice cover quantifications from diatom assemblages via a transfer function (Esper and Gersonde, 2014a) are still missing. Further, the promising concept of a PIP_{25} analogue was not tested against sea ice data. To close these knowledge gaps **Part I** of the thesis consists an **evaluation of $IPSO_{25}$.** A number of marine surface sediment samples will be related to satellite observations of recent sea ice cover and diatom assemblages. This pilot study aims to provide robust evidence of $IPSO_{25}$ as a spring sea ice marker and to identify possible limitations and significance at the WAP. Further, the approach of the sea ice index PIP_{25} from the Arctic will be applied for the first time as the novel “$PIPSO_{25}$ index” for the Southern Ocean and tested with different phytoplankton biomarkers.

More open questions concern the regional coverage and the significance of $IPSO_{25}$ and $PIPSO_{25}$ for studies of past sea ice and environmental conditions. It is also not clear how changes in sea ice, sea ice seasonality and the influence of ENSO and SAM affect $IPSO_{25}$ based sea-ice reconstructions on decadal scales. To address these issues, **Part II** is a multiple short-core study designed for the **reconstruction of spring sea ice cover over the last 200 years** and shall provide information about the suitability and applicability of $IPSO_{25}$ and $PIPSO_{25}$. The study on three short sediment cores at the WAP is supposed to reveal the regional coverage of sea ice records. This study benefits from the access to high-resolution sea ice and climate data from satellite observations, marine sediments and ice cores as well as the application of numerical modelled data for comparison.

Sea ice reconstructions on longer, i.e. centennial to multi-millennial, time scales are needed for validation of modelling studies and, in particular, to reveal the interactions of sea ice with changing climate conditions as well as in relation to atmospheric or oceanic circulation patterns on regional and global scales. Hence, **Part III** of this thesis will aim for the application of $IPSO_{25}$ and $PIPSO_{25}$ in a **multi-proxy intercomparison sea ice reconstruction over the last 17,000 years**. This allows the application of sea ice proxies for time periods with fundamental climate changes, i.e. during the deglaciation and the Holocene. The response of sea ice to long- and short-term climate changes will be assessed and compared with regional paleo data. The dynamics in sea ice and climate conditions shall reveal the impact of ENSO and the SWWs on sea ice cover, biomarker production and oceanographic configurations.

The WAP as study region was chosen mainly for two reasons. First, this region is strongly affected by recent global warming and therefore a key site for the detailed reconstruction of paleo sea ice and climate conditions for future projections. Second, numerous studies with multiple different climate proxies were already examined at the WAP that allow the assessment of climate and sea ice indicators from several sources.

3. MATERIAL AND METHODS

3.1. Conceptualization of biomarker study

The study is designed as a step by step approximation to the significance of $IPSO_{25}$ in Antarctic sediments from recent sea ice conditions, over the period of 200 years and finally to millennial scales. Since the reconstruction of sea ice is the main focus of this thesis the analytical description includes the detailed examination of HBIs and sterols necessary for the application of $IPSO_{25}$ and the phytoplankton-$IPSO_{25}$ index ($PIPSO_{25}$, chapter 3.2), all other analytical steps are described briefly (chapter 3.3) and documented more precisely in the individual studies. For analyses, 26 surface sediment samples (multicores and boxcores) were taken from different ocean regimes, additionally three short cores and one 10 m piston core were analysed downcore. The samples were retrieved during the cruise PS97 of RV *Polarstern* (expedition report Lamy, 2016) in 2016. Multicores and boxcores were sampled aboard and stored frozen in glass vials, the piston corer was stored at 4° C and sampled at the Alfred Wegener Institute (AWI) in Bremerhaven. The study includes numerous laboratory analyses (Table 3.1) and the use of additional data of satellite sea ice observations, numerical modelling of sea ice and ocean temperature and ice core and sediment data of paleo sea ice, climate, SWWs, ENSO and SAM for comparison (chapter 3.4).

Table 3.1 Overview of the laboratory analytics for this study.

Type	Parameter	Laboratory
Organic bulk parameters	Carbon, nitrogen, total organic carbon (TOC), biogenic opal	AWI Bremerhaven Universidad de Concepción
Highly branched isoprenoids	$IPSO_{25}$, HBI Z-triene, HBI E-triene	AWI Bremerhaven
Phytosterols	Brassicasterol, dinosterol, campesterol, ß-sitosterol, desmosterol	AWI Bremerhaven
Glycerol dialkyl glycerol tetraethers	GDGTs, OH-GDGTs, crenarchaeol	AWI Bremerhaven
Diatom fossils	Ecological groups Transfer function for winter sea ice and summer sea surface temperature	Universidad de Concepción Colgate University, New York AWI Bremerhaven
Stable carbon isotopes	$\delta^{13}C$ of TOC $\delta^{13}C$ of $IPSO_{25}$	University of Hamburg Universidad de Concepción Washington State University GFZ Potsdam, MARUM
Radiocarbon dating	^{14}C, acid-insoluble organic carbon	AWI Bremerhaven
Pb dating	^{210}Pb excess	AWI Bremerhaven Instituto Antártico Chileno, Punta Arenas Université de Montpellier
Sediment composition	XRF-scan, magnetic susceptibility, ice rafted debris	AWI Bremerhaven

3.2. An advanced concept of sea ice biomarker interpretation

One difficulty in the interpretation of sea ice biomarkers is their absence that can refer to a permanentely open ocean or an ocean permanentely covered by thick sea ice (Müller et al., 2011) or a floating ice shelf canopy covering the ocean surface which does not allow diatom growth at the bottom of the ice shelf due to light limitation. An advanced concept beyond the simple ratio of biomarkers for sea ice reconstruction and a semi-quantitative estimation of sea ice cover was established in the Arctic by Müller et al. (2011). It is applied to the sea ice biomarker IP_{25}, (ice proxy with 25 carbon atoms, Belt et al., 2007) which is the northern hemisphere counterpart of $IPSO_{25}$. Sea ice is not just a habitat for sympagic diatom species but also promotes diatom blooms at the sea ice edge through nutrient release and water column stratification in late spring and summer (Arrigo et al., 1997; Vernet et al., 2008). Therefore, an index based on the relative contribution of both environmental biomarkers helps to avoid the over- or underestimation of single indicators and refines the differentiation between various states of sea ice cover, dynamics and characteristics depending on the surrounding conditions. For the Arctic, the index is calculated with the sea ice biomarker (IP_{25}) and open marine phytoplankton markers (either phytosterols or HBI trienes), constituted as the phytoplankton-IP_{25} index (PIP_{25}) (Müller et al., 2011) and provides a detailed assessment of sea ice conditions with a range of the index between 0 and 1. Figure 3.1 illustrates the gradation of environmental conditions from open ocean towards permanent sea-ice cover.

Due to the absence (or low concentrations) of IP_{25}, zero to low PIP_{25} values indicate dominantly ice-free ocean conditions, while rising values point to the presence of a stable sea-ice edge and long-lasting sea-ice cover in spring and summer. The value 1 marks a sea ice cover that suppresses phytoplankton growth but still allows photosynthesis of sea ice diatoms. When both biomarkers are absent and the sea ice index is not calculable

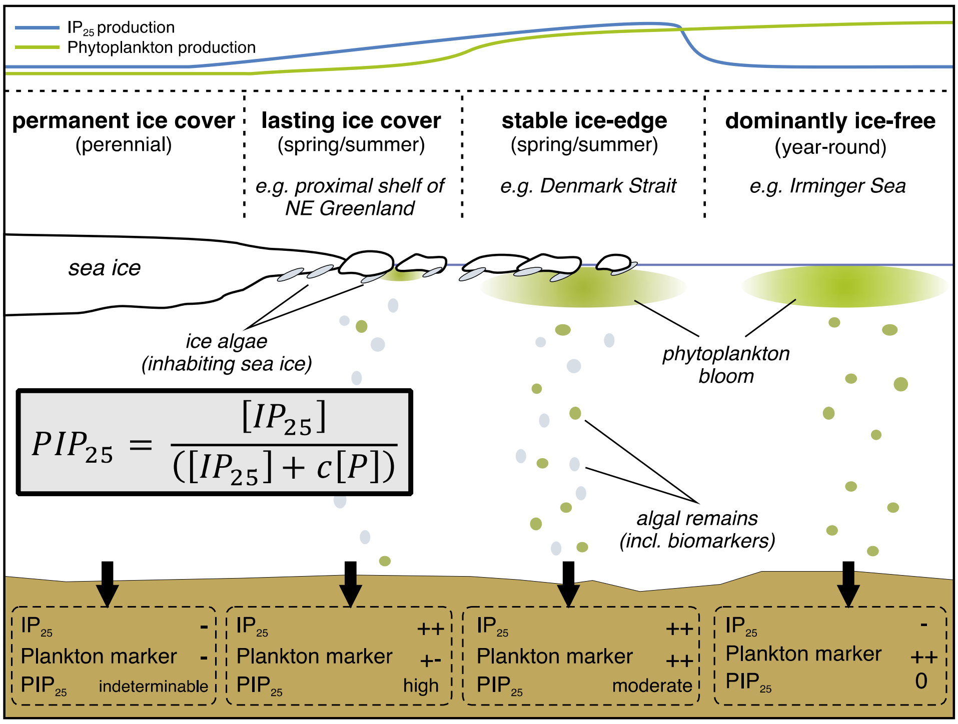

Figure 3.1 The illustrated conception of the phytoplankton-ice proxy approach PIP_{25} and its equation (grey box) for Arctic sea ice reconstructions after Müller et al. (2011). Square brackets represent biomarker concentrations, the balance factor c (c = mean IP_{25}/mean phytoplankton) equalizes concentration differences between sea ice and phytoplankton biomarkers.

and refelcts perennial, thick sea ice without any diatom growth (Müller et al., 2011). Calibration studies in the Arctic have revealed a positive correlation of the PIP_{25} approach to modern spring sea ice distributions (Kolling et al., 2017; Müller et al., 2011; Navarro-Rodriguez et al., 2013; Xiao et al., 2015b), most successful with PIP_{25} indicators based on HBI trienes (Köseoğlu et al., 2018).

3.3. Laboratory study on $IPSO_{25}$ and phytoplankton markers

For the analysis of $IPSO_{25}$ and phytoplankton markers the methodological approach of biomarker lipid extraction, identification and quantification is based on the analytical protocol to perform HBI and sterol-based sea ice reconstructions in the Arctic (Belt et al., 2013, 2014; Stein et al., 2012). Besides $IPSO_{25}$, the E- and Z-isomeres of HBI trienes, ((9E)-2,6,10,14-tetramethyl-7-(3-methylpent-4-enyliden)pentadeca-9-ene) and (9Z)-2,6,10,14-tetramethyl-7-(3-methylpent-4-enyliden)pentadeca-9-ene), brassicasterol (24-methylcholesta-5,22E-dien-3β-ol), dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol), β-sitosterol (24-ethylcholest-5-en-3β-ol), campesterol (24-methylcholest-5-en-3β-ol) and desmosterol (cholesta-5,24-dien-3β-ol) were examined (Belt et al., 2017; Volkman, 1986; Xiao et al., 2013). To account for different laboratory facilities the method was modified to fit the laboratory standard at the AWI Bremerhaven including analyses of HBI trienes and sterols.

Sediment samples were freeze-dried and homogenised before extraction. Between 3 g and 5 g of sediment was taken and internal standards 7-hexylnonadecane (7-HND for HBIs, 0.076 µg per sample), 5α-androstan-3β-ol (for sterols, 0.78 µg per sample) and C_{46} (for GDGTs, 0.78 µg per sample) were added for quantification and quality control of the extraction procedure. The sediment was treated three times with 6 ml dichloromethane:methanol (CH_2Cl_2:MeOH, *v/v* 2:1) in a 15 min ultrasonification and the solvent was decanted after centrifugation (2500 rpm, 1 min). The separation of the apolar hydrocarbons was done via column chromatography with silica gel (SiO_2) acting as the stationary phase. The different biomarker lipids were eluted as following: first, 5 ml hexane (HBI fraction), second, 8 ml ethylacetate:hexane (sterol fraction, *v/v* 20:80), and third, 5 ml CH_2Cl_2:MeOH (GDGT fraction, *v/v* 1:1). The separation of sterol and GDGT fraction was modified during the project: for the second study sterols and GDGTs were eluted together (with 5 ml CH_2Cl_2:MeOH) and this extract was purified and filtrated for GDGT measurement and later silylated (with 200 µl BSTFA under 60° C for 2h, Belt et al., 2013; Brault and Simoneit, 1988; Fahl and Stein, 2012) for sterol measurement. In the third study, again, sterols and GDGTs were eluted together and split into half for individual examination and measurement of each biomarker fraction.

HBIs and sterols were analyzed via gas chromatography mass spectrometry (GC-MS) with an Agilent 7890B gas chromatograph (30m DB 1MS column, 0.25mm diameter, 0.250 µm film thickness, carrier gas helium) coupled to an Agilent 5977B mass spectrometer (MSD, 70 eV constant ionization potential, ion source temperature 230 ° C). The individual oven temperature program for HBIs was 60° C for 3 min, a temperature increase to 325° C within 23 min and holding of the temperature for 16 min. For sterols the initial temperature (60° C) was hold for 2 min, then increased to 150° C within 6 min, and further increased to 325° C within 57 min. The identification of individual biomarkers is based on the comparison of measured and published mass spectra from HBIs (Belt, 2018; Belt et al., 2000). Published mass spectra from sterols (Belt et al., 2007; Boon et al., 1979; Brown and Belt, 2016; Volkman, 1986) were also compared in a reference compound run within the analytical sequence. The molecular ions were *m/z* 348 for $IPSO_{25}$, *m/z* 346 for HBI trienes and fragment ion *m/z* 266 for 7-HND. For sterols, the molecular ions were *m/z* 470 for brassicasterol, *m/z* 500 for dinosterol, *m/z* 486 for β-sitosterol, *m/z* 472 for campesterol and *m/z* 456 for desmosterol. The quantification was done via integration of peak areas from the selected ion monitoring (SIM) mode allowing the detection of low concentrations (Figure 3.2). Concentrations of biomarkers were calculated in relation to the internal standard 7-HND which is assumed to be affected equally under the extraction and analytical process as the biomarkers:

$$Biomarker\ [\mu g/g\ sed] = \left(\frac{Std\ \mu l * Std\ \mu g/\mu l}{Peak\ Std * Peak\ Biomarker}\right)/g\ sed \qquad (1)$$

The concentrations were corrected via multiplication with the specific response factor determined by running an external standard sediment with known HBI concentrations from the Lancaster Sound, Canada (PS72/287-2). The manual quantification also acted as a visual quality control on e.g. for the occurrence of HBI C_{25} sulfides from potential sulfurization of $IPSO_{25}$ (Sinninghe Damsté et al., 2007). The calculation of $PISPO_{25}$ is based on the original equation from IP_{25} (Figure 3.1). For a better distinction of different phytoplankton sources in the sea ice index the respective letter of the biomarker is part of the expression as P_ZIPSO_{25} (based on HBI Z-triene), P_EIPSO_{25} (based on HBI E-triene), P_BIPSO_{25} (based on brassicasterol), and P_DIPSO_{25} based on dinosterol.

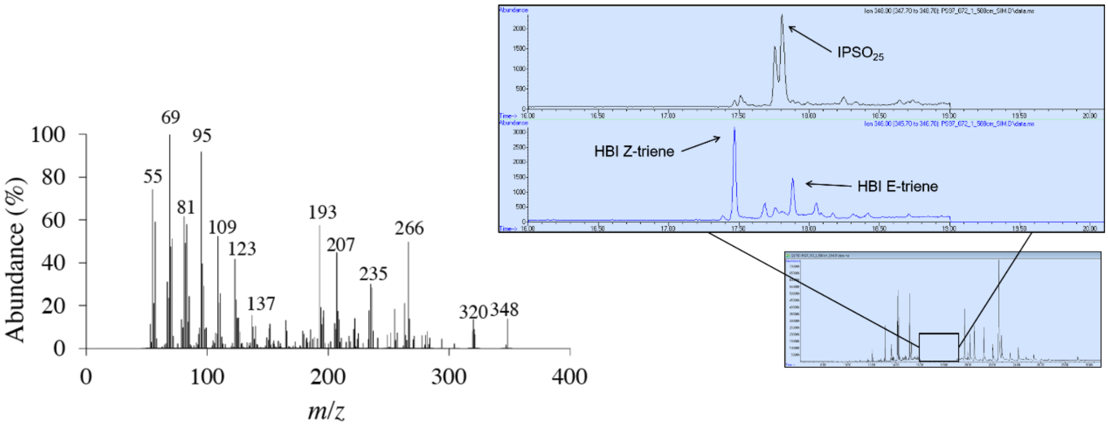

Figure 3.2 On the left: the characteristic mass spectrum of the diunsaturated HBI alkene $C_{25:2}$, expressed as $IPSO_{25}$ (from Belt and Cabedo-Sanz, 2015). Right: Chromatograms of $IPSO_{25}$ and HBI Z- and E-trienes. Peak areas were integrated manually.

3.4. Additional laboratory analyses

This chapter contains a brief overview of additional laboratory analyses that are described in the individual studies in detail including all technical data.

The analyses of sediment bulk content of carbon (C) and nitrogen (N) was done with a CNS analyser (Elementar Vario EL III). The content of total organic carbon (TOC) was determined with a carbon-sulphur determinator (CS-2000, ELTRA) on acidified samples (500 µl hydrochloric acid) (details in paper 2 and 3). Biogenic opal was determined following the alkaline extraction procedure (Mortlock and Froelich, 1989; modified after Müller and Schneider, 1993) and measured via molybdate-blue spectrometry at the University of Concepción (Cárdenas et al., 2019).

Stable carbon isotopes of organic $\delta^{13}C$ were examined from acidified samples (three times 100 µl 1 N HCl) via an elemental analyser coupled with an IsoPrime isotope ratio mass spectrometer (details in Cárdenas et al., 2019 and paper 3). The examination of compound specific stable carbon isotopes $\delta^{13}C$ on $IPSO_{25}$ was done with GC-irm-MS (ThermoFisher Scientifi GC) coupled with an isotope ratio mass spectrometer (Finnigan

MAT 252) at the MARUM and GFZ Potsdam (details in paper 1 and 3). All $\delta^{13}C$ (in ‰) relied on the Vienna PeeDee Belemnite (VPDB).

GDGTs (lipid extraction, see chapter 3.3) were analysed after filtration (polytetrafluoroethylene filters) with high performance liquid chromatography (Agilent 1200 HPLC system) connected with a single quadrupole mass spectrometer (Agilent 6120 MSD) and via an atmospheric pressure chemical ionization (APCI) interface. Results were used to calculate ocean temperatures based on TEXL86 (Kim et al., 2010), RI-OH' (Lü et al., 2015) and an index for terrestrial organic matter (Hopmans et al., 2004)(details paper 2 and 3).

Diatom fossils were washed with hydrogen peroxide and hydrochloric acid, microscope slides were prepared after Gersonde and Zielinski (Gersonde and Zielinski, 2000) and diatom valves were counted (Schrader and Gersonde, 1978). Diatom ecological groups were defined (Buffen et al., 2007; Campagne et al., 2016; Heroy et al., 2008) and marine diatom transfer function was applied for winter sea ice (Esper and Gersonde, 2014a) and summer sea surface temperature (Esper and Gersonde, 2014b)(details paper 1, 2 and 3).

^{14}C radiocarbon dating was done on calcite samples with the mini carbon dating system (MICADAS) after Wacker et al. (2010) and on acid-insoluble organic carbon following Heroy et al. (2008) at AWI. Surface sediment samples were calibrated based on MARINE13 (Reimer et al., 2013), for downcore sediment samples the reservoir age was corrected based on reservoir age simulations (Butzin et al., 2017) and calibration was done based on and SHCal13 (downcore sediment samples, Hogg et al., 2013) with Calib 7.1 (http://calib.org/, Stuiver et al., 2018). For downcore records the relative fraction of marine and terrestrial organic matter was estimated from a two end-member mixing model (Thornton and McManus, 1994) based on stable carbon isotope endmembers from marine plankton and terrestrial mosses and peat. Since input of reworked, older organic carbon led to an overestimation of ^{14}C ages, radiocarbon dates of the long sediment core PS97/072-1 were matched to independent chronologies of the West Antarctic Ice Sheet Divide ice core (WAIS Divide Project Members et al., 2015). Interpolation of ages based on the Bayesian age model HummingBird (https://hummingage.awi.de/)(details paper 3).

The geochronology for the short sediment cores (PS97/056-1, PS97/068-2 and PS97/072-2) was derived from $^{210}Pb_{xs}$ activities by alpha spectrometry (Flynn, 1968) and ages based on $^{210}Pb_{xs}$ inventories according the Constant Rate of Supply Model (CRS, Appleby and Oldfield, 1978). On samples analyzed at the Université de Montpellier an age model was applied using the software R (R Core Team, 2017) and the package clam (Blaauw, 2010). On ages from AWI a Monte-Carlo approximation was applied (Sanchez-Cabeza et al., 2014)(details paper 2).

The sediment composition was examined via core description (sediment core PS97/072-1) and smear slides (short cores). Additionally, the magnetic susceptibility for the long core was conducted on the whole round core sections (GEOTEK multi-sensor core logger) aboard and profiling X-ray fluorescence (AVAATECH core-scanner) was done at AWI.

3.5. Additional data sets

Paper 2 includes monthly environmental data (ocean and atmospheric temperature, sea ice cover and thickness) from the numerical model AWI-ESM2 consisting of the atmospheric model ECHAM6 (Stevens et al., 2013) and the finite element sea ice-ocean model (FESOM2, Danilov et al., 2017) coupled to a climate model (Sidorenko et al., 2019)(details paper 2).

MATERIAL AND METHODS

For papers 1 and 2 monthly mean satellite sea ice concentrations were derived from passive microwave satellite data from the National Snow and Ice Data Center (NSIDC, Cavalieri et al., 1996) and the mean spring sea ice data (September to November) was taken for evaluation of $IPSO_{25}$ and $PIPSO_{25}$.

For large-scale atmospheric modes the paleo ENSO index (Li et al., 2013) and modelled SAM data (Abram et al., 2014) was used for the short time scale (paper 2). For the Holocene, a sand record from El Junco was considered for ENSO variability (Conroy et al., 2008) and the clay/silt ratio from a sediment core from the Chilean fjord were used for paleo SWWs strength (Lamy et al., 2010)(paper 3).

Information from short ice core records were retrieved from stable isotope data (δD, James Ross Island, Abram et al., 2013; $\delta^{18}O$, Bruce Plateau, Goodwin et al., 2016) and methansulfonic acid (MSA, Dyer Plateau, Abram et al., 2010)(paper 2). Stable isotope data from long cores were used in paper 3 (WAIS Divide Project Members et al., 2013). Holocene sea salt sodium flux data were taken from the EPICA Dronning Maud Land ice core (EPICA Community Members et al., 2004) and the WAIS Divide ice core (δD, Mulvaney et al., 2012; $\delta^{18}O$, WAIS Divide Project Members et al., 2015)(paper 3).

4. AUTHOR´S CONTRIBUTION

The sediment cores and boxcorers used in all three studies were taken and mainly sampled by Juliane Müller and members of the Marine Geology section of AWI during the *Polarstern* cruise PS97 in the year 2016. Juliane Müller also supervised the PhD project and all studies throughout the time and contributed to the manuscripts and interpretations. For all manuscripts I arranged the data, did calibration and calculations of indices and correlations, wrote the drafts and created the figures. In every study, all co-authors were part of the interpretation, discussion and review process.

Part I (Chapter 5): For first study I performed the preparation of sediment samples, the measurement of total organic carbon as well as the lipid extraction of HBIs and sterols and prepared the microscopy slides for the diatom analyses. Measurements of stable carbon isotopes of $IPSO_{25}$, the ^{14}C radiocarbon dating, the retrieval of satellite sea ice data and the analysis of diatoms assemblages were done in cooperation with different sections at AWI and MARUM, Bremen.

Part II (Chapter 6): For second study I sampled the trigger core PS97/072-1 and performed the lipid extraction of HBIs, sterols and GDGTs on two of three cores in the laboratory. The third core was analysed by Denise Diekstall from PALICE, AWI. In cooperation with the Instituto Antártico Chileno in Punta Arenas, Chile, and different sections at AWI the ^{210}Pb dating, the modelling study, retrieval of satellite sea ice data, analysis of GDGTs, and the complete diatom analyses and transfer function were done.

Part III (Chapter 7): For the third study I performed the lipid extraction on the sediment core, measured stable carbon isotopes on TOC and employed an age model for the sediment core. Further analyses of stable carbon isotopes on TOC and $IPSO_{25}$, biogenic opal, diatom assemblages and their transfer functions, GDGTs and radiocarbon dating were done at AWI and in cooperation with the University of Hamburg, Universidad de Concepción, Chile, Colgate University and Washington State University, USA, and GFZ Potsdam.

PART I

5. PART I: HIGHLY BRANCHED ISOPRENOIDS FOR SOUTHERN OCEAN SEA ICE RECONSTRUCTIONS: A PILOT STUDY FROM THE WESTERN ANTARCTIC PENINSULA

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Abstract

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

5.1. Introduction

In the last century, the Western Antarctic Peninsula (WAP) has undergone a rapid warming of the atmosphere of 3.7 ± 1° 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 $C_{25:2}$, Figure 5.1a) – for Southern Ocean sea ice reconstructions. The HBI diene was first described by Nichols et al. (1988) from sea ice diatoms. ^{13}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 monoene termed IP_{25} (Belt et al., 2007) – proposed the term $IPSO_{25}$ (Ice Proxy for the Southern Ocean with 25 carbon atoms) as a new name for this biomarker.

In previous studies, an HBI triene (HBI $C_{25:3}$; Figure 5.1b-c) found in polar and sub-polar phytoplankton samples (Massé et al., 2011) has been considered alongside $IPSO_{25}$ and the ratio of $IPSO_{25}$ to this HBI triene hence has been interpreted as a measure for the relative contribution of organic matter derived from sea ice algae versus open water phytoplankton (Massé et al., 2011; Collins et al., 2013; Etourneau et al., 2013; Barbara et al., 2013, 2016).

Collins et al. (2013) further suggested that the HBI triene might reflect phytoplankton productivity in marginal ice zones (MIZ) and, based on the observation of elevated HBI triene concentrations in East Antarctic MIZ surface waters, this has been strengthened by Smik et al. (2016a). Known source organisms of HBI trienes (Figure 5.1 shows molecular structures of both the E- and Z-isomer) are, for example, *Rhizosolenia* and *Pleurosigma* diatom species (Belt et al., 2000, 2017). In the subpolar North Atlantic, the HBI Z-triene has been used to further modify the so-called PIP_{25} index (Smik et al., 2016b) - an approach for semi-quantitative sea ice estimates. Initially, PIP_{25} was based on the employment of phytoplankton-derived sterols, such as brassicasterol (24-

methylcholesta-5,22E-dien-3β-ol) and dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol) (Kanazawa et al., 1971; Volkman, 2003), to serve as open-water counterparts, while IP_{25} reflects the occurrence of a former sea ice cover (Belt et al., 2007; Müller et al., 2009, 2011). Consideration of these different types of biomarkers helps to discriminate between ice-free and permanently ice-covered ocean conditions, both resulting in a lack of IP_{25} and $IPSO_{25}$, respectively (for further details see Belt, 2018; Belt and Müller, 2013). Uncertainties in the source-specificity of brassicasterol (Volkman, 1986) and its identification in Arctic sea ice samples, however, require caution when pairing this sterol with a sea ice biomarker lipid for Arctic sea ice reconstructions (Belt et al., 2013). In this context, we note that Belt et al. (2018) reported that brassicasterol is not evident in the $IPSO_{25}$ producing sea ice diatom *Berkeleya adeliensis*. While the applicability of HBIs (and sterols) to reconstruct past sea ice conditions has been thoroughly investigated in the Arctic Ocean (Belt, 2018; Stein et al., 2012; Xiao et al., 2015b), only two studies document the distribution of HBIs in Southern Ocean surface sediments (Belt et al., 2016; Massé et al., 2011). The circum-Antarctic data set published by Belt et al. (2016), however, does neither report HBI triene nor sterol abundances. Significantly more studies so far focused on the use of $IPSO_{25}$ and the HBI Z-triene for paleo sea ice reconstructions and these records are commonly compared to micropaleontologial diatom analyses (e.g., Barbara et al., 2013; Collins et al., 2013; Denis et al., 2010).

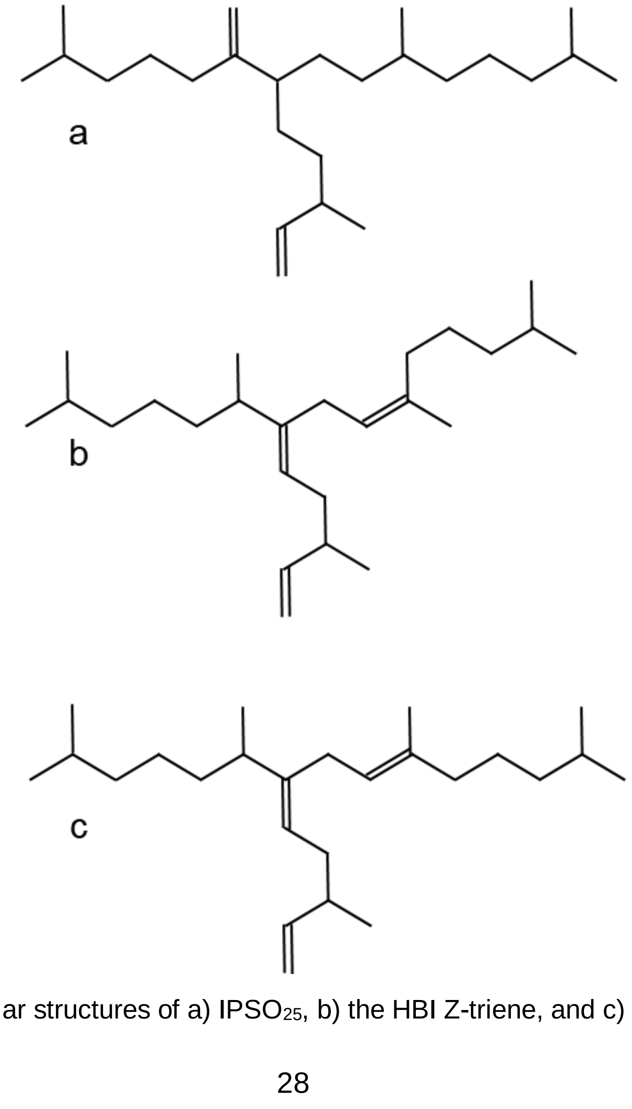

Figure 5.1 The molecular structures of a) $IPSO_{25}$, b) the HBI Z-triene, and c) the HBI E-triene.

Here, we provide a first overview of the distribution of $IPSO_{25}$, HBI trienes, brassicasterol and dinosterol in surface sediments from the permanently ice-free ocean in the Drake Passage towards the seasonal sea ice inhabited area of the Bransfield Strait at the northern WAP. Sea ice estimates based on biomarkers are compared to sea ice concentrations derived from diatom transfer functions and satellite-derived data on the recent sea ice conditions in the study area. We further introduce and discuss the so-called $PIPSO_{25}$ index (phytoplankton-$IPSO_{25}$ index), which, following the PIP_{25} approach in the Arctic Ocean (Müller et al., 2011), may serve as a further indicator of past Southern Ocean sea ice cover.

5.2. Oceanographic setting

The study area includes the southern Drake Passage and the Bransfield Strait located between the South Shetland Islands and the northern tip of the WAP (Figure 5.2a and b). The oceanographic setting in the Drake Passage is dominated by the Antarctic Circumpolar Current (ACC) and several oceanic fronts showing large geostrophic water mass flows and subduction and upwelling of water masses (Orsi et al., 1995). The Antarctic Polar Front (APF) divides relatively warm subantarctic waters from the cold and salty Antarctic waters, while the southern Antarctic Circumpolar Current Front (SACCF) often associates with the maximum sea ice extent (Kim and Orsi, 2014). The current system in the Bransfield Strait is relatively complex and the mixture of water masses is not yet well understood (Moffat and Meredith, 2018; Sangrà et al., 2011). A branch of the ACC enters the Bransfield Strait in the west as the Bransfield Current, carrying transitional waters under the influence of the Bellingshausen Sea (Transitional Bellingshausen Sea Water, TBW). The

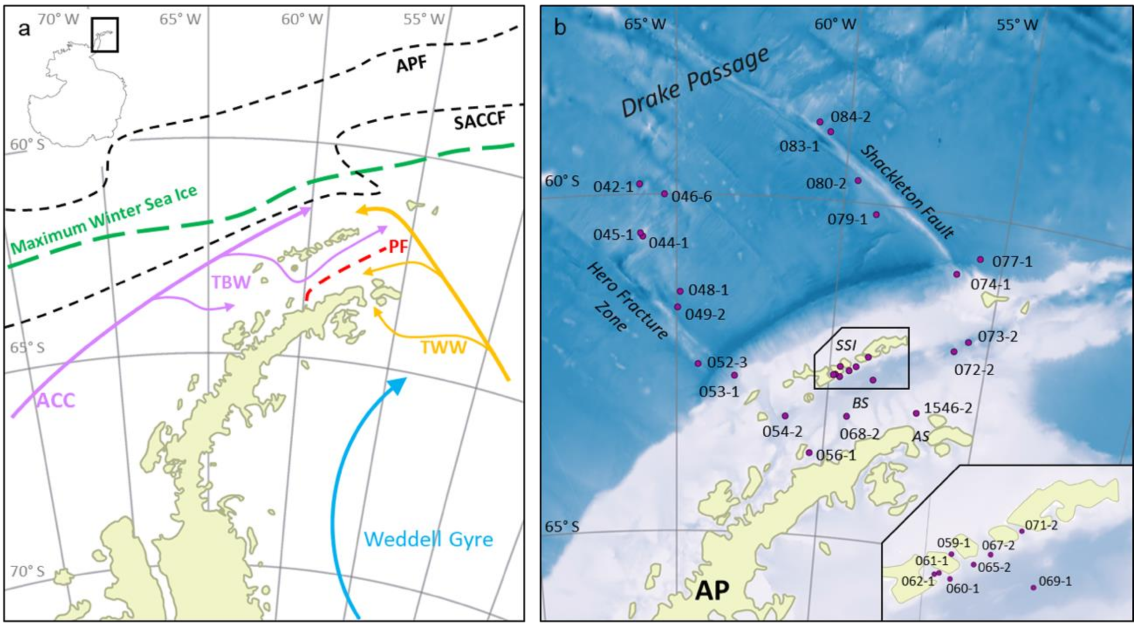

Figure 5.2 a) Oceanographic setting of the study area (modified after Hofmann et al., 1996; Sangrà et al., 2011) with ACC = Antarctic Circumpolar Current, TBW = Transitional Bellingshausen Water, TWW = Transitional Weddell Water, APF = Antarctic Polar Front, SACCF = Southern Antarctic Circumpolar Front, and PF = Peninsula Front, and the maximum winter sea ice extent (after Cárdenas et al., 2018). b) The bathymetric map of the study area with locations of all stations; AP = Antarctic Peninsula, AS = Antarctic Sound, BS = Bransfield Strait, and SSI = South Shetland Islands. A detailed station map at the South Shetland Islands is integrated.
The overview maps were done with QGIS 3.0 from 2018 and the bathymetry was taken from GEBCO_14 from 2015.

TBW is characterized by a well-stratified, fresh and warm water mass with summer sea surface temperatures (SST) above 0° C. Below the shallow TBW, a narrow tongue of circumpolar deep water (CDW) flows along the slope of the South Shetland Islands (Sangrà et al., 2011). In the eastern part, transitional water from the Weddell Sea (Transitional Weddell Sea Water, TWW) enters the Bransfield Strait through the Antarctic Sound and from the Antarctic Peninsula (AP). This water mass corresponds to the Antarctic Coastal Current (Collares et al., 2018; Thompson et al., 2009). The TWW is significantly colder (summer SST < 0° C) and saltier due to extended sea ice formation in the Weddell Sea Gyre. The two water masses are separated at the sea surface by the Peninsula Front characterized by a TBW anticyclonic eddy system (Sangrà et al., 2011). While the TWW occupies the deep water column of the Bransfield Strait (Sangrà et al., 2011), it joins the surface TBW in the southwestern Bransfield Strait (Collares et al., 2018).

Due to high concentrations of dissolved iron on the shelf (Klunder et al., 2014), the area around the WAP is characterized by a high primary production with high vertical export fluxes during early summer associated with the formation of fast sinking mineral aggregates and fecal pellets (Kim et al., 2004; Wefer et al., 1988). The Peninsula Front divides the Bransfield Strait into two biogeographic regimes of high chlorophyll and diatom abundance in the TBW and low chlorophyll values and a pre-dominance of nanoplankton in the TWW (Gonçalves-Araujo et al., 2015), which is also reflected in the geochemistry of surface sediments (Cárdenas et al., 2019).

5.3. Materials and Methods

5.3.1. Sediment samples and radiocarbon dating

In total, 26 surface sediment samples obtained by multicorers and boxcorers during the RV *Polarstern* cruise PS97 (Lamy, 2016) were analyzed (Figure 5.2). All samples were stored frozen and in glass vials. The composition of the sediments ranges from foraminiferal mud in the Drake Passage to diatomaceous mud with varying amounts of ice rafted debris in the Bransfield Strait (Lamy, 2016).

^{14}C radiocarbon dating of two samples from the PS97 cruise and one from the *Polarstern* cruise ANT-VI/2 (Fütterer, 1988) was conducted using the mini carbon dating system (MICADAS) at the Alfred Wegener Institute (AWI) in Bremerhaven, Germany, following the method of Wacker et al. (2010). The ^{14}C ages were calibrated to calendar years before present (cal BP) using the Calib 7.1 software (Stuiver et al., 2018) with an estimated reservoir age of 1178 years, derived from the six closest reference points listed in the Marine Reservoir Correction Database (www.calib.org).

5.3.2. Organic geochemical analyses

For biomarker analyses, sediments were freeze-dried and homogenized using an agate mortar. After freeze-drying, samples were stored frozen to avoid degradation. The extraction, purification and quantification of HBIs and sterols follow the analytical protocol applied by the international community of researchers performing HBI and sterol-based sea ice reconstructions (Belt et al., 2013, 2014; Stein et al., 2012). Prior to extraction, internal standards 7-hexylnonadecane (7-HND) and 5α-androstan-3β-ol were added to the sediments. For the ultrasonic extraction (15 min), a mixture of CH_2Cl_2:MeOH (v/v 2:1; 6 ml) was added to the sediment. After centrifugation (2500 rpm for 1 min), the organic solvent layer was decanted. The ultrasonic extraction step was repeated twice. From the combined total organic extract, apolar hydrocarbons were separated via open column chromatography (SiO_2) using hexane (5 ml). Sterols were eluted with ethylacetate:hexane (v/v 20:80; 8 ml). HBIs were analyzed using an Agilent 7890B gas chromatography (30 m DB 1MS column, 0.25 mm diameter, 0.250 µm film thickness, oven temperature 60° C for 3 min, increase to 325° C within 23 min, holding 325° C for 16 min) coupled to an Agilent 5977B mass spectrometer (MSD, 70 eV constant ionization potential, ion source temperature 230° C). Sterols were first silylated (200 µl BSTFA; 60° C; 2 hours; Belt et al., 2013; Brault and Simoneit, 1988; Fahl and Stein, 2012) and then analyzed on the same instrument using a different oven temperature program (60° C for 2 min, increase to 150° C within 6 min, increase to 325° C within 56 min 40 sec). As recommended by Belt (2018), the identification of $IPSO_{25}$ and HBI trienes is based on comparison of their mass spectra with published mass spectra (Belt, 2018; Belt et al., 2000; see Figure Appendix 1). Regarding the potential sulfurization of $IPSO_{25}$, we examined the GC-MS chromatogram and mass spectra of each sample for the occurrence of the HBI C_{25} sulfide (Sinninghe Damsté et al., 2007). The C_{25} HBI thiane was absent from all samples. For the quantification, manually integrated peak areas of the molecular ions of the HBIs in relation to the fragment ion m/z 266 of 7-HND were used. Instrumental response factors are determined by means of an external standard sediment from the Lancaster Sound, Canada. The HBI concentrations in this sediment are known and a set of calibration series was applied to determine the different response factors of the HBI molecular ions (m/z 346; m/z 348) and the fragment ion of 7-HND (m/z 266) (Figure Appendix 2; Belt, 2018; Fahl and Stein, 2012). The identification of sterols was based on comparison of their retention times and mass spectra with those of reference compounds run on the same instrument. Comparison of peak areas of individual analytes and the internal standard was used for sterol quantification. The error determined by duplicate GC-MS measurements was below 0.7 %. The detection limit for HBIs and sterols was 0.5 ng/g sediment. Absolute concentrations of HBIs and sterols were normalized to total organic carbon content (for TOC data see Cárdenas et al., 2018).

The herein presented phytoplankton-$IPSO_{25}$ index ($PIPSO_{25}$) is calculated using the same formula as for the PIP_{25} index following Müller et al. (2011):

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

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

Stable carbon isotope composition of $IPSO_{25}$, requiring a minimum of 50 ng carbon, was successfully determined on five samples using GC-irm-MS. The ThermoFisher Scientific Trace GC was equipped with a 30 m Restek Rxi-5 ms column (0.25 mm diameter, 0.25 µm film thickness) and coupled to a Finnigan MAT 252 isotope ratio mass spectrometer via a modified GC/C interface. Combustion of compounds was done under continuous flow in ceramic tubes filled with Ni wires at 1000° C under an oxygen trickle flow. The same GC program as for the HBI identification was used. The calibration was done by comparison to a CO_2 monitoring gas. The values of $\delta^{13}C$ are expressed in per mill (‰) against Vienna PeeDee Belemnite (VPDB) and the mean standard deviation was <0.9 ‰. An external standard mixture was measured every six runs, achieving a long-term mean standard deviation of 0.2 ‰ and an average accuracy of <0.1 ‰. Stable isotopic composition of neither HBI trienes nor sterols could be determined due to coeluting compounds.

5.3.3. 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 Gersonde, 2014a). The WSI estimates refer to September sea-ice concentrations averaged over a time period from 1981 to 2010 at each surface sediment site (National Oceanic and Atmospheric Administration, NOAA; Reynolds et al., 2002, 2007). The reference data set is suitable for our approach as it uses a 1° by 1° grid, representing a higher resolution than previously used and results in a root mean squared error of prediction (RMSEP) of 5.52 % (Esper and Gersonde, 2014a). We defined 15 % concentration as threshold for maximum sea-ice expansion following the approach of Zwally et al. (2002) for the presence or absence of sea ice, and 40 % concentration representing the average sea-ice edge (Gersonde et al., 2005; Gloersen et al., 1993). MAT calculations were carried out with the statistical computing software R (R Core Team, 2017) using the additional packages Vegan (Oksanen et al., 2012) and Analogue (Simpson and Oksanen, 2012).

Further enhancement of the sea-ice reconstruction was obtained by consideration of the abundance pattern of the diatom sea-ice indicators allowing for qualitative estimate of sea-ice occurrence, as proposed by Gersonde and Zielinski (Gersonde and Zielinski, 2000).

5.3.4. Sea ice data

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

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

5.4. Results and Discussion

In the following we present and discuss the sedimentary concentrations of $IPSO_{25}$, 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 $PIPSO_{25}$ by analogy with the Arctic sea ice index PIP_{25} (Müller et al., 2011).

5.4.1. Biomarker distribution in surface sediments

Distribution of $IPSO_{25}$

The sea ice biomarker $IPSO_{25}$ was detected in 14 samples, with concentrations ranging between 0.37 and 17.81 µg g^{-1} TOC. The distribution of $IPSO_{25}$ in the study area shows a clear northwest-southeast gradient (Figure 5.3a) with concentrations increasing from the continental slope and around the South Shetland Islands towards the continental shelf. Maximum $IPSO_{25}$ 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 $IPSO_{25}$ 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 $IPSO_{25}$ 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 $IPSO_{25}$ 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 $IPSO_{25}$ concentrations at these sites. $IPSO_{25}$ was not detected in sediments from the permanently ice-free areas in the Drake Passage.

The $\delta^{13}C$ values of $IPSO_{25}$ are between -10.3 ‰ and -14.7 ‰ which is the commonly observed range for $IPSO_{25}$ 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 $\delta^{13}C$ values of marine phytoplankton lipids in Antarctic sediments

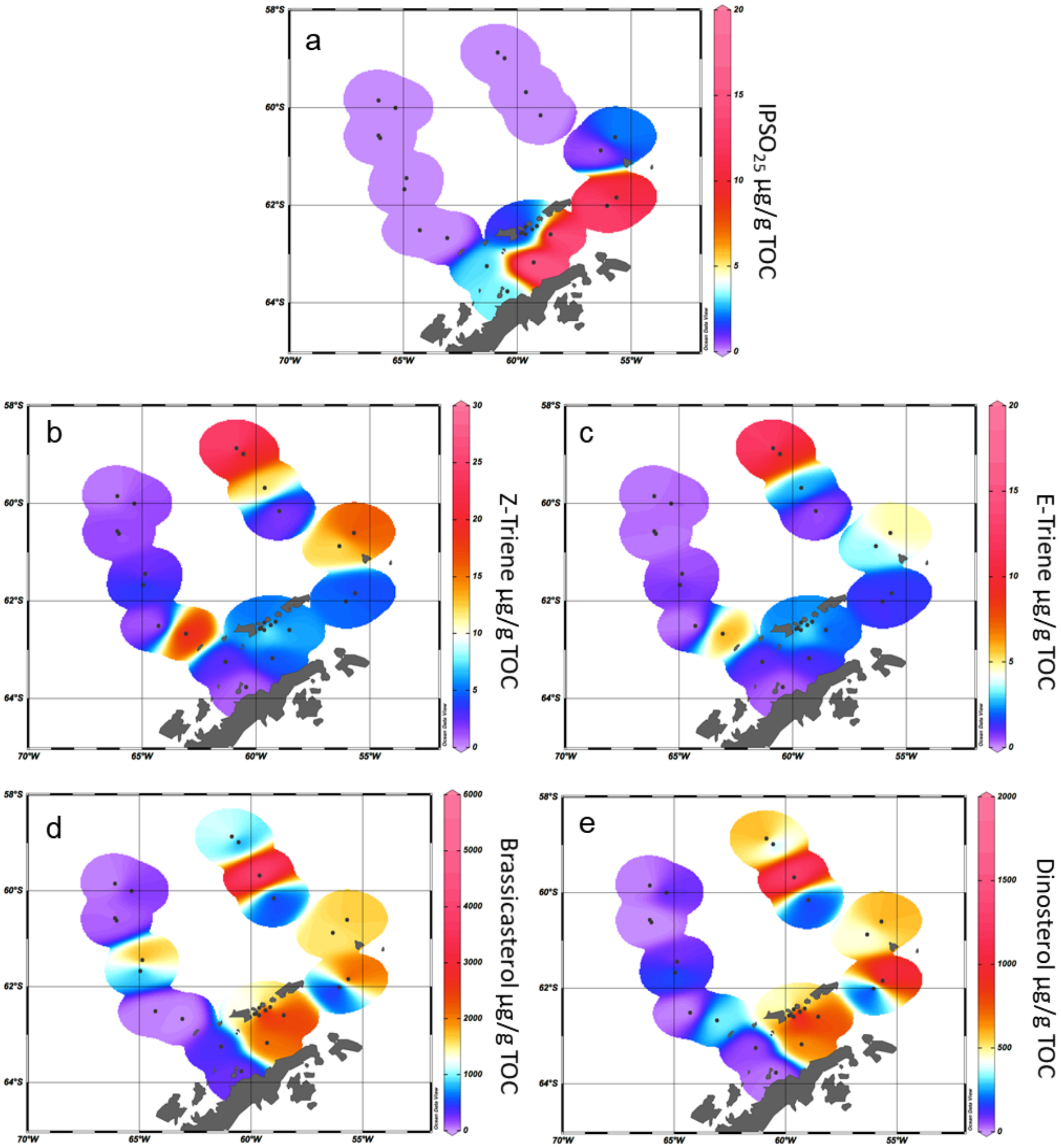

Figure 5.3 Distribution of a) $IPSO_{25}$, b) HBI Z-triene, c) HBI E-triene, d) brassicasterol, and e) dinosterol concentrations normalized to TOC. All distribution plots were made with Ocean Data View 4.7.10 (2017).

(-38 ‰ to -41 ‰ after Massé et al., 2011) and support the sea ice origin of $IPSO_{25}$ in the study area.

Distribution of HBI trienes

The HBI Z-triene was present in all 26 samples (0.33-26.86 µg g^{-1} TOC) and the HBI E-triene was found in 24 samples (0.15-13.87 µg g^{-1} TOC). Highest concentrations of both HBI trienes are found in the eastern Drake Passage and along the continental slope, where $IPSO_{25}$ is absent, while their concentrations in the Bransfield Strait are generally low (Figure 5.3b and c) suggesting unfavorable environmental conditions for their source diatoms (e.g., cooler SSTs, sea ice cover, grazing pressure). Contrary to the finding of elevated HBI Z-triene concentrations in surface waters along an ice-edge (Smik et al., 2016a) and earlier suggestions that this biomarker may be used as a proxy for MIZ conditions (Belt et al., 2015; Collins et al., 2013; Schmidt et al., 2018), we observe highest concentrations of the HBI Z- and E-triene at the permanently ice-free northernmost stations PS97/083 and PS97/084 in the eastern Drake Passage. These core sites are located in close vicinity to the Antarctic Polar Front (Figure 5.2) and we assume that the productivity of HBI triene source diatoms may benefit from mixing and upwelling of warm and cold water masses in this area (Moore and Abbott, 2002). Sediments collected south of the Antarctic Polar Front and along the Hero Fracture Zone in the western Drake Passage (Figure 5.2) contain moderate and very low concentrations of HBI trienes, respectively. The Hero Fracture Zone is mainly barren of fine-grained sediments and dominated by sands (Lamy, 2016), which may point to intensive winnowing by ocean currents impacting the deposition and burial of organic matter. Moderate concentrations of HBI trienes at the continental slope along the WAP (PS97/053, PS97/074, PS97/077) and in the Bransfield Strait likely refer to primary production associated with the retreating sea ice margin during spring and summer. This indicates seasonally ice-free waters in high production coastal areas influenced by upwelling (Gonçalves-Araujo et al., 2015) and feeding of the local food web (Schmidt et al., 2018). The similarity in the distribution of the HBI Z- and the E-triene in our surface sediments – the latter of which so far is not often considered for Southern Ocean paleoenvironmental studies – supports the assumption of a common diatom source for these HBIs (Belt et al., 2000, 2017).

We consider that degradation of biomarker lipids may affect their distribution within surface sediments. While laboratory studies on HBIs in solution point to a low reactivity of $IPSO_{25}$ towards auto- and photooxidative degradation (Rontani et al., 2014, 2011), a more recent investigation into Antarctic surface sediments shows that $IPSO_{25}$ may potentially be affected by partial autoxidative and bacterial degradation but oxidation products are found in only minor proportions (Rontani et al., 2019a). Since HBI trienes exhibit a generally higher sensitivity to degradation than the C_{25} HBI diene (Rontani et al., 2014, 2019b) - and this is supported by a recent observation of increasing $IPSO_{25}$/HBI triene ratios with increasing water depths in a polynya system off Eastern Antarctica (Rontani et al., 2019b) – their lower concentrations in the Bransfield Strait have to be considered with care. Vice versa, regarding maximum HBI triene concentrations and the absence of $IPSO_{25}$ in Drake Passage sediments, we conclude that the absence of the latter in these samples can be linked to the lack of sea ice (and not to the degradation of $IPSO_{25}$ as HBI trienes would have been removed first).

Distribution of sterols

Brassicasterol is present in all samples with concentrations ranging from 3.39 to 5017.44 µg g^{-1} TOC, while dinosterol was detected in 22 samples (0.0002-1983.75 µg g^{-1} TOC). It is noticeable that the concentrations of sterols exceed the concentrations of $IPSO_{25}$ and HBI trienes by more than two orders of magnitude. We observe higher concentrations of brassicasterol and dinosterol in the eastern part of the Drake Passage supporting an open marine source for these sterols. Surprisingly, elevated concentrations of brassicasterol are also found at stations PS97/048-1 and 049-2 in the Hero Fracture Zone, which may argue against a winnowing signal leading to lower accumulation of organic matter. We can only speculate if transport and deposition of reworked sediment containing brassicasterol via iceberg rafting could explain these higher values. In contrast to the observation made for HBI trienes, high sterol concentrations are found in the eastern and central Bransfield Strait (Figure 5.3d and e). Previously, elevated concentrations of steroidal components including brassicasterol and dinosterol in sediment cores from the Bransfield Strait have been interpreted to reflect a high productivity and significant inputs from diatoms and dinoflagellates (Brault and Simoneit, 1988). In a more recent overview, also Cárdenas et al. (2018) report peak concentrations of pigments, sterols and total organic carbon in the Bransfield Strait, which they relate to large seasonal phytoplankton blooms and higher accumulation rates. Dinosterol and, in particular, brassicasterol are known to have different source organisms including diatoms, dinoflagellates, cryptophytes, prymnesiophycean algae and cyanobacteria (Volkman, 1986) and we assume that this diversity accounts for the higher concentration of these lipids in Bransfield Strait sediments, while concentrations of HBI trienes, mainly derived from diatoms, are significantly lower. Regarding the potential input of brassicasterol from cryptophytes (Gladu et al., 1990; Goad et al., 1983), changes in the dominance of this phytoplankton group over diatoms have been reported for our study area and have been associated with a shallowing of the mixed layer and lower salinity due to intensified glacial ice-melting along the WAP (Mendes et al., 2013).

Similar to the observations made for HBIs, selective degradation may also affect the concentration of phytosterols within surface sediments. With respect to the preservation potential of terrigenous and marine derived sterols, Rontani et al. (2012) note an only weak effect of biotic and abiotic degradation of brassicasterol in Arctic Ocean shelf sediments – if this is also true for Southern Ocean shelf areas needs to be determined. In general, further investigations into degradation processes affecting both HBIs and phytosterols within (the same) sediment samples would address an important knowledge gap regarding in-situ biochemical modifications of the biomarker signal.

5.4.2. Comparison of satellite-derived modern sea ice conditions and biomarker data

The spring and winter sea ice concentrations are shown in Figure 5.4a and b. Winter sea ice is estimated to not extend north of 61° S (Figure 5.4b) and varies between 1 % and 50 % in the study area, while sea ice is reduced to less than 20 % in spring (Figure 5.4a). Sea ice concentrations of up to 50 % are common in winter between the South Shetland Islands and north of the Antarctic Sound where the influence of TWW is highest. Permanent sea ice cover is uncommon in the Bransfield Strait and around the WAP and this area is mainly characterized by a high sea ice seasonality, drift ice from the Weddell Sea (Collares et al., 2018) and a seasonally fluctuating sea ice margin.

Comparisons of $IPSO_{25}$ and winter sea ice concentrations derived from satellite data reveal a positive correlation ($r^2 = 0.53$). The strongest relationship is observed in the eastern Bransfield Strait where the influence of TWW is high. Correlations with spring sea ice ($r^2 = 0.27$) and other seasons are weak. As photosynthesis is not possible and a release of sea ice diatoms from melting sea ice is highly reduced during the Antarctic winter, the observation of a stronger correlation between recent winter sea ice concentrations and $IPSO_{25}$ is unexpected. We hence suggest that this offset may be

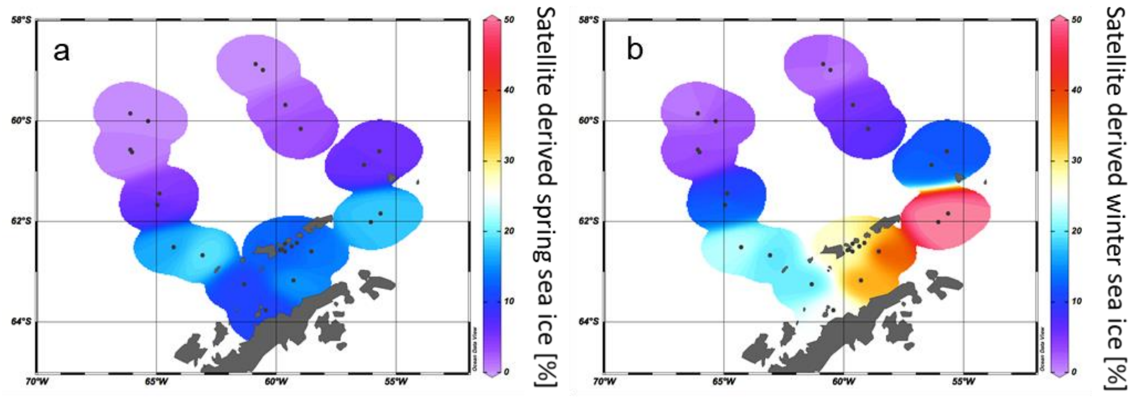

Figure 5.4 The satellite derived mean sea ice concentrations at each sampling station for a) spring and b) winter.

related to the fact that the sediment samples integrate a longer time interval than is covered by satellite observations. Radiocarbon dating of selected samples that contain calcareous material reveals an age of 100 years BP in the vicinity of the South Shetland Islands (station PS97/059-2) and 142 years BP at the Antarctic Sound (station PS1546-2, Table 5.1). A significantly older age was determined for a sample of *N. pachyderma* from station PS97/044-1 (4830 years BP) which likely denotes the winnowing and/or very low sedimentation rates in the Drake Passage. Bioturbation effects and uncertainties in reservoir ages potentially mask the ages of the near-coastal samples. Nevertheless, since also other published ages of surface sediments within the Bransfield Strait (Barbara et al., 2013; Barnard et al., 2014; Etourneau et al., 2013; Heroy et al., 2008) are in the range of 0-270 years, we consider that our surface samples likely reflect the paleoenvironmental conditions that prevailed during the last two centuries (and not just the last 35 years covered by satellite observations). In the context of the rapid warming during the last century (Vaughan et al., 2003) and the decrease of sea ice at the WAP (King, 2014; King and Harangozo, 1998), we suggest that the biomarker data of the surface sediments relate to a spring sea ice cover, which must have been enhanced compared to the recent (past 35 years) spring sea ice recorded via remote sensing. Presumably, the average spring sea ice conditions over the past 200 years might have been similar to the modern (past 35 years) winter conditions, which would explain the stronger correlation between $IPSO_{25}$ and winter sea ice concentrations. The absence of $IPSO_{25}$ at stations PS97/052 and PS97/053, off the continental slope, is in conflict with the satellite data depicting an average winter sea ice cover of 23 %. Earlier documentations that the $IPSO_{25}$ producing sea ice diatom *Berkeleya adeliensis* favors land-fast ice communities in East Antarctica and platelet ice occurring mainly in near-coastal areas (Belt et al., 2016; Riaux-Gobin and Poulin, 2004) could explain this mismatch between biomarker and satellite data, which further strengthens the hypothesis that the application of $IPSO_{25}$ seems to be confined to continental shelf or near-coastal and meltwater affected environments (Belt, 2018; Belt et al., 2016). Alternatively, strong ocean currents (i.e. the ACC) could have impacted the deposition of $IPSO_{25}$ in this region.

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

Table 5.1 Details of the radiocarbon dates and calibrated ages.

Sample Name	AWI-No.	Material	$F^{14}C$ ±error	Conventional ^{14}C age [a]	Calibrated age (cal) [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

5.4.3. Comparison of biomarker distributions and diatom-based sea ice estimates

The diatoms preserved in sediments from the study area can be associated with open ocean and sea ice conditions (Figure 5.5a-d). North of the South Shetland Islands, the strong influence of the ACC is reflected in the high abundance of open ocean diatom species such as *Fragilariopsis kerguelensis* and *Thalassiosira lentiginosa* (Esper et al., 2010). The two diatom species *Fragilariopsis curta* and *Fragilariopsis cylindrus* – known to not produce HBIs (Belt et al., 2016; Damsté et al., 2004) - mark the vicinity to sea ice (Buffen et al., 2007; Pike et al., 2008) and indicate fast and melting ice, a stable sea ice margin and stratification due to melting processes and the occurrence of seasonal sea ice. These observations are in accordance with previous diatom studies revealing a dominance of *Fragilariopsis kerguelensis* in the permanently open-ocean zone in the Drake Passage and an assemblage shift to more cold water adapted and sea ice-associated species in the seasonal sea ice zone of the Bransfield Strait (Cárdenas et al., 2019).

The high abundance of these sea ice diatoms in our samples is in good agreement with high and moderate IPSO$_{25}$ concentrations in the Bransfield Strait and around the South Shetland Islands, respectively. The only HBI source diatom identified is the HBI Z-triene producing *Rhizosolenia hebetata* (Belt et al., 2017), which is present in four samples in relatively small amounts which do not show a relation to the measured HBI Z-triene concentrations. The source diatom of IPSO$_{25}$ *Berkeleya adeliensis* was not observed (or preserved) in the samples, and we suggest that additional, hitherto unknown, producers for IPSO$_{25}$ as well as for the HBI trienes may exist.

We applied the transfer function of Esper and Gersonde (2014a) with four analogs (4an) to our samples to estimate winter sea ice concentrations (WSI; Figure 5.5e). The diatom approach shows a clear trend of high winter sea ice concentrations in the range of 78-91 % in the Bransfield Strait and low sea ice concentrations (between 6-39 %) north of the continental slope. The fact that diatom data propose sea ice in the Drake Passage may result from the high ages of surface sediments but also from drift, resuspension and sedimentation of diatom remains. Because of the absence of IPSO$_{25}$ in the Drake Passage the correlation of its concentrations with WSI is only weak ($r^2 = 0.29$).

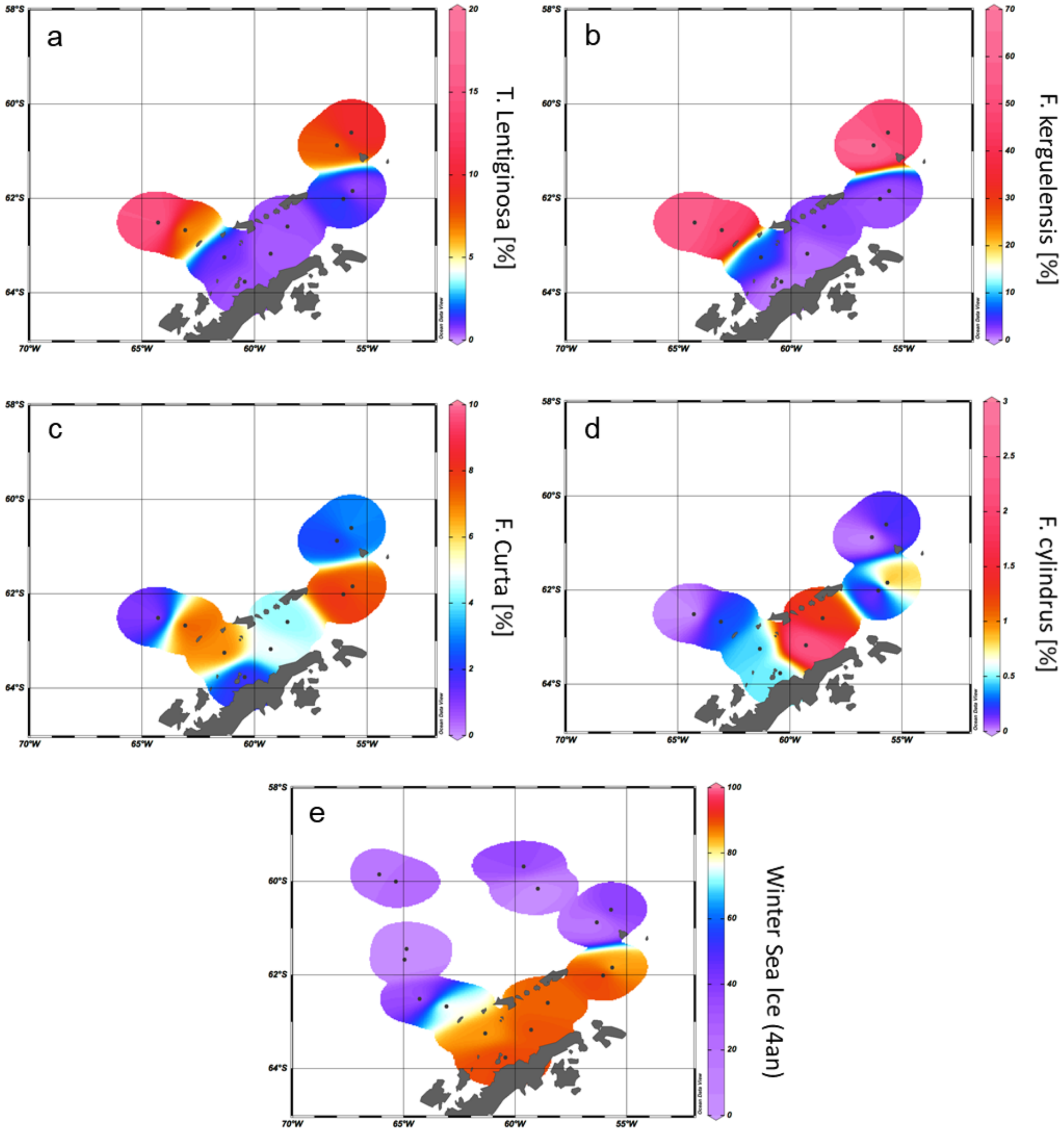

Figure 5.5 Distribution of the diatoms a) T. lentiginosa, b) F. kerguelensis, c) F. curta, and d) F. cylindrus in the study area (percentage per sample). The winter sea ice concentrations from the application of transfer function of Esper and Gersonde (2014a) are shown in e).

5.4.4. Testing a semi-quantitative sea ice approach for the Southern Ocean: PIPSO$_{25}$

Following the PIP$_{25}$-approach applied in the Arctic Ocean (Müller et al., 2011; Belt and Müller, 2013; Xiao et al., 2015), we used IPSO$_{25}$, HBI triene and sterol data to calculate the PIPSO$_{25}$ index. The main concept of combining the sea ice proxy with an indicator of an ice-free ocean environment (i.e. a phytoplankton biomarker; Müller et al., 2011), aims at a more detailed assessment of the sea ice conditions. By reducing the light penetration through the ice, a thick and perennial sea ice cover limits the productivity of bottom sea ice algae (Hancke et al., 2018) , which results in the absence of both sea ice and pelagic phytoplankton biomarker lipids in the underlying sediments. Vice versa, sediments from permanently ice-free ocean areas only lack the sea ice biomarker but contain variable concentrations of phytoplankton biomarkers (Müller et al., 2011). The co-occurrence of both biomarkers in a sediment sample suggests seasonal sea ice coverage promoting algal production indicative of sea ice as well as open ocean environments (Müller et al., 2011). Consideration of a phytoplankton biomarker alongside the sea ice proxy hence helps to avoid an underestimation of the past sea ice cover deduced from the absence of the sea ice proxy, which, in fact, may also be due to a permanent sea ice cover (Belt, 2018, 2019; Belt and Müller, 2013). Depending on the biomarker reflecting pelagic (open ocean) conditions, we here define P_ZIPSO_{25} (using the HBI Z-triene), P_EIPSO_{25} (using the HBI E-triene), P_BIPSO_{25} (using brassicasterol), and P_DIPSO_{25} (using dinosterol).

The $PIPSO_{25}$ values are 0 in the Drake Passage and increase to intermediate values at the South Shetland Islands and the continental slope and reach highest values in the Bransfield Strait (Figure 5.6a-d). Minimum $PIPSO_{25}$ values are supposed to refer to a predominantly ice-free oceanic environment in the Drake Passage, while moderate $PIPSO_{25}$ values mark the transition towards a marginal sea ice coverage at the continental slope and around the South Shetland Islands. Elevated $PIPSO_{25}$ values in samples from the northeastern Bransfield Strait suggest an increased sea ice cover (probably sustained through the drift of sea ice originating in the Weddell Sea). This pattern reflects the oceanographic conditions of a permanently ice-free ocean north of the South Shetland Islands and a seasonal sea ice zone at the WAP influenced by the Weddell Sea as described by Cárdenas et al. (2018). Both HBI triene-based $PIPSO_{25}$ indices show constantly high values at the coast of the WAP of >0.7 (P_ZIPSO_{25}) and >0.8 (P_EIPSO_{25}), respectively, and in the southern Bransfield Strait paralleling the southwest-northeast oriented Peninsula Front described by Sangrà et al. (2011). This front is

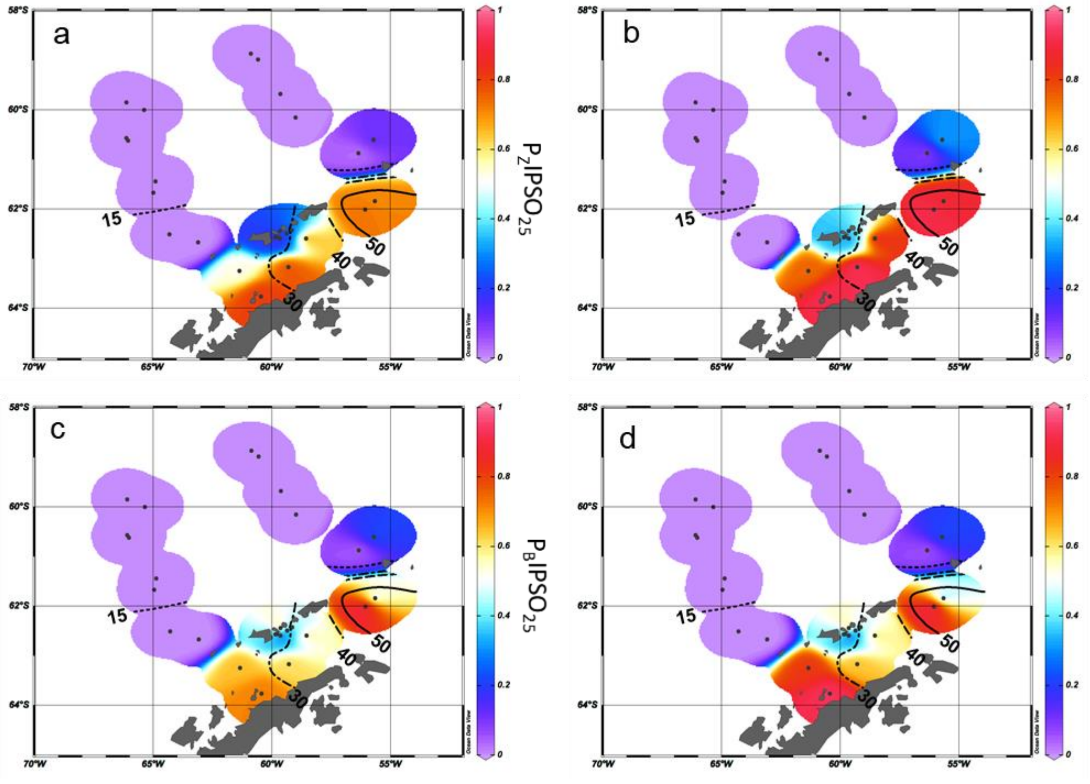

Figure 5.6 Distribution of a) P_ZIPSO_{25}, b) P_EIPSO_{25} , c) P_BIPSO_{25}, and d) P_DIPSO_{25} values in the study area. The extent of 15 %, 30 %, 40 % and 50 % satellite sea ice concentrations during winter is added as contour lines (see also Figure 3.4b).

reported to act as a barrier for phytoplankton communities (Gonçalves-Araujo et al., 2015) and is associated with the encounter between TWW carrying Weddell Sea sea ice through the Antarctic Sound and the TBW. The high $PIPSO_{25}$ values suggesting an extended sea ice cover west of the Peninsula Front (station PS97/054 and PS97/056) result from minimum concentrations of pelagic biomarkers and moderate concentrations of $IPSO_{25}$. $PIPSO_{25}$ values based on the HBI E-triene are about 0.2 higher compared to P_ZIPSO_{25}, due to the generally lower concentrations of the HBI E-triene.

The sterol-based $PIPSO_{25}$ values display a generally similar pattern as P_ZIPSO_{25} and P_EIPSO_{25}, respectively, and we note a high comparability between the P_EIPSO_{25} and P_BIPSO_{25} values ($r^2 = 0.73$). Some differences, however, are observed in the southwestern part of the Bransfield Strait (station PS97/056) where P_BIPSO_{25} indicates a lower sea ice cover and in the central Bransfield Strait (stations PS97/068 and PS97/069) where P_BIPSO_{25} and P_DIPSO_{25} point to only MIZ conditions. Regarding the modern sea ice conditions, the HBI triene-based $PIPSO_{25}$ indices hence seem to reflect the oceanographic conditions within the Bransfield Strait more satisfactorily. It has to be noted that the brassicasterol- or dinosterol-based $PIPSO_{25}$ index links environmental information derived from biomarker lipids belonging to different compound classes (i.e. HBIs and sterols), which have fundamentally different chemical properties. This requires special attention as, for example, selective degradation of one of the compounds may affect the sedimentary concentration of the respective lipids (Rontani et al., 2018b). Previous studies linking HBI and sterol-based sea ice reconstructions with satellite-derived or, with respect to downcore paleo studies, paleoclimatic data, however, demonstrate that the climatic/environmental conditions controlling the production of HBIs and sterols seem to exceed the influence of a potential preferential degradation of these biomarkers within the sediments (e.g., Berben et al., 2014; Cabedo-Sanz et al., 2013; Müller et al., 2009, 2012; Müller and Stein, 2014; Stein et al., 2017; Xiao et al., 2015). A comparison of PIP_{25} records determined using brassicasterol and the HBI Z-triene for three sediment cores from the Arctic realm covering the past up to 14.000 years BP (Belt et al., 2015) reveals very similar trends for both versions of the PIP_{25} index in each core, which may point to, at least, a similar degree of degradation of HBI trienes and sterols through time. More such studies are needed to evaluate the preservation potential of HBIs and sterols in Southern Ocean sediments, especially for down core paleo studies.

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

PART I

Comparison of $PIPSO_{25}$ with satellite sea ice data and diatom sea ice estimations

In the northeastern part of the study area, the HBI triene based $PIPSO_{25}$ indices align well with winter sea ice concentrations and depict the gradient from the marginally ice-covered southern Drake Passage towards the intensively ice-covered Weddell Sea. This is visualized with contour lines from the observed sea ice extent of 15 %, 30 %, 40 % and 50 % winter sea ice compared to the $PIPSO_{25}$ values in Figure 5.6a-d. In the southwestern part of the Bransfield Strait, all $PIPSO_{25}$ indices suggest a higher sea ice cover than it is reflected in the satellite data. This may be explained by the transport (and melt) of drift ice through the TWW, joining the TBW at the southwestern Peninsula Front and/or a higher sea ice cover in this area prior to the remote sensing observational period (and prior to the recent WAP warming).

Correlations of $PIPSO_{25}$ values with satellite-derived sea ice concentrations (for spring, summer, autumn and winter) contrast earlier observations made for the PIP_{25} index in the Arctic Ocean, where the closest linear relationship is found mainly with the spring sea ice coverage (i.e. the blooming season of sea ice algae; Müller et al., 2011; Xiao et al., 2015). We observe a remarkably low correlation between $PIPSO_{25}$ values and spring sea ice concentrations of less than 20 % with a coefficient of determination $r^2 = 0.37$ for P_ZIPSO_{25}, $r^2 = 0.50$ for P_EIPSO_{25} (Figure 5.7a), $r^2 = 0.31$ for P_BIPSO_{25}, and $r^2 = 0.34$ for P_DIPSO_{25} (Figure 5.7b). The highest correlation is observed between winter sea ice concentrations and P_EIPSO_{25} ($r^2 = 0.72$), and P_ZIPSO_{25} ($r^2 = 0.65$, Figure 5.7c) with a weaker correlation for the sterol-based $PIPSO_{25}$ values (P_BIPSO_{25}: $r^2 = 0.52$; P_DIPSO_{25}: $r^2 = 0.44$, Figure 5.7d). As discussed above, we attribute this seemingly conflicting result of a better agreement between biomarker data and winter (instead of spring) sea ice conditions to the offset in the time intervals reflected in satellite and sediment data. For the application of the $PIPSO_{25}$ approach, more aspects concerning the physical environmental conditions controlling the formation of platelet ice, which, at least at this state of research, is regarded as a main source of $IPSO_{25}$ (Belt et al., 2016) need to be considered. The formation and accumulation of platelet ice in supercooled waters below landfast sea ice or underneath an ice-shelf (e.g., Gough et al., 2012; Hoppmann et al., 2015) seem to limit the spatial occurrence of $IPSO_{25}$ and hence the applicability of $PIPSO_{25}$ to coastal environments. However, transport of supercooled waters away from the coast may lead to platelet ice formation (and colonization of *Berkeleya adeliensis*) in more distal areas (Hoppmann et al., 2015) and also the drift of sea ice (including the underlying platelet ice) may impact the distribution of $IPSO_{25}$ in Southern Ocean sediments and these processes require further investigations. Even though $PIPSO_{25}$ values show a stronger relationship to satellite sea ice concentrations than $IPSO_{25}$ concentrations more insight into the production and sedimentation of the involved biomarker lipids is needed to develop such a semi-quantitative approach.

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

A positive correlation is found between WSI concentrations derived from diatoms and the PIPSO$_{25}$ indices based on HBI trienes (P$_Z$IPSO$_{25}$ with r^2 = 0.76; P$_E$IPSO$_{25}$ with r^2 = 0.77, Figure 5.8a). The correlations of sterol-based PIPSO$_{25}$ values with WSI are slightly lower but in the same range (P$_B$IPSO$_{25}$ with r^2 = 0.74; P$_D$IPSO$_{25}$ with r^2 = 0.69, Figure 5.8b). A slightly weaker correlation is noted for diatom- and satellite-based winter sea ice concentrations (r^2 = 0.63; Figure 5.8c). Overall, the diatom approach indicates higher sea ice concentrations than the satellite data with an offset of up to 65 %. This may be due to different sources of satellite reference data used for the transfer function or also due to the fact that the sediment samples integrate a longer time period with a higher sea ice cover than the satellite data (see discussion in chapter 5.4.2). Regarding future sea ice reconstructions based on IPSO$_{25}$ and other biomarkers, we note that the

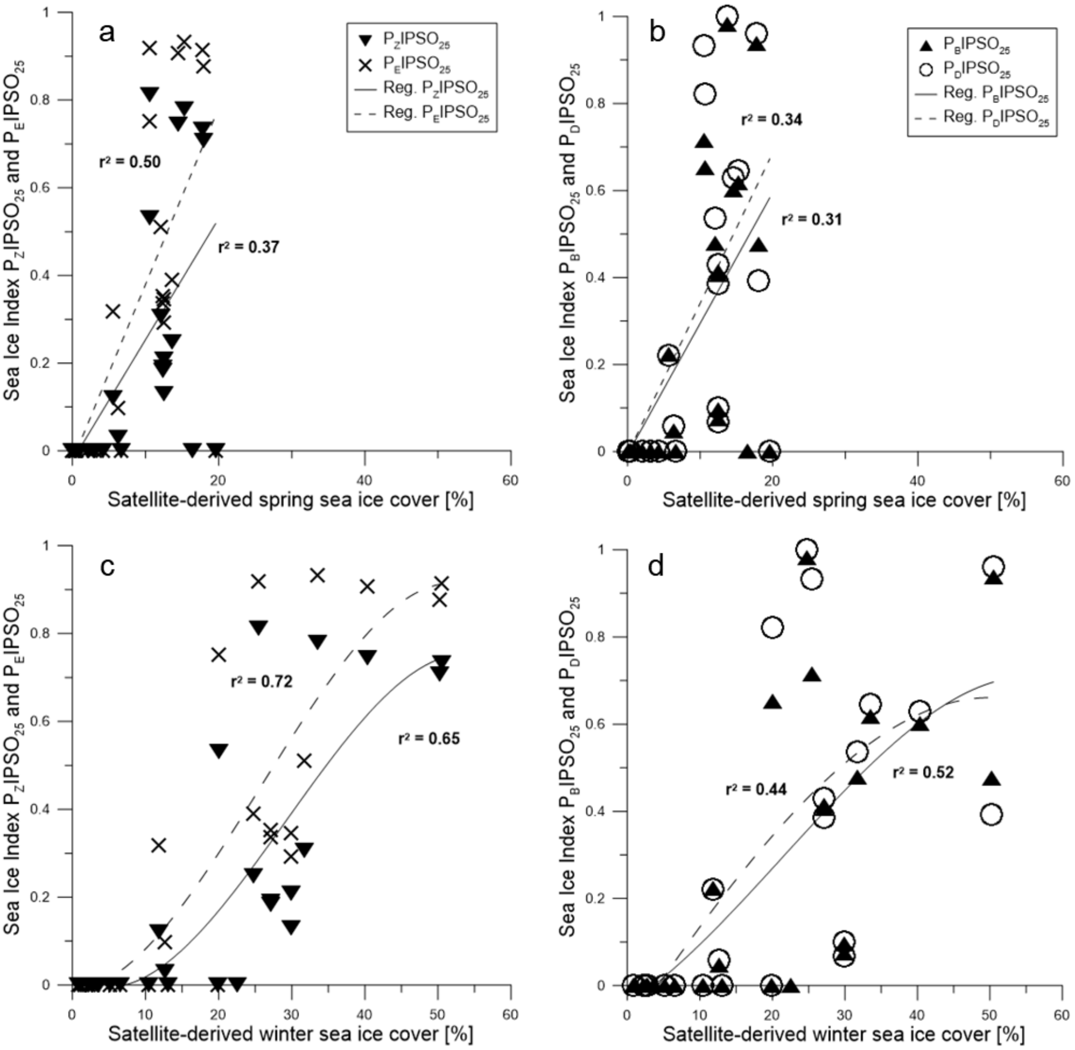

Figure 5.7 Scatter plots of satellite spring sea ice concentrations and a) P$_Z$IPSO$_{25}$ (triangles, solid regression line) and P$_E$IPSO$_{25}$ (crosses, dashed regression line) and b) P$_B$IPSO$_{25}$ (triangles, solid regression line) and P$_D$IPSO$_{25}$ (circles, dashed regression line). Scatter plots of satellite winter sea ice concentrations with c) P$_Z$IPSO$_{25}$ (triangles, solid regression line) and P$_E$IPSO$_{25}$ (crosses, dashed regression line) and d) P$_B$IPSO$_{25}$ (black triangles, solid regression line) and P$_D$IPSO$_{25}$ (circles, dashed regression line). All scatter plots were done with Grapher^{TM} 13.

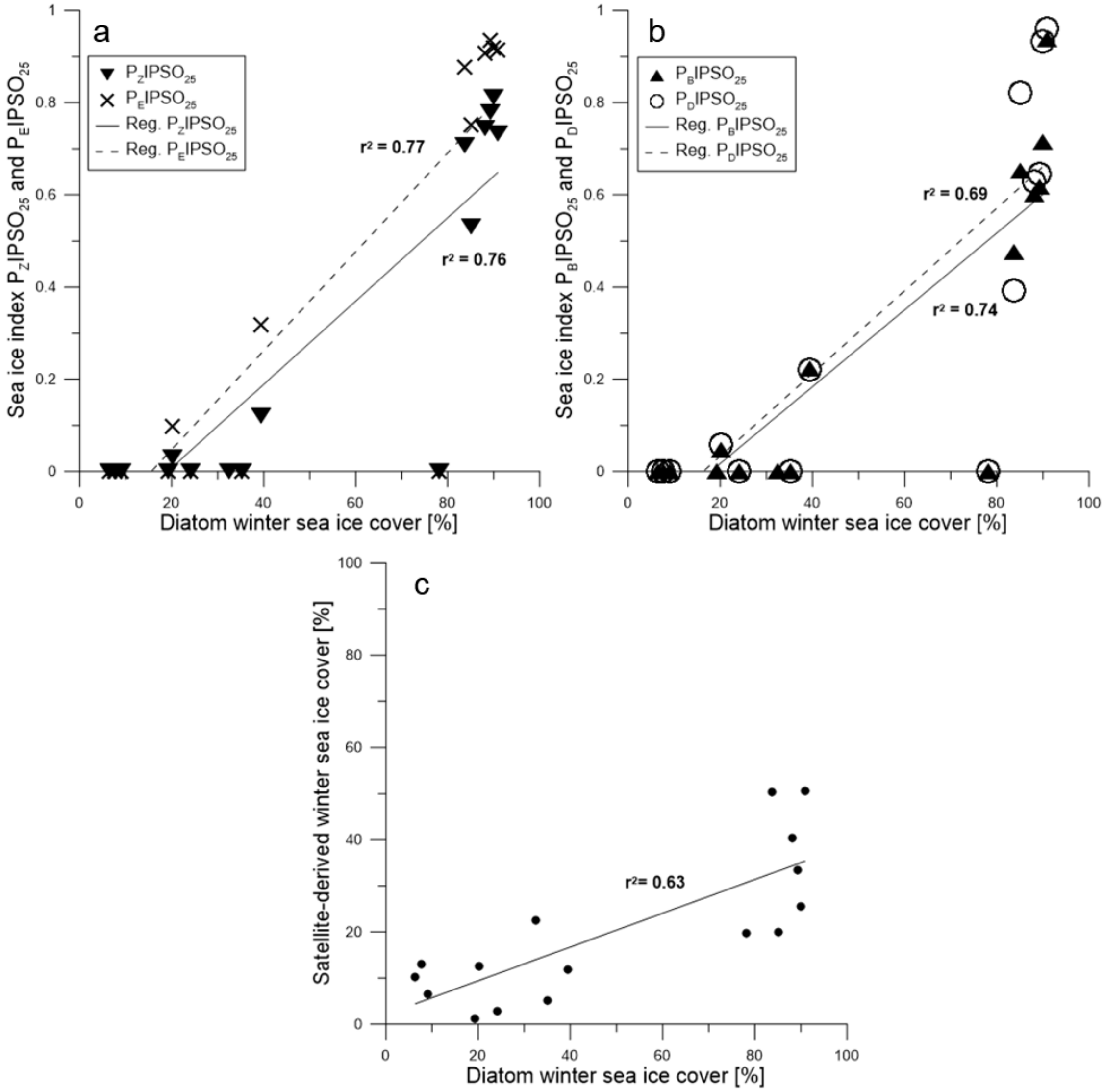

Figure 5.8 Scatter plots of a) P_ZIPSO_{25} (triangles, solid regression line) and P_EIPSO_{25} (crosses, dashed regression line) and b) P_BIPSO_{25} (triangles, solid regression line) and P_DIPSO_{25} (circles, dashed regression line) against diatom derived winter sea ice concentrations. c) Scatter plot of diatom transfer function winter sea ice concentrations and satellite winter sea ice concentrations.

simultaneous study of diatom assemblages provides valuable information on the sea surface conditions and may help to avoid misleading interpretation of the biomarker data (Belt, 2019). Vice versa, while diatom-based transfer functions mainly refer to winter sea ice concentrations, the $IPSO_{25}$ (and $PIPSO_{25}$) signal holds critical information on coastal spring/summer sea ice conditions, which are often crucial for ice-shelf (melting) processes. Pairing the micropaleontological and the biomarker approach hence provides for a more comprehensive reconstruction of Southern Ocean sea ice conditions.

5.5. Conclusions

The distribution of the sea ice biomarker $IPSO_{25}$, related HBI trienes and phytosterols as well as diatoms in a suite of surface sediments from the southern Drake Passage and the WAP reflects recent sea surface water characteristics reasonably well. While highest HBI triene concentrations are observed in the permanently open ocean zone of the Drake

Passage, they are significantly reduced in the seasonally ice-covered Bransfield Strait. This pattern is reversed for the sea ice proxy $IPSO_{25}$ and in accordance with previous surface sediment analyses revealing a preferential occurrence of this biomarker in near-coastal environments. The distribution of phytosterols points to a broader environmental significance of brassicasterol and dinosterol in terms of ocean temperature and sea ice tolerance, and/or nutrient availability. Following the PIP_{25} approach established for Arctic Ocean sea ice reconstructions, the herein proposed sea ice index $PIPSO_{25}$ indicates seasonal sea ice cover along the coast of the WAP and in the Bransfield Strait, whereas mainly ice-free conditions prevail in the Drake Passage. In general, this pattern is consistent with satellite-derived sea ice data and diatom-based sea ice estimates and we note that the $PIPSO_{25}$ index seems a potential approach towards semi-quantitative sea ice reconstructions in the Southern Ocean. The recent rapid warming in the study area, however, affects the comparability of proxy and satellite data. The fact that the surface sediments integrate a significantly longer time interval than the remote sensing data thwarts attempts to calibrate $PIPSO_{25}$ values against observed sea ice concentrations. Additional data from other circum-Antarctic coastal (and distal) environments and investigations into potential calibration methods are needed to further develop this approach. Importantly, more information is needed on the mechanisms of $IPSO_{25}$ and HBI triene synthesis, transport and preservation within sediments. Despite a generally good agreement between $PIPSO_{25}$-, diatom- and satellite-based sea ice distributions, we note that the basically different sea ice patterns and sea ice varieties in the Southern Ocean and accordingly different mechanisms controlling the $IPSO_{25}$ signal need to be considered carefully, when adapting a (not yet fully validated) semi-quantitative approach initially developed for the Arctic Ocean.

Data availability

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

Author contributions

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

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PART II

6. PART II: SEA ICE DYNAMICS AT THE WESTERN ANTARCTIC PENINSULA DURING THE INDUSTRIAL ERA: A MULTI-PROXY INTERCOMPARISON STUDY

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Abstract

In the last decades, changing climate conditions have had a severe impact on sea ice at the Western Antarctic Peninsula (WAP), an area rapidly transforming under global warming. To study the development of spring sea ice and environmental conditions in the pre-satellite era we investigated three short marine sediment cores for their biomarker inventory with particular focus on the sea ice proxy $IPSO_{25}$ and micropaleontological proxies. The core sites in the Bransfield Strait are located in shelf to deep basin areas characterized by a complex oceanographic frontal system, coastal influence and sensitivity to large-scale atmospheric circulation patterns. We analyzed geochemical bulk parameters, biomarkers (highly branched isoprenoids, glycerol dialkyl glycerol tetraethers, sterols), and diatom abundances and diversity over the past 200 years (^{210}Pb dating), and compared them to observational data, sedimentary and ice core climate archives as well as results from numerical models. Based on biomarkers we could identify four different stratigraphic units with (1) stable conditions and moderate sea ice cover before 1860, (2) low to moderate sea ice cover between 1860 and 1930, (3) high seasonal variability and changes in sea ice regimes from 1930 to 1990 and (4) a shift to increasing sea ice cover despite anthropogenic warming since 1990. Although $IPSO_{25}$ concentrations correspond quite well with satellite sea ice observations for the past 40 years, we note discrepancies between the biomarker-based sea ice estimates and the long-term model output for the past 200 years, ice core records and reconstructed atmospheric circulation patterns such as El Niño Southern Oscillation

(ENSO) and Southern Annular Mode (SAM). We propose that the sea ice biomarker proxies $IPSO_{25}$ and $PIPSO_{25}$ are not linearly related to sea ice cover and, additionally, each core site reflects specific, local environmental conditions. High $IPSO_{25}$ and $PIPSO_{25}$ values may not be directly interpreted as referring to high spring sea ice cover because variable sea ice conditions and enhanced nutrient supply may affect the production of both the sea-ice associated and phytoplankton-derived (open marine, pelagic) biomarker lipids. For a more meaningful interpretation we recommend to carefully consider individually biomarker records to distinguish between cold, sea ice favoring and warm, sea ice diminishing environmental conditions.

6.1. Introduction

Observations of global mean surface temperatures show a warming since the industrialization of approximately 1.0±0.2°C (IPCC, 2018) above the 1850-1900 baseline. An acceleration of this trend due to anthropogenic forcing has been projected (IPCC, 2019). The ocean, and especially the Southern Ocean, takes up the majority of the atmospheric heat, and warming has already been observed at all depths (IPCC, 2019). Antarctica´s hot spot of warming is the Western Antarctic Peninsula (WAP) (Jones et al., 2016) with atmospheric temperature increases of 3.7±1.6°C per century (Vaughan et al., 2003) and a slight cooling from 2000 to 2010 (Turner et al., 2019). A warming of up to 1°C of subsurface water is evident in different water masses around the WAP (Cook et al., 2016). On land, glaciers and ice shelves on both sides of the Antarctic Peninsula (AP) retreat rapidly (Cook et al., 2016; Rignot et al., 2019), pointing towards a potential collapse of the WAP ice shelves. In the ocean, the loss of sea ice cover is significant (Parkinson and Cavalieri, 2012). Shortened sea ice seasons (Parkinson, 2002) and a reduction of sea ice extent accelerating from 4 % up to 10 % per decade (Liu et al., 2004) have been observed via satellite since 1979. A recent compilation shows that the slight increase in sea ice around the entire Antarctic continent since 1979 seems to be interrupted since 2014 (Parkinson, 2019). However, the region of the WAP, the Bellingshausen Sea and Amundsen Sea show contrasting sea ice trends and high sea ice variability in 2014 and afterwards (Hobbs et al., 2016). The changes in sea ice cover are not only related to warm water intrusion and higher sea surface temperatures (SSTs) at the WAP (Martinson and McKee, 2012; Meredith and King, 2005), but also to large-scale modes of atmospheric circulation such as the Southern Annular Mode (SAM) (e.g. Barbara et al., 2013) and the El Niño Southern Oscillation (ENSO) (e.g. Liu et al., 2004), or a combination of both (Etourneau et al., 2013; Stammerjohn et al., 2008b, 2008a).

Sea ice is an important factor that shapes and influences the Southern Ocean. Melting sea ice releases nutrients and leads to enhanced primary production and ocean stratification during spring and summer (Arrigo et al., 1997; Vernet et al., 2008). Interestingly, a higher number of sea ice days is associated with to an increased photosynthetic efficiency and enhanced carbon fixation rates due to enhanced nutrient delivery stimulating primary production (Schofield et al., 2018) but also thinning of sea ice affects marine productivity positively (Hancke et al., 2018). Release of dense brine during sea ice formation influences the thermohaline circulation by feeding of deep and intermediate waters (Nicholls et al., 2009) but also induce upwelling at sea ice edges (Alexander and Niebauer, 1981). Sea ice cover also regulates the ocean-atmosphere exchange of heat and gases as well as regional precipitation and albedo (Allison et al., 1982; Butterworth and Miller, 2016; Turner et al., 2017) and is a potential source of the radiative-relevant volatile dimethylsulphide (Trevena and Jones, 2006) – a precursor of methanesulphonic acid (MSA) (Abram et al., 2010). Sea ice changes at the WAP may lead to the destabilization and/or collapse of local ice shelves due to warm water intrusions and basal melting (Cook et al., 2016; Etourneau et al., 2019; Hellmer et al.,

2012) promoting an accelerated ice-sheet flow towards the ocean (Huss and Farinotti, 2014). Sea ice decline in this region may thus also indirectly impact global sea level rise.

Atmospheric circulation patterns such as ENSO and SAM have been suggested to influence the distribution of SST and sea ice at the WAP (Ding et al., 2012; Stammerjohn et al., 2008b, 2008a). Etourneau et al. (2013) concluded from the occurrence of higher sea ice cover together with higher SSTs that a rising number of ENSO events would increase the seasonal amplitude of warmer summers and colder winters in the region. SAM is the leading mode in the Southern Hemisphere (Jones et al., 2016) and has significant impacts on temperatures at the northeast AP (Clem et al., 2016). Stammerjohn et al. (2008b) link ENSO and SAM related teleconnections to opposite sea ice trends in the Pacific and Atlantic sector of the Southern Ocean on decadal scales during the satellite era. The high-latitude responses and ice-atmosphere anomalies are strongest when a positive ENSO occurs “in-phase” with a negative SAM (+ENSO/-SAM) and the subtropical jet over the Pacific Ocean is strengthening whereas the polar frontal jet and the westerlies are weaker. In this state, a positive sea level pressure establishes a high-pressure cell in the Pacific Southern Ocean and warmer, moister conditions with less sea ice establish there. Meanwhile, the Weddell Sea and the WAP experience a cooling with an advance of sea ice. During the opposite state (-ENSO/+SAM) a stronger polar frontal jet establishes a low-pressure cell in the Bellingshausen Sea. In this case, increased, south-ward migrated westerlies transport heat towards the WAP and the Weddell Sea and sea ice cover is reduced under high atmospheric and sea surface temperatures (Marshall et al., 2006; Stammerjohn et al., 2008b; Yuan, 2004). Clem et al. (2016) describe that the combined effect of in-phase ENSO and SAM is strongest in spring.

For modelling past and future Antarctic climate, its ice sheet stability, the thermohaline circulation or the impacts of sea ice loss for ecosystems, data of past sea ice cover are crucial but barely available (Bracegirdle et al., 2015, 2019). For the WAP, insights into climate and sea-ice dynamics during the industrial era are available from ice cores (stable isotopes and marine aerosols) but information from high resolution marine sediments and in particular sedimentary, geochemical or diatom-based sea ice proxies remain sparse (Thomas et al., 2019). Sinking marine particles carry environmental information from the sea surface to the ocean floor and, when buried in the sediments, the environmental history including sea ice can be deduced from these marine climate archives. For sea ice reconstructions, the use of sea ice-associated diatom species and biogeochemical parameters are common (Crosta et al., 1998; Esper and Gersonde, 2014a; Gersonde and Zielinski, 2000). Since diatom frustules may be affected by the dissolution of biogenic opal in the photic zone (Ragueneau et al., 2000), on the ocean floor (Leventer, 1998) and in the sediments (Burckle and Cooke, 1983; Esper and Gersonde, 2014b), an increasing attention is directed to their molecular remains, i.e. specific biomarker lipids, as promising tools for past sea ice reconstructions (Massé et al., 2011). A specific diunsaturated highly branched isoprenoid alkene (HBI diene, $C_{25:2}$) has been proposed as potential tool for past spring sea ice reconstructions in the Southern Ocean (Massé et al., 2011). It is produced by sea ice diatoms (Nichols et al., 1988) and its sea ice origin is evident from the high $\delta^{13}C$ isotopic signature of the molecule (Massé et al., 2011; Sinninghe Damsté et al., 2007; Vorrath et al., 2019). The sea ice diatom *Berkeleya adeliensis* which is found in Antarctic landfast ice and platelet ice (Riaux-Gobin and Poulin, 2004) was identified as a producer of the HBI diene (Belt et al., 2016). HBI diene is present in surface and downcore sediments around Antarctica and can be used as $IPSO_{25}$ (**I**ce **P**roxy for the **S**outhern **O**cean with **25** carbon atoms) in analogy to the Arctic IP_{25} (Belt et al., 2016; Lamping et al., 2020; Massé et al., 2011; Vorrath et al., 2019). To differentiate among an extended spring sea ice cover, the occurrence of a stable sea ice margin and/or an open marine environment, $IPSO_{25}$ is combined with phytoplankton-derived biomarker from lipids such as HBI trienes and/or sterols, which are assumed to refer to open water conditions (Belt and Müller, 2013; Volkman, 1986). Analogous to the PIP_{25} index (P stands for open marine phytoplankton marker) for semi-quantitative sea ice estimations in the Arctic (Müller et al., 2011), the recently proposed $PIPSO_{25}$ approach (Vorrath et al., 2019) allows for a differentiation between several sea ice conditions of a permanently open ocean, a sea ice marginal zone and a permanent sea ice cover (Müller et al., 2011).

Here, we provide the first $IPSO_{25}$-based high-resolution assessment of the spring sea ice development at the WAP during the industrial era and examine the response of sea ice to changes in atmospheric and oceanic oscillation patterns. To achieve this, we conducted a multiproxy study on three short sediment cores from different depths and oceanic regimes within the Bransfield Strait. In addition to $IPSO_{25}$, we analyzed HBI trienes, sterols and glycerol dialkyl glycerol tetraethers (GDGTs) for subsurface ocean temperature (SOT) reconstruction as well as diatom assemblages for estimating winter sea ice concentrations (WSI) and summer sea surface temperatures (SSST) by means of transfer functions. We furthermore consider sea ice and temperature data from an atmosphere-sea ice-ocean numerical model (AWI-ESM2), historical surface air temperatures from local meteorological stations, ice core records (stable isotopes $\delta^{18}O$ and δD, MSA), and paleo records of atmospheric circulation patterns such as ENSO and SAM.

6.2. Material and Methods

6.2.1. Study Area

The study area is the Bransfield Strait at the northern tip of the WAP (Figure 6.1a and b). The region includes the shallow shelf of the WAP as well as the Bransfield Basin with depths exceeding 2000 m at its deepest parts. The Bransfield Basin is located between the South Shetland Islands (SSI) to the northwest and the AP to the southeast. The shallow ocean has been shaped by ice sheet dynamics during the last glaciation (Canals

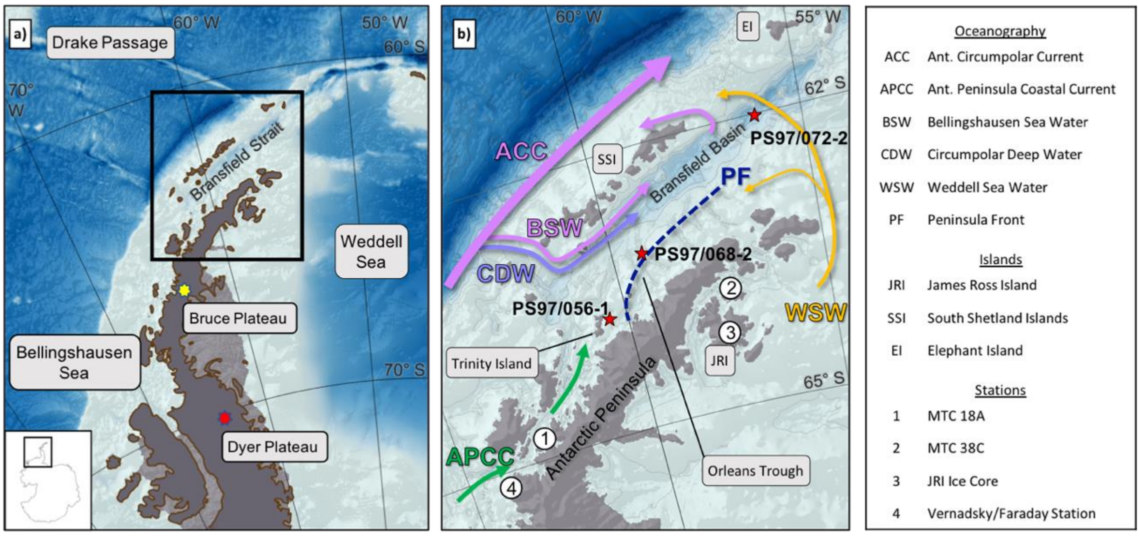


Figure 6.1 a) Overview map of the Antarctic Peninsula with the position of the Dyer Plateau (Abram et al., 2010), Bruce Plateau (Goodwin et al., 2016) and bathymetric features in the Bellingshausen Sea, the Weddell Sea and the Drake Passage. b) Oceanographic setting in the study area (modified after Hofmann et al., 1996; Moffat and Meredith, 2018; Sangrà et al., 2011), sediment and ice core locations and geographic locations mentioned in the text. Maps were generated with QGIS 3.0 (2018) and the bathymetry was taken from GEBCO_14 from 2015.

and Amblas, 2016b; Ingólfsson et al., 2003) and several troughs discharge sediment load from the AP into the basin (Canals et al., 2016; Canals and Amblas, 2016a). The oceanographic setting in this area is complex and yet not fully constrained (Moffat and Meredith, 2018; Sangrà et al., 2011) because water masses enter the basin from the west and east (Figure 6.1b). From the east, relatively cold (< 0°C) and salty Weddell Sea Water (WSW) flows at the surface alongshore the Antarctic mainland as a coastal current but also fills the Bransfield Basin completely below 150 m. It is also observed on the northern slope of the SSI at 200-600 m depth and around Elephant Island as a result of wind driven modulation (Meijers et al., 2016). The main source from the west is the Bellingshausen Sea Water (BSW), a branch of the Antarctic Circumpolar Current (ACC). This well-stratified, fresh and warm surface water flows along the slope of the SSI and forms the Peninsula Front with the WSW in the central Bransfield Strait, trending southwest-northeast parallel to the Antarctic mainland (Sangrà et al., 2011). Additionally, Circumpolar Deep Water (CDW) enters from the southwest as a subsurface current, forming the Bransfield Front to the BSW at 200m to 550m depth along the SSI slope (Sangrà et al., 2017). Both BSW and CDW are observed to turn and flow back at the northern side of the SSI (Sangrà et al., 2011). The mixing and transformation of the three water masses in the Bransfield Strait is yet not well understood but a study of iceberg drifts from Collares et al. (2018) showed that water from the Weddell Sea join waters from the Bellingshausen Sea in the vicinity of Trinity Island (Figure 6.1b). It has been suggested that eddies between the Peninsula Front and the Bransfield Front are a key mechanism for water exchange and/or upwelling (Sangrà et al., 2011; Zhou et al., 2002) and meltwater discharge from the adjacent glaciers has to be considered (Meredith et al., 2018). In the southwest, south of the Bransfield Strait, a narrow, fast flowing Antarctic Peninsula Coastal Current (APCC) is present, enriched in glacial freshwater and characterized by downwelling (Moffat and Meredith, 2018).

Primary productivity at the WAP is mainly controlled by eddies and fronts (Gonçalves-Araujo et al., 2015), due to upwelling (Sangrà et al., 2011), sea ice dynamics (Vernet et al., 2008) and iron distribution (Klunder et al., 2014). High productivity regimes and high chlorophyll concentrations are found north of the Peninsula Front along the SSI under the influence of the BSW, while the area influenced by the WSW is characterized by lower production of nanoplankton (Gonçalves-Araujo et al., 2015). Upwelling, iron fertilization and sea-ice retreat lead to high interannual variability in the production patterns and a strong onshore-offshore gradient is evident. In consequence high production is related to coastal areas, shallow mixed layers and higher stratification owing to sea ice melting (Sanchez et al., 2019; Vernet et al., 2008). High production is also reflected in high vertical export of sinking particles (e.g. Wefer et al., 1988; Kim et al., 2004) and in the biogeochemical distribution of surface sediments, dominated by high concentrations of TOC, pigments, sterols and diatoms but low calcium carbonate (Cárdenas et al., 2019). Organic matter is mainly of marine origin as supported by low values of C/N and the stable carbon isotope composition (Cárdenas et al., 2019) whereas the AP is an important source of terrestrial silt and clay input (Wu et al., 2019).

6.2.2. Sampling and age model

The cores were collected in 2016 during the RV *Polarstern* cruise PS97 (ANT-XXXI/3) using multicorers at stations PS97/056-1 (63°45.42’S, 60°26.51’W, 633 m water depth) east of Trinity Island, PS97/068-2 (63°10.05’S, 59°18.12’W, 794 m water depth) in the Orleans Trough, and PS97/072-2 (62°00.39’S, 56°03.88’W, 1992 m water depth) in the East Bransfield Basin (Figure 6.1b). Smear slides were examined and microscopic description of the surface sediments was done onboard (Lamy, 2016). Immediately after recovery of the sediments were sectioned in 1 cm slices and samples designated for biomarker analyses were stored frozen in glass vials, while separate samples for micropaleontological investigation were stored at 4° C in plastic bags. A second suite of samples from a trigger core from station PS97/072-1 was used for total organic carbon (TOC) and diatom analyses (diatom samples from core PS97/072-2 were not available).

Geochronology for the sediment cores from sites PS97/056-1 and PS97/072-2 was established using $^{210}Pb_{xs}$ activities quantified by alpha spectrometry of its daughter ^{210}Po in secular equilibrium with ^{210}Pb and using ^{209}Po as a yield tracer (Flynn, 1968). The activities were corrected to the time of plating considering the ^{210}Po decay (half life: 138 days). $^{210}Pb_{xs}$ (unsupported) activities were determined as the difference between ^{210}Pb and ^{226}Ra activities measured by gamma spectrometry in some intervals of the sediment core. Alpha and gamma counting were performed at the Laboratoire Géosciences of the Université de Montpellier (France). The ages were based on $^{210}Pb_{xs}$ inventories according the Constant Rate of Supply Model (CRS, Appleby and Oldfield, 1978). Standard deviations (SD) were estimated propagating the counting uncertainties (Bevington et al., 1993). Since the dating on core PS97/056-1 and PS97/072-2 was done on selected samples the age model was established using the software R (R Core Team, 2017) and the package clam (Blaauw, 2010, version 2.3.2, calibration curve Marine13.14C). Trigger core PS97/072-1 was correlated to the age model of core PS97/072-2 based on TOC data.

$^{210}Pb_{xs}$ for core PS97/068-2 was measured at the Alfred Wegener Institute (AWI, Germany) on dried and ground bulk sediment samples in sealed gas-tight petri dishes, using a HPGe gamma spectrometer with planar geometry. ^{210}Pb was measured at 46 keV, ^{226}Ra for the excess correction in each depth interval via its indirect decay products at 295, 352 and 609 keV. Analytical errors were calculated considering error propagation. For core PS97/068-2 the calculation of CRS ages and the Monte-Carlo approximation of age uncertainties was based on Sanchez-Cabeza et al. (2014), modified to accommodate the variable sample sizes and fractions for different depths. Due to residual inventory of $^{210}Pb_{xs}$ below the available samples in cores PS97/056-1 and PS97/072-2, the CRS model had increasing uncertainties below ~130 years (Figure Appendix 3). We therefore extrapolated ages before 1880 based on the average respective sedimentation rates for the oldest 3 cm.

6.2.3. Organic geochemical analyses

Organic geochemical analyses were done on freeze-dried and homogenized sediments. Bulk content of carbon (C) and nitrogen (N) were determined with a CNS analyzer (Elementar Vario EL III, standard error < 2%), whereas the analysis of TOC content was done on 0.1 g acidified (500 µl hydrochloric acid) sediment using a carbon-sulphur determinator (CS-2000, ELTRA, standard error < 0.6 %). The C/N ratio was calculated as TOC/total nitrogen.

The extraction procedure of HBIs follows the analytical protocol of the international community conducting HBI-based sea ice reconstructions (Belt et al., 2013, 2014; Stein et al., 2012). For the quantification of biomarkers the internal standards 7-hexylnonadecane (7-HND), 5α-androstan-3β-ol and C_{46} were added to the sediments. Sediment samples of 5 g were extracted ultrasonically three times using 6 ml of CH_2Cl_2:MeOH (v/v 2:1, 15 min) followed by centrifugation (2500 rpm, 1 min) and decantation of the total organic solvent extract. The different biomarkers were separated via open column chromatography with silica gel used as a stationary phase. First, the apolar fraction containing HBIs was separated with 5 ml hexane, while the second polar fraction containing GDGTs and sterols was eluted with 5 ml CH_2Cl_2:MeOH (v/v 1:1). The polar fraction (GDGT and sterols) was dried using nitrogen, re-dissolved in 120 µl hexane:isopropanol (v/v 99:1) and filtered through a polytetrafluoroethylene filter (0.45

µm in diameter). After measuring GDGTs, the polar fraction was silylated (200 µl BSTFA; 60° C; 2 hours) and used for sterol analysis.

The HBIs and sterols were analyzed by GC-MS with an Agilent 7890B gas chromatograph equipped with a 30 m DB 1 MS column (0.25 mm diameter, 0.250 µm film thickness) and coupled to an Agilent 5977B mass spectrometer (MSD, 70 eV constant ionization potential, ion source temperature 230° C). Apolar and polar lipid fractions were analyzed using different temperature programs. For HBIs, the temperature was held at 60° C for 3 min, ramped to 325° C over 23 min, and was held at this level for 16min. Sterol analysis started at a temperature of 60° C for 2 min, followed by a temperature increase to 150° C over 6 min, and to 325° C within 57 min. HBIs were identified via comparison of mass spectra of the measured compounds and published mass spectra (Belt et al., 2000). Quantification of HBIs was based on manual peak integration. Instrumental response factors of molecular ions of HBI diene (*m/z* 348) und trienes (*m/z* 346) were determined by means of calibration measurements using a sample with known concentrations of HBIs. Identification of sterols was based on comparison of their retention times and mass spectra with those of reference compounds analyzed on the same instrument. The mean relative error of duplicates was < 5% for HBIs and < 1% for sterols (desmosterol had exceptional high relative errors of up to 14%), the detection limit was determined at 0.5 ng/g sediment. Co-elution of other compounds hampered identification and quantification of sterols in several samples (PS97/056-1; 0-13cm and PS97/072-2; 0-16cm).

GDGTs were analyzed using high performance liquid chromatography (HPLC, Agilent 1200 series HPLC system) coupled to a single quadrupole mass spectrometer (MS, Agilent 6120 MSD) via an atmospheric pressure chemical ionization (APCI) interface. Individual GDGTs were separated at 30° C on a Prevail Cyano column (150 mm x 2.1 mm, 3 µm). Each sample was injected (20 µl) and passed a 5 min isocratic elution with mobile phase A (hexane/2-propanol/chloroform; 98:1:1) at a flow rate of 0.2 ml/min. The mobile phase B (hexane/2-propanol/chloroform; 89:10:1) increased linearly to 10% within 20 min and after this to 100% within 10 min. After 7 min the column was cleaned with a backflush (5 min, flow 0.6 ml/min) and re-equilibrated with solvent A (10 min, flow 0.2 ml/min). The APCI had the following conditions: nebulizer pressure 50 psi, vaporizer temperature 350°C, N_2 drying gas temperature 350°C, flow 5 l/min, capillary voltage 4 kV, and corona current 5 µA. GDGT detection was done by selective ion monitoring (SIM) of $(M+H)^+$ ions (dwell time 76ms). The molecular ions *m/z* of GDGTs-I (*m/z* 1300), GDGTs-II (*m/z* 1298), GDGTs-III (*m/z* 1296), and Crenarchaeol (*m/z* 1292) as well as of the branched GDGTs-Ia (*m/z* 1022), GDGTs-IIa (*m/z* 1036), GDGTs-IIIa (*m/z* 1050) and hydroxylated GDGTs OH-GDGT-0 (*m/z* 1318), OH-GDGT-1 (*m/z* 1316), and OH-GDGT-2 (*m/z* 1314) were quantified in relation to the internal standard C_{46} (*m/z* 744). The hydroxylated GDGTs quantified in the scans of their related GDGTs (see Fietz et al., 2013). The standard deviation was 0.01 units of TEX^L_{86}.

We follow Kalanetra et al. (2009), proposing that GDGT-derived temperatures represent near-surface waters which is underlined by studies from Kim et al. (2012) and Park et al. (2019) and consider our results to reflect subsurface ocean temperatures (SOT). For calculation of TEX^L_{86} (Kim et al., 2010) only GDGTs with the *m/z* 1296 (GDGT-3), *m/z* 1298 (GDGT-2), *m/z* 1300 (GDGT-1) were considered:

$$TEX^L_{86} = \log\left(\frac{[GDGT-2]}{[GDGT-1]+[GDGT-2]+[GDGT-3]}\right) \tag{1}$$

and calibrated it with $SOT^{TEX} = 67.5 \times TEX^L_{86} + 46.9$ (Kim et al., 2010). (2)

The calculation based on OH-GDGT was done after Lü et al. (2015)

$$RI-OH' = \frac{[OH-GDGT-1]+2\times[OH-GDGT-2]}{[OH-GDGT-0]+[OH-GDGT-1]+[OH-GDGT-2]} \quad (3)$$

and calibrated with SOT^{OH} = (RI-OH' - 0.1) / 0.0382. (4)

To determine the influence of terrestrial organic matter the BIT index was calculated following Hopmanns et al. (2004) as

$$BIT = \frac{[GDGT-Ia]+[GDGT-IIa]+[GDGT-IIIa]}{[Crenarchaeol]+[GDGT-Ia]+[GDGT-IIa]+[GDGT-IIIa]}. \quad (5)$$

The phytoplankton-$IPSO_{25}$ index ($PIPSO_{25}$) was calculated following Vorrath et al. (2019) with

$$PIPSO_{25} = \frac{IPSO_{25}}{IPSO_{25}+(c\times phytoplankton\ marker)} \quad (6)$$

using sterols and HBI trienes as phytoplankton marker (Vorrath et al., 2019). The balance factor c (c = mean $IPSO_{25}$ / mean phytoplankton biomarker) is used to account for concentration offsets between $IPSO_{25}$ and phytoplankton biomarkers (Belt and Müller, 2013; Müller et al., 2011; Smik et al., 2016b; Vorrath et al., 2019). Since the concentrations of HBI trienes are within the same range as the sea ice proxy we set the c-factor to 1 (Smik et al., 2016b) and c-factors for sterols were calculated individually for every core site. To distinguish the different indices based on their phytoplankton marker we use the terms P_ZIPSO_{25} for an index based on Z-trienes, P_EIPSO_{25} based on E-trienes, P_BIPSO_{25} based on bassicasterol, and P_DIPSO_{25} based on dinosterol.

6.2.4. Diatom analysis and transfer function

Diatom analyses were done on cores PS97/056-1, PS97/068-2 and the trigger core from the core site of PS97/072-1 (correlated with PS97/072-2 via TOC content). About 300 mg of freeze-dried sediments were treated after the method described by Cárdenas et al. (2018) to prepare slides for microscopy analysis. Two permanent slides per sample were prepared and observed with a Carl Zeiss Axio Lab.1 microscope with phase contrast at 1000× magnification at the Instituto Antártico Chileno in Punta Arenas. Diatoms were identified and counted on transects on microslides until reaching at least 400 valves on each slide, following counting procedures of Schrader and Gersonde (1978). Diatom identification was done to species or species group level following the taxonomy described by Armand and Zielinski (2001), Taylor et al. (2001), Crosta et al. (2004), Buffen et al. (2007), Cefarelli et al. (2010), Esper et al. (2010), Allen (2014), and Campagne et al. (2016). The Hyalochaete of the genus *Chaetoceros* were identified as vegetative cells and/or resting spores.

We applied the marine diatom transfer function TF MAT-D274/28/4an to estimate winter sea ice (WSI) concentrations. It comprises 274 reference samples with 28 diatom taxa and/or taxonomic groups and an average of 4 analogues from surface sediments in the Atlantic, Pacific, and western Indian sectors of the Southern Ocean(Esper and Gersonde, 2014a). Winter sea ice (WSI) estimates reflect September sea-ice concentrations averaged over the period from 1981-2010 (National Oceanic and Atmospheric Administrations, NOAA; Reynolds et al., 2002, 2007) in a 1 by 1 grid. We follow the approach of Zwally et al. (2002) and define a sea ice concentration of 15% as the threshold for presence or absence of sea ice and 40% as the representative average of sea-ice edge (Gersonde et al., 2005; Gloersen et al., 1993). For summer sea surface temperature (SSST), we used the transfer function TF IKM336/29/3q from 336 reference samples (Pacific, Atlantic and Indian Southern Ocean) with 29 diatom taxa and three factors (Esper and Gersonde, 2014b). For calculations of MAT and IKM the software R (R Core Team, 2017) was used with the packages Vegan (Oksanen et al., 2012) and Analogue (Simpson and Oksanen, 2012).

6.2.5. Modelled data

We used data from numerical modelling to compare and evaluate our biogeochemical analyses. The AWI-ESM2 is a state-of-the-art coupled climate model developed at AWI (Sidorenko et al., 2019). The model consists of the atmospheric model ECHAM6 (Stevens et al., 2013) and the finite element sea ice-ocean model (FESOM2) (Danilov et al., 2017). The model also includes a Land-Surface Model (JSBACH) with dynamical vegetation (Raddatz et al., 2007).

The atmosphere grid in the high-resolution experiment is T63 (about 1.9 degree) with 47 vertical levels. A multi-resolution approach is employed in the ocean module. In detail, the high-resolution experiment applies up to 20 km horizontal resolution over the Arctic region and 150 km for the far field ocean (Figure Appendix 4). Moreover, the tropical belt has a refined resolution of 30-50 km in this configuration. There are 46 uneven vertical depths in the ocean component. The model has been validated under modern climate condition (Sidorenko et al., 2019). Previous versions of the model have been applied for the Holocene (Shi et al., 2020; Shi and Lohmann, 2016).

We run the climate model from the Mid-Holocene as a starting point (*midHolocene* simulation), and performed a transient simulation from the Mid-Holocene to the pre-industrial (*past6k* simulation) along the recipe as described in Otto-Bliesner et al. (2017). The transient orbital parameters are calculated according to Berger (1978). Moreover, as the change of topography from mid-Holocene to present is minor, we use constant topography under pre-industrial conditions for the entire transient period. In our modeling strategy, we follow Lorenz and Lohmann (2004) and use the climate condition from the pre-industrial state as spinup and initial state for the transient simulation covering the period 1850-2017 CE. Greenhouse gases concentrations are taken from the ice core records (Köhler et al., 2017) and from Meinshausen et al. (2011).

6.2.6. Additional data sets

Regional monthly satellite sea ice concentrations were derived from Nimbus-7 SMMR and DMSP SSM/I-SSMIS passive microwave data from the National Snow and Ice Data Center (NSIDC, grid cell size 25x25 km, Cavalieri et al., 1996) and mean winter (JJA) and spring (SON) sea ice concentrations were used in this study.

For the large-scale atmospheric modes we used the paleo ENSO index from Li et al. (2013) and the modelled SAM data from Abram et al. (2014). After Stammerjohn et al. (2008b), years with positive ENSO and negative SAM indices cause higher sea ice cover at the WAP and years with a negative ENSO and positive SAM lead to warmer seasons with reduced sea ice cover.

We used ice core stable isotope data representing relative air temperature at James Ross Island (δD, Abram et al., 2013) and at Bruce Plateau ($\delta^{18}O$, Goodwin et al., 2016). We compared the marine sea ice proxies (biomarkers, diatoms) with MSA data from coastal West Antarctic Dyer Plateau ice core (Abram et al., 2010).

6.3. Results

6.3.1. Age model and core description

The ^{210}Pb signals indicated continuously increasing ages with depth in all sediment cores (Figure 6.2). All sediment cores roughly cover the last 240 years (including the extrapolated time) with resolution between 2 and 12 years per centimeter and sedimentation rates from 0.1 to 0.5 cm/a. Core PS97/056-1 located east of Trinity Island is characterized by silt-bearing diatomaceous clay (Lamy, 2016) and covers the timespan from 1830 to 2006 CE with sedimentation rates increasing from 0.1 to 0.4 cm/a over time. Core PS97/068-2 from Orleans Trough consists mainly of diatom-bearing silty clay

(Lamy, 2016) and spans from 1780 to 2007 CE with sedimentation rates from 0.1 to 0.5 cm/a. Sediment core PS97/072-2 from the East Bransfield Basin is the deepest record characterized as silt-bearing diatomaceous clay (Lamy, 2016) with increasing sedimentation rates (from 0.1 to 0.4 cm/a) covering the time from 1823 to 2000 CE. The TOC contents of all cores ranged between 0.7 and 1.1 wt%. Low C/N ratios (< 8.6) and BIT values (< 0.02) point to a marine origin of the organic matter.

6.3.2. Biomarker lipids

A summary of biomarker results that will be discussed in detail is visualized in Figure 6.3 (results of HBI E-trienes, sterols and their related sea ice indices can be found in Figure Appendix 5). All biomarker records show an overall increasing trend towards the present with a few exceptional peaks along the record. $IPSO_{25}$ is abundant at all core sites with values ranging from 0.2 µg g^{-1} TOC up to 6.4 µg g^{-1} TOC. All three cores display similar patterns with low values before 1850 CE followed by moderate concentrations until 1970 CE and maxima in the 2000s (Figure 6.3). Concentrations of HBI trienes are much lower than $IPSO_{25}$ concentrations with values below 1.4 µg g^{-1} TOC for Z-trienes (Figure 6.3) and below 0.7 µg g^{-1} TOC for E-trienes (Figure Appendix 5). The exception is core PS97/072-2 from of the East Bransfield Basin where both HBI trienes reach up to 3.7 µg g^{-1} TOC and 1.6 µg g^{-1} TOC, respectively, in the second half of the 19th century. The concentrations of brassicasterol (10.2–241.3 µg g^{-1} TOC) and dinosterol (5.0–145.2 µg g^{-1} TOC) are two to three magnitudes higher than the HBIs; markedly lower concentrations characterize the Orleans Trough (PS97/068-2) (Figure Appendix 5). The $PIPSO_{25}$ indices calculated with Z- and E-trienes run parallel to $PIPSO_{25}$ based on

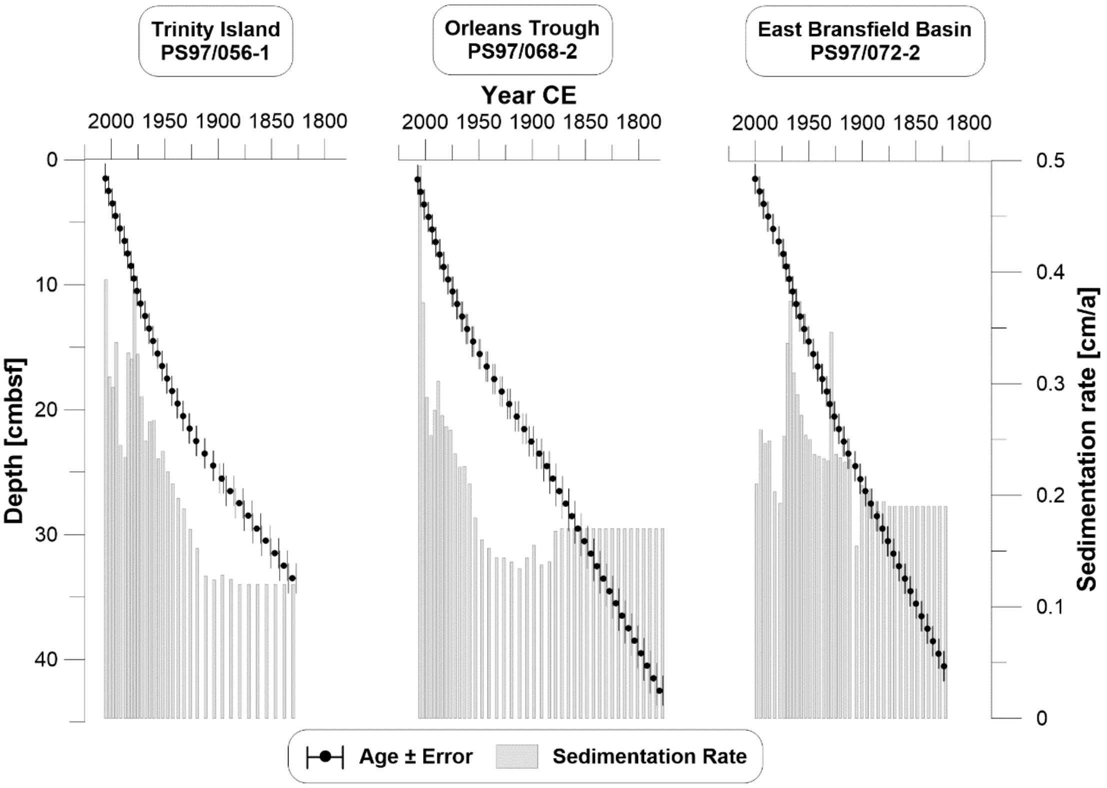


Figure 6.2 Age-depth models with error bars of all three core sites. The sedimentation rate is displayed in grey bars. Ages were extrapolated prior to 1880 CE for all cores based on thei average respective sedimentation rate for the oldest 3 cm. All plots were done with Grapher™ 13.

brassicasterol and dinosterol and show increasing trends with time. In general, HBI triene-based $PIPSO_{25}$ have higher values (P_ZIPSO_{25} from 0.32 to 0.91; P_EIPSO_{25} from 0.25 to 0.95) than $PIPSO_{25}$ based on sterols (P_BIPSO_{25} from 0.15 to 0.70; P_DIPSO_{25} from 0.11 to 0.75). The $PIPSO_{25}$ indices suggest an increasing spring sea ice cover over time (Figure 6.3, Figure Appendix 5). This is most prominent at the East Bransfield Basin (PS97/072-2) where lowest sea ice cover is indicated around 1870 CE and increase towards the present is indicated. Indications of short-term low spring sea ice cover are found for the 1960s and 1970s at the near-coastal core sites (PS97/056-1 and PS97/068-2) but do not change the overall trend.

Temperatures based on GDGTs show a wide range of values. At Trinity Island (PS97/056-1) and the East Bransfield Basin (PS97/072-2), SOT^{TEX} range from -3.87°C to 2.34°C (Figure 6.3) whereas temperatures are always above zero from 0.73° C to 3.62° C at the Orleans Trough (PS97/068-2). Distinct cold events occur in the 1860s at the East Bransfield Basin (PS97/072-2) and as a longer cool period from 1940 to 1970 CE at the coastal core sites but general trends are hard to distinguish. In contrast, SOT^{OH} displays a decreasing temperature trend at all core sites with a narrow range of -2.58 °C to -0.99° C reversed by rapid warming since the 1990s (Figure 6.3).

6.3.3. Diatom assemblages

Winter sea ice estimations derived from diatom assemblages point to a high variability (74% to 92% WSI at PS97/056-1, 64% to 92% at PS97/068-2, 68% to 90% at PS97/072-1) with a minimum around 1840 and 1880 CE and a slight increment toward 1990s (Figure 6.3). This variability coinciding with the high abundances of sea ice diatom species *Fragilariopsis curta* that show a high contribution at cores PS97/056-1 and 068-2. In addition, WSI records reveal similar features compared to $IPSO_{25}$ and $PIPSO_{25}$, which points to a relationship of winter and spring sea ice estimates based on different approaches. The SSST from diatom assemblages have a small amplitude in all cores (-0.9 to 0.5°C at PS97/056-1, -1.1 to 0.2°C at 068-2 and -0.8 to 0.1°C at 072-1) and show a similar pattern to SOT^{TEX} at the sites PS97/068-2 and 072-1 (Figure 6.3).

6.3.4. Modelled data

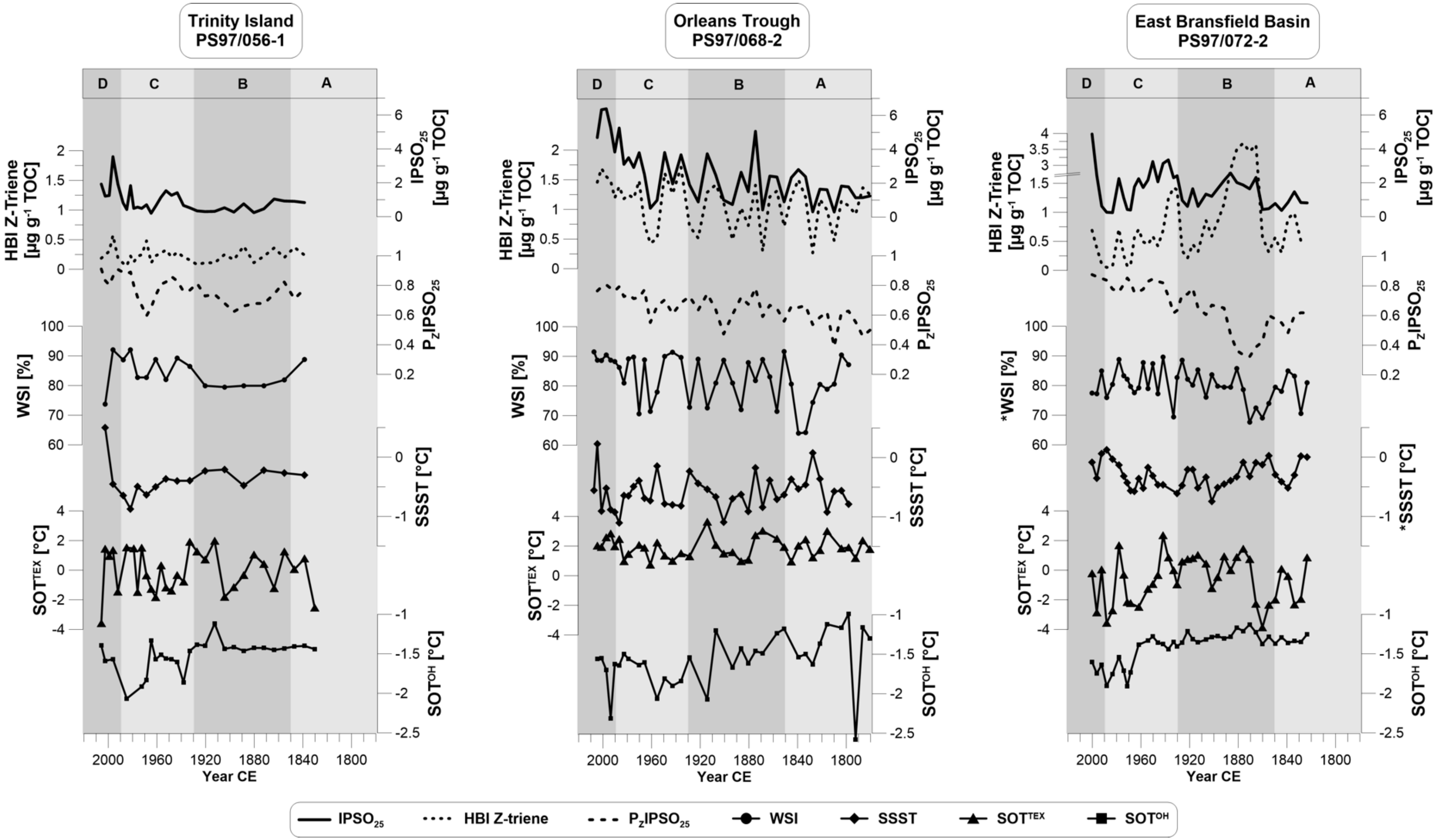
We use model data as derived from the AWI-ESM2 which include spring sea ice concentration (mSSIC), spring sea ice thickness (mSSIT), subsurface ocean temperature (mSOT, mean temperature from 30-100 m below sea surface), and surface air temperature (mSAT). Based on 10-year means, we detect negative trends for the last 200 years in both mSSIC (decrease by 30% to 50%) and mSSIT (decrease from 0.5 m down to 0.1 m). At the same time, positive trends for mSOT and mSAT at all core sites show temperatures rising by 0.3°C to 0.6°C. Further, a time series of the latitudinal shift of the sea ice edge at the WAP (between 50°W and 70°W) which shows a southward shift of 1.5° from 61.9°S to 63.4°S in the 20th century.

6.4. Discussion

6.4.1. Spatial and temporal distribution of paleoenvironmental biomarkers

The core site at Trinity Island (PS97/056-1) is dominated by the APCC and receives freshwater input from the Peninsula with influence of BSW from the ACC (Moffat and Meredith, 2018). We suggest that sea ice proxies originate from free floating or land fast sea ice in this region since the core site is only 8 km away from Trinity Island. Coastal upwelling of macro- and micronutrients, especially iron, and a stratified water column fuel

Figure 6.3 Biomarker composition of the three sediment cores showing concentrations of (from top to bottom) IPSO$_{25}$ and HBI Z-trienes, the sea ice index P$_Z$IPSO$_{25}$, diatom-derived winter sea ice (WSI) concentrations and temperatures of summer sea surface temperatures (SSST), subsurface ocean temperature derived from TEX$^L_{86}$ (SOT^{TEX}), and OH-GDGTs (SOT^{OH}). Data marked with * are from the trigger core PS97/072-1. Vertical grey bars denote the stratigraphic units A to D.



open marine primary production (Sanchez et al., 2019; Vernet et al., 2008) and may explain highest concentrations of sterols at this core site. $IPSO_{25}$, HBI Z-triene, P_ZIPSO_{25} and WSI records exhibit similar trends and fluctuations over time (Figure 6.3). A direct relation between reconstructed sea ice conditions and temperature (SSST, SOT^{TEX} and SOT^{OH}) is not evident. However, slightly higher temperatures deduced from SOT^{OH} and diatom data seem to coincide with lower $IPSO_{25}$ concentrations, lower $PIPSO_{25}$ values and reduced WSI in the 19th century, while variable but higher temperatures in the 20th century are accompanied by higher $IPSO_{25}$ and WSI concentrations at site PS97/056-1 (Figure 6.3). The remarkably low SOT^{TEX} in the year 2006 CE might be a result of cold meltwater injections due to enhanced glacier melting (e.g. Pastra Glacier on Trinity Island). A general weak cooling trend is present in SSST and SOT^{OH} from 1920 CE to the 1990s.

The data obtained from the sediment core in the Orleans Trough (PS97/068-2) suggest that the core site is affected by the Peninsula Front where water masses from both salty and cold WSW and fresh and warm BSW meet. The water here is characterized by enhanced mixing within a narrow eddy zone and deepening of the mixed layer (Sangrà et al., 2011). High concentrations of biomarkers point towards a strengthening of primary productivity associated with BSW (Gonçalves-Araujo et al., 2015) in a less stratified and mixed water column (Vernet et al., 2008). The patterns of $IPSO_{25}$, HBI Z-triene as well as P_ZIPSO_{25} and WSI have a good visual correspondence. They indicate higher phytoplankton productivity and higher sea ice cover towards present time. Also, SSST corresponds quite well with SOT^{OH} at PS97/056-1 and with SOT^{TEX} at PS97/072-2 (Figure 6.3). The SOT^{TEX} is remarkably high (above 0° C) throughout the studied period contrasting modern ocean temperatures of the upper 400 m at the WAP below -0.5°C (Cook et al., 2016). Compared to SOT^{TEX}, SOT^{OH} temperatures are closer to modern ocean temperatures in this area (Cook et al., 2016) within a narrow range. As this core site is in the middle of BSW and WSW influenced, no clear dominance from one or the other regime is evident and we suggest that GDGT-derived temperatures are affected by influences of both BWS and WSW.

The core site in the East Bransfield Basin (PS97/072-2) is further away from the coast (145 km) compared to the other two core sites. Marine productivity is expected to be lower due to the presence of WSW (Gonçalves-Araujo et al., 2015) but relatively high concentrations of $IPSO_{25}$ and HBI Z-triene may be related to fertilization through iron input (Sanchez et al., 2019). A remarkable maximum in HBI Z-triene concentrations in the late 19th century have resulted from drastic changes in the local oceanographic settings and productivity patterns. As indicated by SOT^{TEX}, this period is marked by a rapid shift from cold to warm water temperatures, pointing to a possible dominance of warmer BSW. A corresponding retreat of sea ice cover and likely ice-free summers, as reflected by P_ZIPSO_{25} and WSI values, could have promoted the productivity of open marine or coastal phytoplankton communities, e.g. *Rhizosolenia* and *Pleurosigma*, synthesizing the HBI Z-triene (Belt et al., 2000, 2017).

Despite the different oceanographic settings, all cores sites exhibit increasing trends in $IPSO_{25}$ and HBI Z-triene concentrations as well as rising P_ZIPSO_{25} values and WSI towards the present reflecting an overall advance of sea ice cover. At the same time, SOT^{TEX} and SOT^{OH} tend to decrease until the 1990s and rise since the 1990s, which we interpret as a delayed ocean warming compared to other parts of the global ocean (Cook et al., 2016). The overall trend in our records is a rise of both open marine and sea ice biomarkers and an ocean cooling (mainly indicated by SOT^{OH}). A clear stratigraphy is hard to distinguish but four units could be roughly divided by sea ice and temperature biomarker records:

Unit A: Moderate sea ice cover before 1850 CE. In the period before 1850 CE, the WAP experienced low productivity of sea ice algae as well as ice-edge or open marine algae (low IPSO$_{25}$ and HBI triene values). Diatom and biomarker sea ice indices reveal decreasing winter sea ice and moderate spring sea ice cover with low variability in seasonal sea ice changes. The fluctuating water temperatures display no clear trend except for a weak cooling at the East Bransfield Basin, which may have resulted from an enhanced WSW inflow into the Bransfield Strait.

Unit B: Moderate winter sea ice cover and ice-free summers from 1850 to 1930 CE. In this period, changes in the oceanographic pattern may have led to a dominance of BSW in the East Bransfield Basin (PS97/072-2) and a weakened WSW inflow causing sea ice retreat and ocean warming. During this time, seasonal shifts from winter sea ice to ice-free summers occurred faster and promoted enhanced open marine biomarker production (Gonçalves-Araujo et al., 2015) fueled by high nutrient release through melting (Vernet et al., 2008). Sea ice cover remained at a moderate level near the coast (core sites PS97/056-1 and 068-2), as suggested by Barbara et al. (2013) who interpreted near-coastal diatom assemblages and HBIs at both sides of the AP to reflect long persisting sea ice cover in spring (Figure Appendix 6). They furthermore postulated that enhanced productivity occurs due to a stratified water column and nutrient injections by meltwater and autumn storm activity in the southern Bransfield Strait. Despite this, we see high fluctuations of winter sea ice (up to 20% WSI between two data points). Furthermore, high (low) winter sea ice cover as indicated by WSI at PS97/068-2 and 072-2 occurs contrary to low (high) spring sea ice reflected by P$_Z$IPSO$_{25}$ pointing to fast seasonal changes.

Unit C: Higher variability and increasing sea ice cover from 1930 to 1990 CE. In contrast to Unit B, all biomarkers indicate an increasing sea ice cover in Unit C. It is characterized by a general ocean cooling (except for SSST in the East Bransfield Basin), which may suggest a delayed onset of anthropogenic warming in Antarctic waters (Abram et al., 2016; Cook et al., 2016) and the atmosphere (Abram et al., 2013). High fluctuations in IPSO$_{25}$ and HBI Z-triene concentrations indicate conditions favorable for both sea ice and phytoplankton productivity potentially resulting from a higher seasonal variability characterized by high winter sea ice cover and ice-free summers. High winter sea ice cover now coincides with high spring sea ice coverat all core sites. WSI and IPSO$_{25}$ indicate enhanced coastal winter and spring sea ice cover in the 1940s and 1950s and low sea ice cover in the 1960s and 1970s in correspondence with other paleo records (e.g. Abram et al., 2010; Hobbs et al., 2016). A distinct increase in IPSO$_{25}$ and HBI Z-triene concentrations since 1930 CE was also reported by Barbara et al. (2013) on both sides of the AP (Figure Appendix 6). We suggest that higher production of IPSO$_{25}$ and sterols could be related to pulses of cold water and nutrients due to glacier retreat (Cook et al., 2016; Kunz et al., 2012). The increasing sea ice cover at all core sites contrasts a reconstructed sea ice decrease from satellite and ice cores since the 1950s for the Bellingshausen Sea (Abram et al., 2010; Hobbs et al., 2016). This contradicting long-term sea ice growth is also evident in the study by Barbara et al. (2013) who first observed a shortening of the sea ice season but an advance thereafter due to a stable, sea ice favoring environment under mild conditions after 1950 CE.

Unit D: Warm reversal and sea ice peak from 1990 to 2006 CE. The last unit is marked by the trend reversal to a warm subsurface ocean (Cook et al., 2016), present at all core locations in the Bransfield Strait. Sea ice cover tends to increase towards maximum values and seems to reflect recent observations of sea ice cover rebounds in the Bellingshausen Sea and the WAP after 2005 CE (Hobbs et al., 2016; Schofield et al., 2018). Since the last unit is very short, the interpretation of warm ocean temperature together with a high sea ice cover is rather tentative.

We note that for the interpretation of biomarker-based sea ice reconstructions the potential degradation of biomarkers affecting their downcore concentration profile needs to be taken into consideration. We observe that the upper part of the sediment cores contains higher concentrations of $IPSO_{25}$, HBI trienes and sterols compared to the underlying older sediments. A similar pattern in $IPSO_{25}$ and HBI triene concentrations is also reported by Barbara et al. (2013). Their biomarker concentrations from the western AP equal the concentrations in the Bransfield Strait but do not show such high values near the sediment surface, as in our data, are not present. Auto- and photooxidative degradation of $IPSO_{25}$ and HBI trienes was already studied in laboratory experiments (Rontani et al., 2014, 2011) and autoxidative and bacterial degradation was also found in the oxic layers of surface sediments (Rontani et al., 2019a). According to these results, a faster degradation of HBI trienes (because of their higher number of double bonds) in the upper centimeters of the herein studied sediment cores would lead to higher $PIPSO_{25}$ values with progressive degradation. Sterols might also undergo degradation (Rontani et al., 2012) but studies from Antarctic sediments are still missing. As we observe remarkably high HBI triene concentrations in core PS97/072-2 in the late 20th century and lower concentrations towards present (Figure 6.3, Figure Appendix 5), we suggest that degradation does not have major impacts on biomarker concentrations presented in this study.

6.4.2. Comparison of proxy-derived and modelled sea ice estimates with satellite sea ice observations

We compared $IPSO_{25}$ concentrations, P_ZIPSO_{25} values, and diatom-based WSI estimates with satellite data and with mSSIC to evaluate their accuracy in reflecting spring and winter sea ice cover variability at the core sites over the past 40 years (Figure 6.4). Satellite-derived spring sea ice concentrations (satSSIC) show general similarities to fluctuations observed in the $IPSO_{25}$ record indicating lower sea ice cover in the 1980s, a peak in the mid 1990s and a drop in sea ice cover in the early 2000s, except for the coastal remote core site (PS97/072-2) where sea ice concentrations rise towards present (Figure 6.4). At the near-coastal core sites (PS97/056-1 and 068-2), these dynamics are well reflected in $IPSO_{25}$ and $PIPSO_{25}$, in particular for site PS97/056-1, where a good correspondence is observed between biomarker and satellite data (Figure 6.4). However, we cannot exclude aliasing effects due to a lower temporal resolution of the sediment cores (Pisias and Mix, 1988). Maximum sea ice concentrations observed in 1996 CE, are well reflected by elevated $IPSO_{25}$ concentrations but the drop afterwards is not that clearly reflected. Diatom-based WSI compared to satellite-derived winter sea ice concentrations (satWSIC) show that these two data sets are in moderate agreement at the near-coastal core sites (PS97/056-1 and PS97/068-2) and winter sea ice coverage seems to be less dynamic at the Peninsula Frontal mixing zone (PS97/068-2). We note that the modelled spring sea ice cover is mostly opposite to satellite data, in particular during the 1990s and 2000s. While modelled and satellite derived data have similar grid sizes (model: 30x30 km, satellite: 25x25 km) we suppose that global models such as AWI-ESM2 cannot resolve the AP sub-aerial and marine topography and have difficulties in capturing local to regional near coastal sea-ice dynamics in the study region. Another reason is related to internal variability and missing feedbacks which makes a direct comparison of short time series difficult. However, both modelled and satellite data show a decreasing trend in spring sea ice cover (about 10%) and a slightly rising trend in winter sea ice cover over the recorded period (about 7%), while sea-ice proxies suggest an increasing trend of spring sea ice. For winters sea ice, core sites PS97/056-1 and PS97/072-2 display a decreasing trend, whereas PS97/068-1 clearly point to sites PS97/056-1 and PS97/072-2 display a decreasing trend, whereas PS97/068-1 clearly point to an increase of winter sea ice.

For the offshore core site at the East Bransfield Basin (PS97/072-2), IPSO$_{25}$ and PIPSO$_{25}$ correspond better with satSSIC than with mSSIC sea ice data (Figure 6.4). Between 1985 and 1995 CE, both PIPSO$_{25}$ indices suggest a similar increase in spring sea ice as the satellite observations. Sea ice estimates from WSI seem to be more related to satSSIC than to satWSIC. Also, WSI estimates are remarkably lower than at the other core sites, although satellite winter sea ice cover is the highest of all. Regarding the oceanographic setting, we consider that also drift ice originating in the Weddell Sea may have affected the deposition of IPSO$_{25}$ at this core site. Input of allochthonous material from the shelf is also possible, which might impact the fidelity of the proxy records.

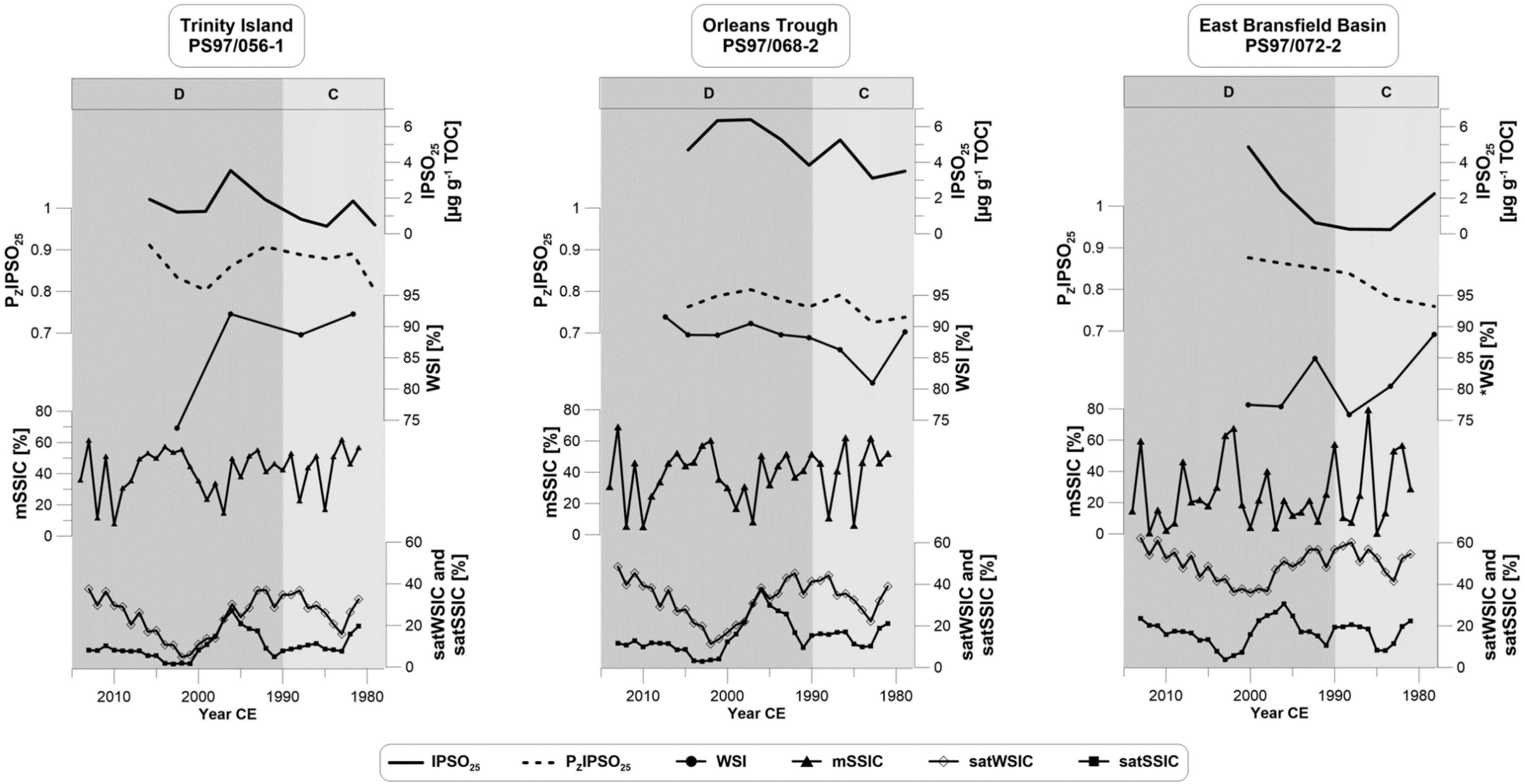
Based on the overall accordance with satellite data, we conclude that the biomarker and diatom-based sea ice estimations are related to regional dynamics of sea ice cover, as far as we can assess it from the low resolution of the sediment cores. Since HBI Z-trienes and sterol concentration profiles are similar to IPSO$_{25}$ concentrations (Figure 6.3, Figure Appendix 5) we suggest that sea ice dynamics also promote growth of open marine phytoplankton species due to nutrient release or nutrient upwelling (Sanchez et al., 2019; Vernet et al., 2008). As the record of satellite observations is short, it is not clear if decadal or centennial sea ice trends can be directly derived from our biomarker records. Hence, we use modelled and ice core data for further insights over the full sediment records.

6.4.3. Comparison of sea ice proxy records with modelled and ice core data covering the pre-satellite era

By comparing IPSO$_{25}$, P$_Z$IPSO$_{25}$-based sea ice estimates and WSI with modelled spring sea ice data, we note opposite long-term sea ice trends reflected in the proxy records and the modelled data for the past 240 years (Figure 6.5). Modelled spring sea ice concentration and thickness show a clear decreasing trend at all core sites with a loss of sea ice cover between 15% and 20%. Modelled sea ice cover fluctuates strongly at the East Bransfield Basin (PS97/072-2) while the coastal core sites run almost parallel. Although the modelled spring sea ice does not agree with satellite data on local to regional scale (Figure 6.4) it does reflect the satellite observations of the large-scale general trend of sea ice decline and warming in the Bellingshausen Sea and at the WAP (Parkinson and Cavalieri, 2012; Vaughan et al., 2003).

The increasing concentrations of IPSO$_{25}$ as well as the rise of both parallel running P$_Z$IPSO$_{25}$ values and diatom-derived WSI concentrations recorded in all three sediment cores suggest a long-term sea ice advance. On the other hand, the rise in the concentrations of the HBI Z-triene and sterols also rise (Figure Appendix 5), which indicates more open marine and/or stable ice edge conditions promoting phytoplankton productivity. We suppose that a thinning of the ice and a hence higher light penetration permitting photosynthesis at the ice-water interface (Hancke et al., 2018) could have triggered the productivity of IPSO$_{25}$ source diatoms. In addition, increased melting of sea could have contributed to a higher deposition of sea ice diatoms and IPSO$_{25}$. Thinner ice and accelerated melting during spring may have resulted in a largely ice-free sea surface during summer promoting phytoplankton (biomarker) productivity. The declining mSSIC and mSSIT (Figure Appendix 7) support this interpretation. Increasing concentrations of both IPSO$_{25}$ and phytoplankton-derived biomarker lipids accordingly may reflect more

Figure 6.4 Concentrations of (from top to bottom) $IPSO_{25}$, P_ZIPSO_{25}, WSI compared to modelled spring sea ice concentrations (mSSIC) and satellite derived winter and spring sea ice concentrations (satWSIC and satSSIC, 5 year running mean) from the National Snow and Ice Data Center (NSIDC, Cavalieri et al., 1996) for all three core sites. Data marked with * are from the trigger core PS97/072-1. Vertical grey bars denote the stratigraphic units C and D.



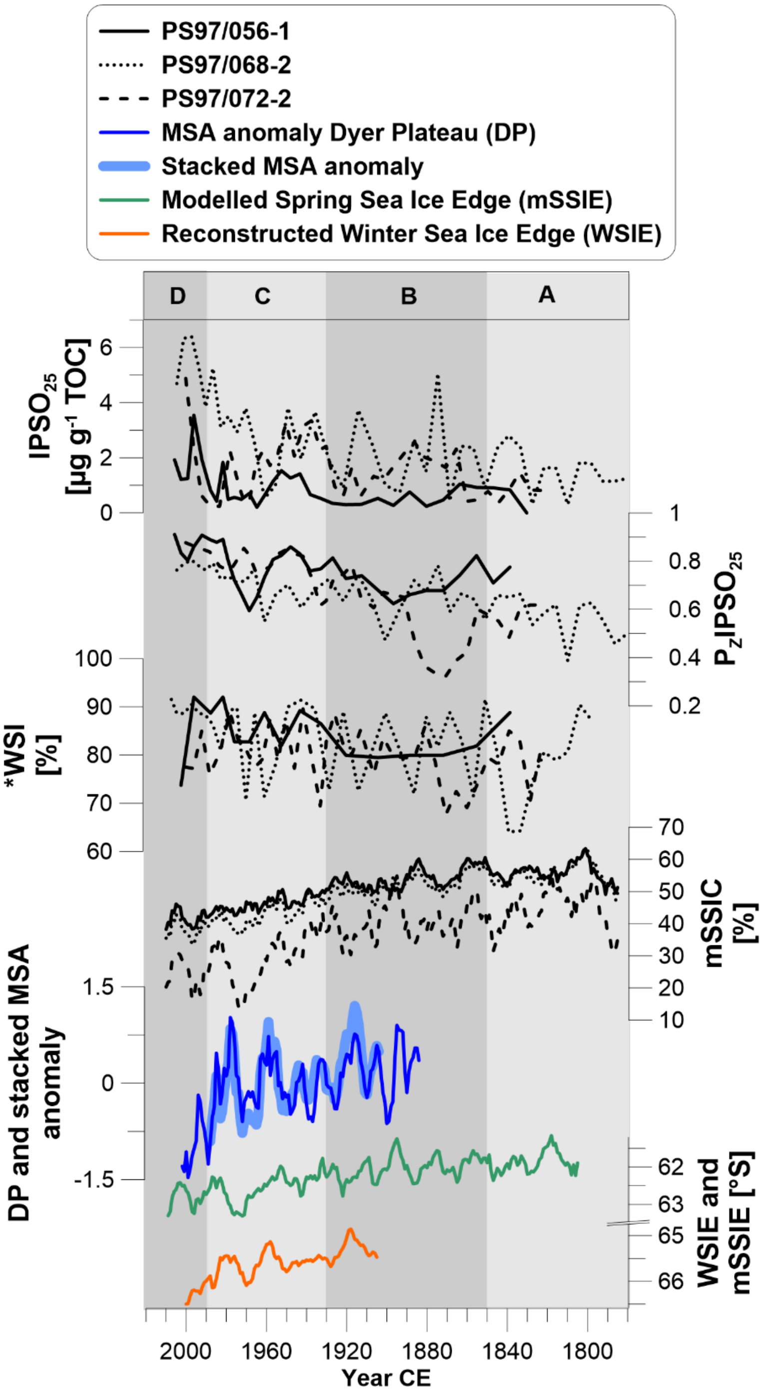


Figure 6.5 The biomarker (from top to bottom) $IPSO_{25}$, sea ice index P_ZIPSO_{25}, and winter sea ice concentration (WSI) from diatom assemblages compared to modelled spring sea ice cover (mSSIC, 10 year running mean), MSA anomaly from Dyer Plateau and stacked MSA covering the Bellingshausen Sea sector (5 year running mean, Abram et al., 2010), modelled spring sea ice edge latitude (mSSIE, 10 year running mean) and econstructed winter sea ice edge latitude from MSA (WSIE, 10 year running mean, Abram et al., 2010). Data marked with * are from the trigger core PS97/072-1. Vertical grey bars denote the stratigraphic units A to D.

pronounced ice-edge conditions and/or a distinct seasonality in spring and summer conditions at the WAP through the past 200 years.

For the WAP, we generally expect influences of meltwater inputs from glacial melting (Meredith et al., 2018), additional nutrient input from the APCC and intense mixing at the Peninsula Front. As the distribution of $IPSO_{25}$ is sensitive to local oceanographic conditions (Smik et al., 2016a), biomarker-based sea ice studies require an interpretation that takes the specific environmental characteristics of the region into account. Obviously, high fluctuation in sea ice cover, sea ice thickness and water temperature stimulate phytoplankton growth rather than stable conditions with very high and long lasting or low ice covers and/or ice-free sea surface (e.g. Xiao et al., 2013). We hence propose to compare the individual concentration records of $IPSO_{25}$ and phytoplankton biomarkers rather than using the $IPSO_{25}$ (and $PIPSO_{25}$) record alone to deduce sea ice conditions.

We further consider records of MSA, an organic aerosol, which is associated with marine biological activity during sea ice breakup and is used as a proxy for paleo marine productivity and seasonal sea ice reconstructions in ice cores. Influenced by timing, duration and spatial extent of sea ice breakup MSA concentrations are linked with winter sea ice extent in some regions and summer productivity within the sea ice zone in other regions of Antarctica (Thomas et al., 2019 and references therein). Here we use records of MSA from the Dyer Plateau on the AP as well as a stacked MSA record based on three regional ice cores including Dyer Palteau (Abram et al., 2010) that reflect winter sea ice dynamics in the Bellingshausen Sea. Both records display an overall decreasing trend in MSA concentrations since 1900 CE indicating less sea ice (Figure 6.5). The pattern shows some agreement with the mSSIC from the East Bransfield Basin (PS97/072-2) but is opposite to our biomarker records and sea ice indices for all three core sites. This is likely due to the fact that our sediment records reflect local to regional changes strongly influenced by the AP as a geographic barrier and the complex oceanography within the Bransfield Strait from interaction of BSW and WSW. As both the Dyer Plateau and the stacked MSA records are dominated by large-scale winter sea ice cover variability in the Bellingshausen Sea (centered between 70° and 100°W) (Abram et al., 2010), we suggest that the regional sea ice variability within the Bransfield Strait covered by our sediment cores is not well reflected in the ice core records.

Additionally, we took the latitudinal movement of the spring sea ice edge from modelled data (mSSIE, Figure 6.5) into account, which displays a southward shift down to 63.5°S reflecting sea ice retreat and proposes the occasional absence of spring sea ice at all core sites since the 1970s. The spatial shift of the sea ice edge must be treated with caution because the model does not account for regional impacts, coastal and peninsula interactions and seasonal input of drift ice from the Weddell Sea. The MSA-based winter sea ice edge (WSIE, Figure 6.5) (Abram et al., 2010) displays the same decreasing trend in the Bellingshausen Sea but is located 3° to the south of the modelled ice edge (from 65° to 66°S). The fact that our core sites are located north of this projected WSIE shift is another argument why the ice core MSA cannot be considered to reflect sea ice conditions in our study area, which, according to the ice core data would have been free of sea ice during the entire 20th century.

6.4.4. Comparison of marine temperature proxy records with model and ice core data

Comparison of GDGT-based temperatures with modelled subsurface ocean temperature mSOT reveals a general disagreement over the 20th century (Figure 6.6). Only at the Orleans Trough (PS97/068-2) we assume SOT^{TEX} to reflect atmospheric temperatures due to an enhanced water mixing at the Peninsula Front since the mean temperature of +1.9° C is remarkably higher compared to the other core sites with -0.1° C at PS97/056-1 and -0.6° C at PS97/072-2. During the 19th century, SOT^{TEX}-based cold (around 1850s

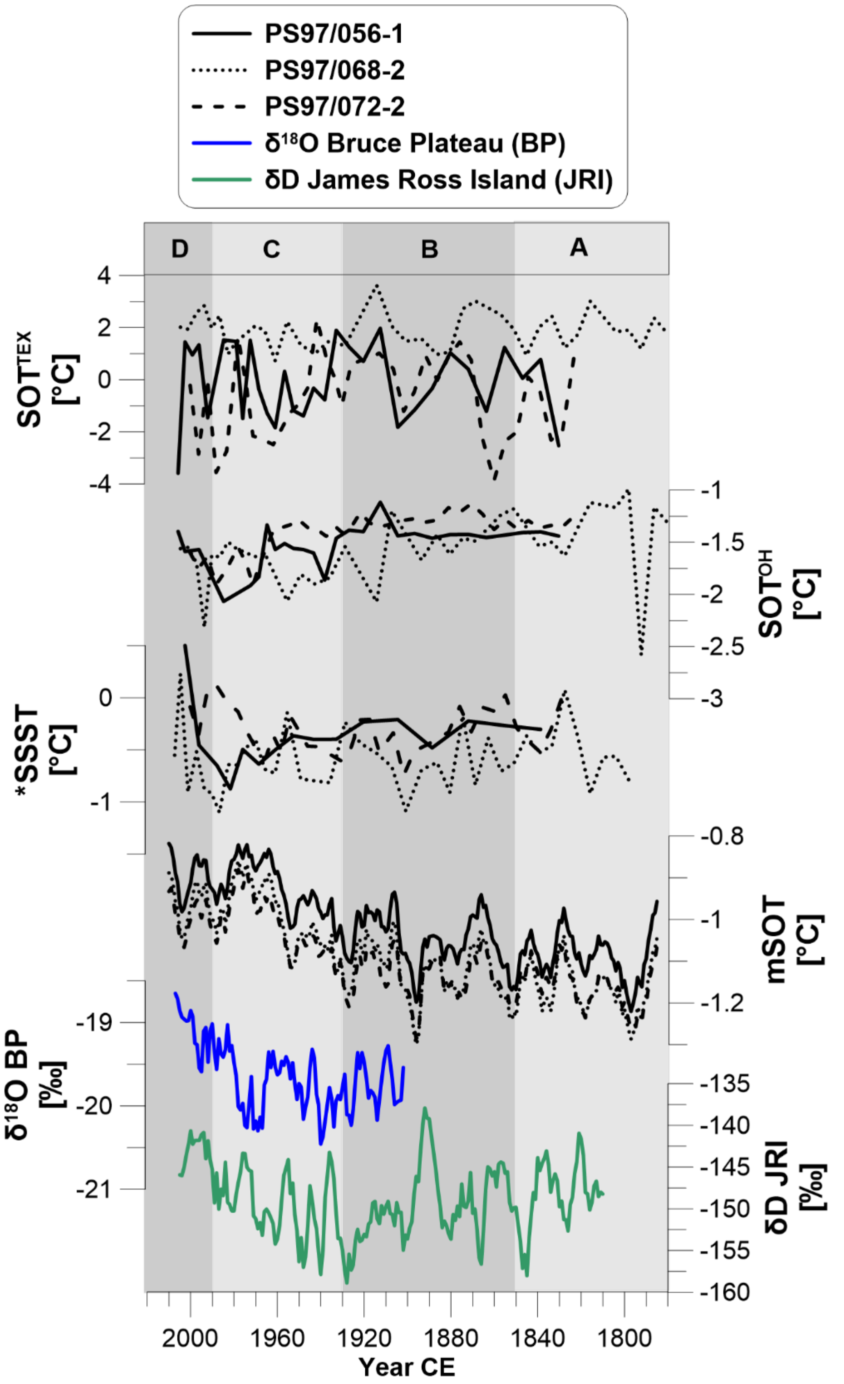


Figure 6.6 Biomarker derived subsurface ocean temperatures based on TEX^{L}_{86} (SOT^{TEX}), and hydroxylated GDGTs (SOT^{OH}), and summer sea surface temperatures (SSST) derived from diatom assemblages compared to modelled subsurface ocean temperature (mSOT), stable isotope ice core records from the Bruce Plateau (BP, $\delta^{18}O$, 5 year running mean; Goodwin et al., 2016) and from James Ross Island (JRI, δD, 5 year running mean; Abram et al., 2013). Data marked with * are from the trigger core PS97/072-1. Vertical grey bars denote the stratigraphic units A to D.

and 1900 CE) and warm events (from 1860 to 1880 CE, and around 1910 CE), respectively, agree better with mSOT at all core sites than in the 20th century. SOT^{OH} does not correspond to mSOT except since the 1990s when both data sets reflect the modern warming. SSST from diatoms show a short cool period around 1900 CE similar to SOT^{TEX} and modelled data. In general, biomarker derived temperatures point to a slight cooling trend over the last 200 years at the WAP which is contradicted by the mSOT data.

Interestingly, highly variable but continuously increasing mSOT (and mSAT) match with the observed trends in atmospheric warming derived from stable isotope ice core data (Figure 6.6). The records of $\delta^{18}O$ records at Bruce Plateau (Goodwin et al., 2016) and δD records from *James Ross Island* (Abram et al., 2013) display the large-scale air temperature evolution in the sector of the Bellingshausen Sea and the Antarctic Peninsula region, and show the same upward trend as air temperatures from several meteorological stations at the WAP (Stastna, 2010). However, we note that ice cores represent a large regional scale and meteorological station records are influenced by e.g. altitude, morphology and local wind patterns, while GDGT-based derived ocean temperatures picture a local to regional marine record controlled by BSW and WSW. We also note that the ocean is decoupled from the atmosphere during periods with sea ice cover and a heating of the ocean by the atmosphere is diminished. Further, sea ice melting in spring enhances the stratification of the upper water column and restricts heat exchange between the subsurface ocean and atmosphere.

6.4.5. Sea ice evolution and large-scale atmospheric circulation patterns

Since atmospheric circulation affects the heat and sea ice distribution at the WAP especially during spring time (Clem et al., 2016), we expect patterns of ENSO and/or SAM to leave a footprint in our spring sea ice $IPSO_{25}$ record. Several studies suggest an enhanced influence of ENSO and SAM on Antarctic temperatures with increasing greenhouse gas concentrations, so their relation to sea ice is a crucial factor for sea ice and climate predictions (Rahaman et al., 2019; Stammerjohn et al., 2008b). For example, the atmosphere-ocean-sea ice interactions impact the WAP strongly through increased northerly winds during an in-phase -ENSO/+SAM mode. They lead to a strong, positive feedback of atmospheric warming amplification due to shorter sea ice seasons, thinner sea ice cover with more leads and an enhanced heat flux from the ocean (Stammerjohn et al., 2008a).

We compared $IPSO_{25}$ from all core sites with a tree-ring based ENSO reconstruction (Li et al., 2013) and SAM data from proxy records including the full mid-latitude to polar domain of the Drake Passage (Abram et al., 2014) (Figure 6.7). Both, ENSO and SAM, have oscillating positive and negative periods and SAM shows a slight decrease until 1860 CE. Since 1930 CE, SAM, and since 1960 CE, ENSO, increase again and reach maximum positive states in the 2000s. When comparing biomarker and circulation patterns, SAM matches best with elevated HBI concentrations, especially at the coastal core sites, relating a higher accumulation of $IPSO_{25}$ with a +SAM. During a +SAM, stronger westerlies lead to a southward shift of the low-pressure cell over the Bellingshausen Sea and the strengthening of the polar frontal jet (Marshall et al., 2006). The blocking effect of the AP is diminished because air masses pass over the northern AP from west to east (Marshall et al., 2006). This results in a remarkable impact on rising summer air temperatures on the eastern AP leeside due to a "Föhn" effect (Klemp and Lilly, 1975). In contrast, the temperature effects on the western AP are very small and not even detectable at e.g. the southwest Vernadsky/Faraday Station (Marshall et al., 2006). Nevertheless, our records suggest that a +SAM is positively related to the production of $IPSO_{25}$ and HBI Z-triene at the WAP, especially since the mid 20th century.

The pattern of ENSO is related negatively with biomarker concentrations in the 19th century (especially at core site PS97/072-2) and more positively in the 20th century. The recent shift to a positive ENSO is accompanied by increased $IPSO_{25}$ concentrations.

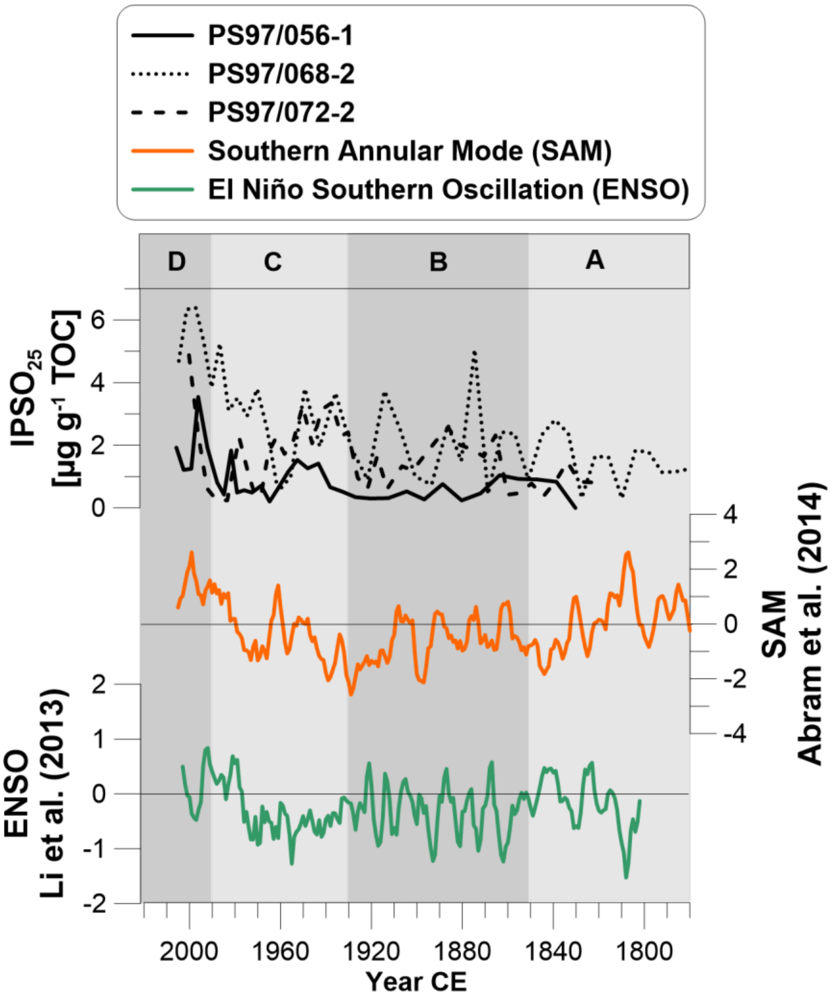


Figure 6.7 Concentrations of biomarker $IPSO_{25}$ in all three sediment cores compared to circulation pattern of the Southern Annular Mode (SAM, 5 year running mean; Abram et al., 2014), and the El Niño Southern Oscillation (ENSO, 5 year running mean; Li et al., 2013). Vertical grey bars denote the stratigraphic units A to D.

After Yuan (2004) a +ENSO causes sea ice advance under cold conditions in the Weddell Sea and the WAP, and warm, moist conditions in the Southern Pacific Ocean. However, due to observations of recently rising atmospheric temperature (Stastna, 2010), ocean temperature (Cook et al., 2016) and declining sea ice cover, a +ENSO seems to be more likely related to warm and sea ice reduced conditions at the WAP in the studied period. Nevertheless, we observe that the $IPSO_{25}$ production at the coastal core sites (PS97/056-1 and 068-1) correspond to ENSO since the 1980s. While neither SAM nor ENSO alone seem to exert a consistent control on $IPSO_{25}$ and phytoplankton production at the WAP, +ENSO together with +SAM seem to be linked to higher $IPSO_{25}$ concentrations especially in the 20th century, which agrees with previous suggestions regarding the impact of atmospheric circulation pattern on sea ice conditions (Barbara et al., 2013; Etourneau et al., 2013).

6.5. Conclusion

In this study we analyzed the spring sea ice biomarker $IPSO_{25}$ and other organic biomarkers as well as diatom assemblages in three sediment cores from the Western

Antarctic Peninsula region covering the industrial era and combined them with numerical model data, satellite observations, temperature records and paleo records of atmospheric circulation patterns. We note that the interpretation of the biomarker data for past sea ice estimates in Antarctica is strongly impacted by the origin of water masses and mixing, nutrient input and dynamics of sea ice-related primary production. Based on sea ice biomarkers and sea ice indices, the 200-year records can be divided into four units:

Unit A Before 1850 CE, the sea ice cover in the WAP was moderate with a low primary productivity and low seasonal sea ice variability influenced by WSW inflow into the Bransfield Strait.

Unit B From 1850 to 1930 CE, low to moderate stable sea ice cover was common at the coastal WAP, while rapid changes in sea ice seasonality were evident at the East Bransfield Basin due to changes in oceanographic pattern and enhanced BSW inflow.

Unit C 1930 CE marked a turning point in sea ice cover with increased sea ice dynamics triggering melting and primary production of both open marine and sea ice species, with periods of high (1940s-1950s) and low sea ice cover (1960s-1970s).

Unit D Since 1990 CE, the anthropogenic warming reversal is evident in subsurface ocean temperatures and low sea ice cover with high seasonal dynamics promoting marine production and causing maximum sea ice indices.

While $IPSO_{25}$ concentrations agree with satellite sea ice data, they seem to contradict with long-term large-scale ice core and model data. We explain this as a result of local coastal influences, high sea ice dynamics and thinner sea ice promoting the production of both sea ice diatoms and open marine phytoplankton affecting the interpretation of $IPSO_{25}$ and the sea ice index $PIPSO_{25}$. When estimating spring sea ice cover, the strong susceptibility of $IPSO_{25}$ to local influences such as water masses, coastal interaction and, e.g. a higher sea ice algae productivity resulting from thinner ice cover need to be taken into account. We hence recommend to consider additional phytoplankton data instead of constructing sea ice estimates on $IPSO_{25}$ and $PIPSO_{25}$ records solely. We do not observe a relation between ocean temperature evolution and retreating sea ice in the 20th century. The examination of ENSO and SAM paleo records reveals that both seem to affect the sea ice regime at the WAP and that SAM in particular could be a main driver for sea ice conditions favoring $IPSO_{25}$ production.

Data availability

All data will be available at the open access repository www.pangaea.de (https://doi.pangaea.de/10.1594/PANGAEA.918808).

Author contributions

The study was conceived by MV and JM. Data collections and experimental investigations were done by MV together with PC, LR, PM and CBL (diatoms, dating), WG (dating), OE (diatom transfer functions), JM and GM (HBIs, GDGTs), XS and GL (modelling and supplement Figure Appendix 4), CH (satellite sea ice data), and TO (ice cores). MV drafted the manuscript and figures. JM supervised the study. All authors contributed to the interpretation and discussion of the results and the conclusion of this study.

PART II

Acknowledgment

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PART III

7. PART III: FROM THE LAST GLACIAL MAXIMUM UNTIL TODAY: A MULTIPROXY STUDY ON SEA ICE AND CLIMATE DYNAMICS AT THE WESTERN ANTARCTIC PENINSULA

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Abstract

The reconstruction of past sea ice distribution in Antarctica provides crucial information to evaluate and improve model projections of Antarctic climate. The Western Antarctic Peninsula (WAP) is heavily exposed to a rapid warming and the associated decrease in sea ice cover contradicts the generally increasing trend of Antarctic sea ice. To reveal long-term sea ice conditions at the WAP under different and changing climate conditions we examined a marine sediment core from the eastern basin of the Bransfield Strait covering the last deglacial and the Holocene. We focused on the specific biomarker lipid $IPSO_{25}$, a highly branched isoprenoid (HBI), from sea ice algae in combination with biomarkers derived from open marine diatom species, i.e. HBI trienes and sterols. Further, we considered the sedimentological and geochemical composition of the sediment, the use of diatom assemblages and glycerol dialkyl glycerol tetraether (GDGTs) as well as independent records such as ice core sea salt sodium aerosol records and large-scale atmospheric circulation reconstructions. Sea salt sodium flux records revealed a positive relationship to our sea ice biomarker $IPSO_{25}$ and the derived sea ice indicator $PIPSO_{25}$, indicating it to be a reliable source of paleo sea ice information. Using biomarker concentrations and sedimentological data we reconstruct

a retreat of the floating ice shelf and an opening of the ocean surface at 16.4 ka BP at the core site. During the deglaciation, an extensive sea ice cover weakened due to the warming which is interrupted by the Antarctic Cold Reversal from 13.2 ka to 12.4 ka BP. Both warming and sea ice retreat continued in the early Holocene (12 ka to 9 ka BP) and stabilized in the middle Holocene, characterized by maximum phytoplankton productivity. Between 12 ka and 5 ka BP, sea ice conditions changed from stable sea ice edges to shorter sea ice seasons with high amplitudes. The late Holocene is characterized by unstable sea ice and climatic conditions with a prominent cooling trend towards today. Large-scale atmospheric circulation patterns such as the El Niño Southern Oscillation (ENSO) and the Southern Annular Mode (SAM) were found to govern temperature and sea ice biomarker production at the WAP. Prevailing positive SAM and negative ENSO indices promoted middle Holocene warm conditions with highly variable sea ice conditions, while the opposite pattern supported cold conditions with moderate sea ice cover in the late-Holocene.

The manuscript and data are under a moratorium for an indefinite period due to copyright restrictions.

8. CONCLUSIONS AND OUTLOOK OF THE THESIS

The gain in knowledge within the framework of this thesis is the evaluation of $IPSO_{25}$ as a tool for paleo sea ice studies in Antarctica and the Southern Ocean. It is the first employment of $PIPSO_{25}$ - in analogy to the Arctic sea ice index PIP_{25} (Müller et al., 2011) - and its first application in a high-resolution, pre-Holocene paleo record (the study of Collins et al. (2013) dates back to 60 ka BP but has a far lower resolution). This provides robust evidence of its applicability and opens the opportunity for further reconstructions of the sea ice extent, sea ice seasonality and climate conditions to improve climate and sea ice projections.

In **Part I** of the thesis I could demonstrate that the distribution pattern of $IPSO_{25}$ and the application of the semi-quantitative sea ice index $PIPSO_{25}$ bear a high reliability for assessing recent sea ice cover. I found $IPSO_{25}$ in near-coastal surface sediments, an environment where the occurrence of its source species *B. adeliensis* is possible. The spatial distribution of $IPSO_{25}$ is in accordance with sea-ice information from satellite observations and diatom assemblage data. Simultaneously, $IPSO_{25}$ was absent in the open marine and ice-free Drake Passage. Both, $IPSO_{25}$ and the sea ice index $PIPSO_{25}$ hold the potential to reflect sea ice cover in the Bransfield Strait, showing a clear offshore gradient. The distribution of phytoplankton markers indicating open marine conditions showed higher concentrations in permanent ice-free environments in case of HBI trienes and a wide distribution of sterols under several sea ice conditions. I suppose these findings to reflect recent sea ice conditions as they are corresponding well to a similar study in East Antarctica (Smik et al., 2016a). Assessing the suitability of phytoplankton markers for calculation of the sea ice index $PIPSO_{25}$, I found that HBI Z-trienes have an advantage over sterols, since HBI trienes are mainly distributed in areas remote from recent sea ice. I suggest that a $PIPSO_{25}$ index based on HBI trienes may therefore better indicate between sea ice covered and ice-free areas. Recently, a study in the Arctic also showed that PIP_{25} based on HBI trienes is more suitable as a sea ice index (Köseoğlu et al., 2018). Nevertheless, $PIPSO_{25}$ indices based on HBI Z-trienes and brassicasterol corresponded well with sea-ice information from satellite observations and fossil diatom assemblages. However, these findings need to be treated with caution: in contrast to findings of a distribution study from the Arctic (Navarro-Rodriguez et al., 2013), where PIP_{25} matched well with satellite spring sea ice data, the appearance of $IPSO_{25}$ and the sea ice index $PIPSO_{25}$ at the WAP is more likely related to winter sea ice as deduced from satellite observations. It is suggested that this discrepancy is related to the fact that the sediment samples from the WAP cover sea ice biomarker records for roughly 200 years but satellite data only 40 years. Due to the recent decline in sea ice, I supposed that past spring sea ice distribution integrated by marine sediments show an extent comparable to modern winter sea ice cover. Nevertheless, the good agreement of $PIPSO_{25}$ to winter sea ice estimations from diatom fossil assemblages indicates that this index reflects sea ice cover reasonably well.

In the study of multiple short cores in **Part II** of the thesis I did the first paleo interpretation of the sea ice index $PIPSO_{25}$ and showed that both, $IPSO_{25}$ and $PIPSO_{25}$, are likely influenced mostly by sea ice dynamics. Other regional factors such as ocean mixing, nutrient input, and different water masses play also a role. Another important result is that $IPSO_{25}$ reflects regional sea ice dynamics and characteristics better than the total sea ice cover. In the study I revealed the good agreement of $IPSO_{25}$ with satellite-based sea ice time series during the last 40 years, whereas it contrasts centennial scale ice-core based sea ice reconstructions. Since existing ice core records do not directly reflect sea ice dynamics at the WAP but those of the Amundsen or Bellingshausen Seas (Abram et al., 2010), it is difficult to relate ice core and marine sediment data. However, a comparison of normalized biomarker concentrations of two adjacent sediment cores from the west and east side of the AP (Barbara et al., 2013) underlined the similar sea ice development and seasonality on both sides of the WAP in the 20th century.

I found that $IPSO_{25}$ is more sensitive to high sea ice dynamics, because sea ice fluctuations promote higher marine production due to nutrient release and higher light penetration through thinner sea ice and at the sea ice edge. Therefore, sea ice reconstructions should not be solely based on $IPSO_{25}$ but should consider biomarkers indicating open marine conditions as well as e.g. ocean temperature for a comprehensive sea ice interpretation. The finding of parallel sea ice and open marine biomarker patterns indicates, that in over the last two centuries sea ice dynamics were favourable for both biomarkers. A study by Schofield et al. (2018) at the southern WAP supports this suggestion since they found higher phytoplankton productivity in relation to high sea ice cover. Earlier studies already hypothesized an impact of SAM on sea ice distribution and ocean temperature in recent (Clem et al., 2016; Stammerjohn et al., 2008b) and past times (Barbara et al., 2013; Etourneau et al., 2013; Shevenell et al., 2011). I could show that the production of $IPSO_{25}$ is related to positive SAM modes at the WAP but the exact relationships between both parameters are still unknown.

In **Part III** of the thesis, I applied $IPSO_{25}$ on millennial time scales and showed the robustness of $PIPSO_{25}$ under both slowly and rapidly changing climate conditions between the LGM and today. Using a sediment core from the East Bransfield Basin, I could identify the retreat of the ice shelf at the AP and the opening of the ocean surface around 17.2 ka BP. The retreat of sea ice cover during the deglacial and Early Holocene is clearly indicated by biomarker concentrations and $PIPSO_{25}$ and fits into the Antarctic wide pattern of sea ice retreat reflected by ice core records (EPICA Community Members et al., 2004; WAIS Divide Project Members et al., 2015). The changing amplitudes of sea ice seasonality could be determined from specific biomarker concentrations as well as from $PIPSO_{25}$ and diatom based WSI and are similar to reconstructions based on a sediment core from the Palmer Deep, WAP (Etourneau et al., 2013). By comparing sea ice biomarkers with reconstructions of ENSO variability and the strength of SWWs, I found indications that especially SWWs have an impact on climate conditions and $IPSO_{25}$ production also on millennial timescales: while an impact of ENSO is hardly distinguishable from our data, we see a clear positive relationship of SWWs strength possibly being a dominant driver of subsurface ocean heat distribution, higher $IPSO_{25}$ concentrations and sea ice cover from enhanced fresh water input under high seasonal sea ice amplitudes.

A result of all three studies is an enhanced understanding of the significance of $IPSO_{25}$ in relation to HBI trienes and sterols. $PIPSO_{25}$ is not linearly connected to sea ice cover because the highest production of $IPSO_{25}$ occurs under thin sea ice and at sea ice margins and not when there is a high and thick sea ice cover. This is supported by findings from Arrigo et al. (2012) and Hancke et al. (2018), who observed a positive effect on phytoplankton blooms due to thinner Arctic sea ice. Therefore, the production of both sea ice and open ocean biomarkers may be promoted equally under certain conditions. In cases of an opposite biomarker pattern, the value of the $PIPSO_{25}$ index can be related to higher or lower sea ice cover, whereas in the case of parallel biomarker patterns, $PIPSO_{25}$ must be handled with caution since the index does not vary and propose a constant level of sea ice cover. Hence, a theoretical concept (Figure 8.1) of an advanced interpretation for past sea ice reconstructions is based on two factors:

1. The absolute concentration of biomarkers during a certain time interval in comparison with the entire record and
2. the interrelation of sea ice and phytoplankton biomarker patterns.

The paleo sea ice studies showed that parallel biomarker patterns are the result of marine production favorable for both biomarker types. In the case of a high sea ice cover with cold, ice-rich summer seasons concentrations of $IPSO_{25}$ are high and those of phytoplankton biomarkers low (Figure 8.1a). With increased seasonal contrasts, the production of phytoplankton marker is also promoted due to enhanced sea ice melt and stable water column conditions promoting phytoplankton growth. As a result, both types of biomarker show a parallel pattern on high concentration levels (Figure 8.1b). During low sea ice cover and warm, long summers, $IPSO_{25}$ concentrations are low and phytoplankton markers are either low due to diminished mixing of the ocean surface and limited nutrient supply (Figure 8.1c). Under conditions of generally low sea ice cover and a high seasonal amplitude, low $IPSO_{25}$ and high phytoplankton marker concentrations appear in the record (Figure 8.1d).

Another result from this thesis is, that $PIPSO_{25}$ based on HBI trienes more likely reflects sea ice cover in relation to summer conditions because HBI trienes were predominantly distributed in open marine, ice-free areas. In contrast, sterols were found to not have environmental preferences but were higher concentrated in the zone of sea ice edges.

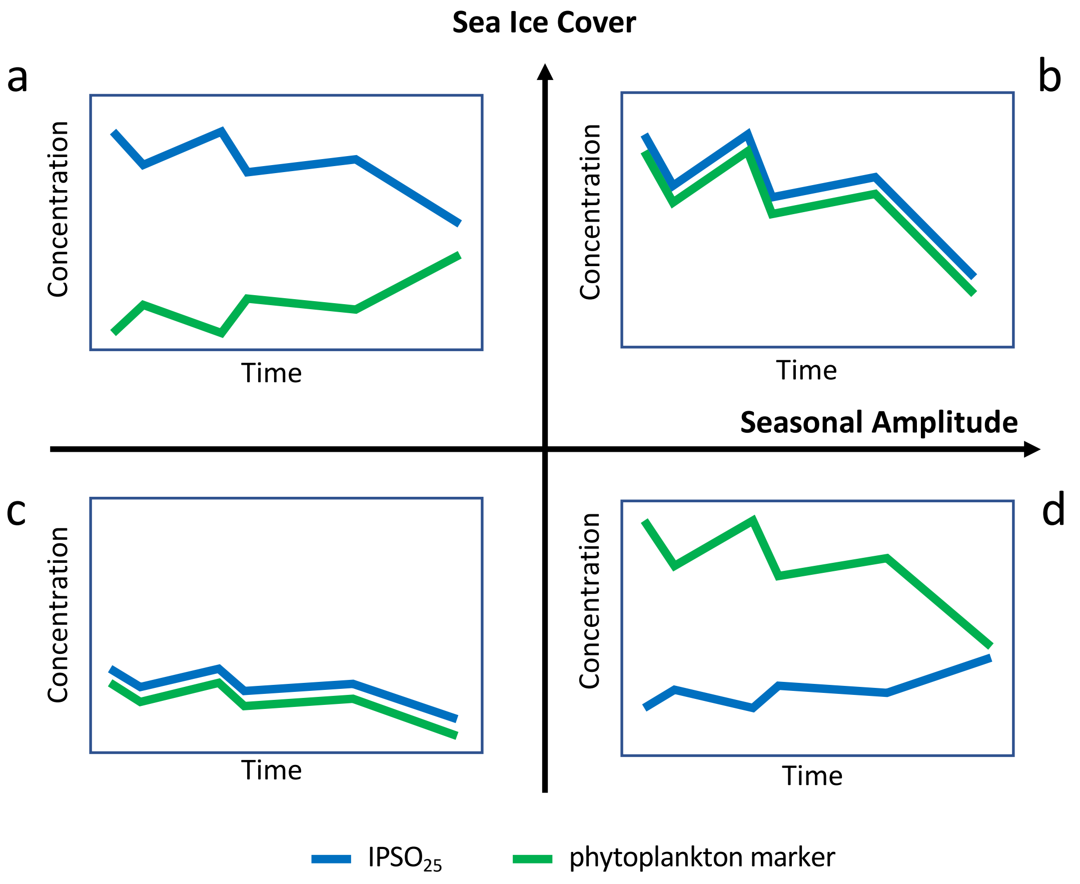

Figure 8.1 The theoretical concept of $IPSO_{25}$ interpretation depending on absolute biomarker concentrations and pattern of both sea ice and phytoplankton biomarker.

So, sterols and sterol-based PIPSO$_{25}$ might therefore be rather indicators for spring sea ice edges as they benefit from sea ice edge-open marine interactions. In summary, IPSO$_{25}$ and PIPSO$_{25}$ are rather indicators of sea ice dynamics and sea ice properties, such as thickness or the velocity of retreat, than of absolute sea ice cover. Also, the differences between WSI and PIPSO$_{25}$ show the gradients between winter and spring sea ice according to the sea ice seasonality.

From the high-resolution records of the second study (Part II) I suggest a positive relationship of IPSO$_{25}$ production to SAM and almost no impact of ENSO. During a positive SAM, the WAP is more likely characterized by warmer ocean temperatures and higher storm frequency (Martinson and McKee, 2012; Meredith and King, 2005). This suggests that warmer temperatures and high seasonal dynamics promote IPSO$_{25}$ production (as indicated in Figure 8.1b) and a high seasonal amplitude might overprint the signal of sea ice cover indicated by PIPSO$_{25}$. So, for a comprehensive reconstruction of sea ice cover one should always consider an ensemble of other sea ice and climate proxies like phytoplankton marker, diatom assemblages, ice core data (MSA, ssNa^{+}), geochemical data or simply the total biomarker concentrations in comparison to the entire record.

Within this thesis, I found promising results that IPSO$_{25}$ and PIPSO$_{25}$ may improve paleo sea ice reconstructions in Antarctica. This might contribute to an enhanced capability of climate models for future projections of Antarctic climate and sea ice interrelations. The newly retrieved data is crucial as reference data for future calibration studies at the WAP but also for the Southern Ocean in general. Based on the results of this thesis, I strongly recommend to conduct a comprehensive assessment of biomarkers in surface sediments (e.g. using satellite observations) for every region prior to paleo sea ice studies for an enhanced interpretation of the different biomarkers and derived indices. As shown in this thesis, the PIPSO$_{25}$ index works well with HBI Z-trienes and brassicasterol at the WAP, whereas a PIPSO$_{25}$ based on dinosterol seems to resolve past sea ice better in the Amundsen Sea (Lamping et al., 2020). Additionally, a data base with reference data of evaluated surface sediments, providing information of the regional characteristics, interpretation and application of PIPSO$_{25}$ could be established. Such a data base may eventually obviate the need for such evaluation pre-studies and would allow to focus on paleoenvironmental studies.

In the light of previous paleo sea ice (e.g. Barbara et al., 2016; Etourneau et al., 2013), recent (Clem et al., 2016; Stammerjohn et al., 2008b) and my own studies, sea ice investigations at the WAP should always take into account large-scale atmospheric circulation patterns. A consideration of these circulation patterns could support interpretations of paleo climate and sea ice reconstructions regarding influences from e.g. storms, upwelling of CDW or the “Föhn” effect on the east side of the AP (Klemp and Lilly, 1975). Under progressing global warming, positive SAM is establishing and higher ocean temperatures are observed at the WAP. The warm SSTs and enhanced heat flux from the ocean to the atmosphere are strengthening low pressure cells (and therefore SAM) and may establish a positive feedback at the WAP (Yuan et al., 1999). I therefore assume, that future sea ice will face a high seasonality, disturbance and likely a retreat, which would hereafter reinforce a positive SAM and a strengthening of the SWWs. Due to the strong atmospheric-sea-ice-ocean interactions, modelling of past and future sea ice at the WAP must specifically consider the forcing from ENSO and SAM for significant results.

Overall, the impact of SAM and ENSO on the west, and especially on the east AP is still not resolved well. Recently, a study from Etourneau et al. (2019) found oceanographic patterns to be the main driver of sea ice and ice sheet stability on the east AP. But still, due to sparse data, a reconstruction of the complex oceanographic and atmospheric interactions and a detailed assessment of ENSO and SAM impacts on sea ice is still not possible for the east AP. To study this, a suite of short and long sediment cores, retrieved on the *Polarstern* cruises PS97 and PS118, are available for temporal and spatial high-resolution sea ice studies. Such a high spatial coverage of the area could be used to develop a detailed conceptual 4D-sea ice model of this region (Figure 8.2) and this data could be integrated in a coupled atmosphere-ocean-model. With such a model, a far more better understanding of sea ice interactions with atmospheric and oceanographic circulation patterns is possible. This would enhance the capability of regional sea ice modelling at the WAP which is often hampered by the unique geographic configuration of the peninsula.

For further sea ice reconstructions, a compilation of existing biomarker data (with comparable stratigraphic units and revised, reliable age models) as aimed by the PAGES C-side working group would gain the benefit the sea ice research community and would make paleo sea ice data more accessible for modelling studies. Further, studies of $IPSO_{25}$ on its source organisms or its pathway from the ocean surface into the sediment could enhance a more detailed view on past sea ice using this biomarker.

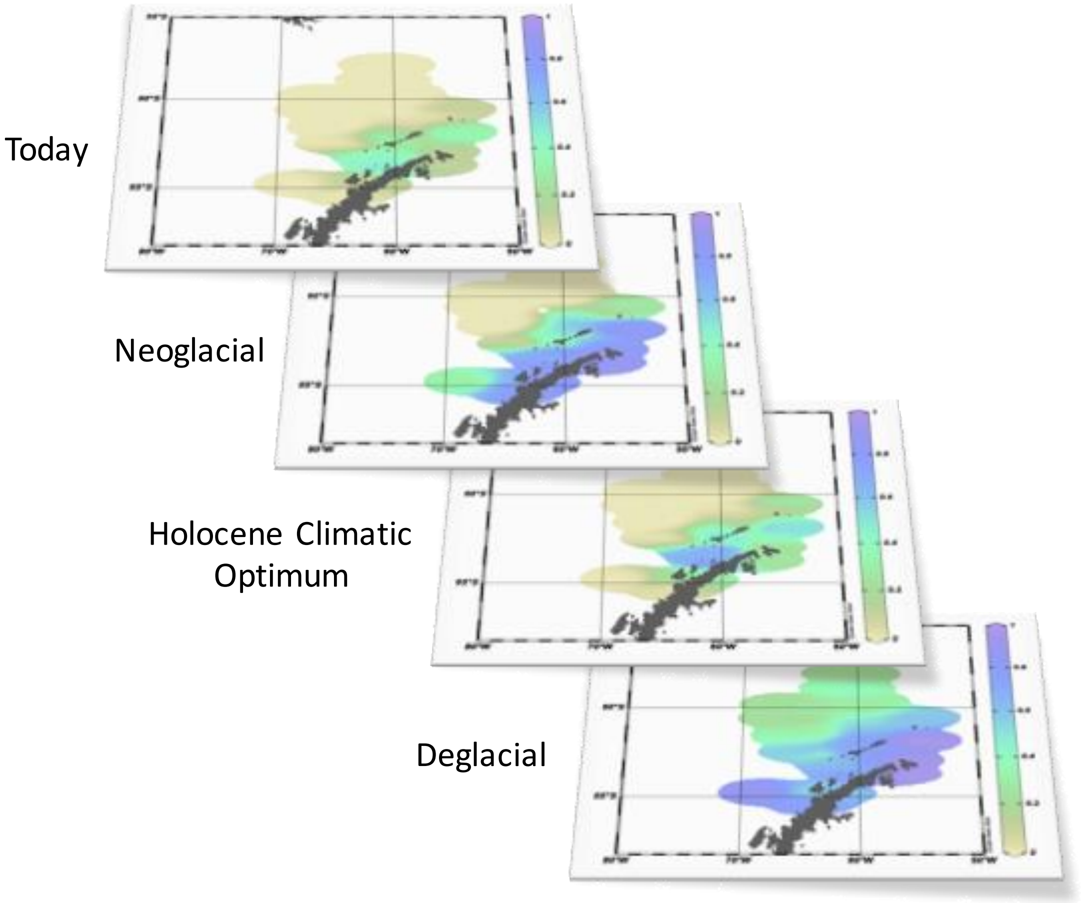

Figure 8.2 Example of a 4D-model based on reconstructed sea ice conditions at the Antarctic Peninsula with the novel tool $IPSO_{25}$ showing the sea ice distribution in different spatial and temporal dimensions. Data could be used from published studies and examination of available sediment cores. Colors and time intervals based on fictional numbers for demonstration.

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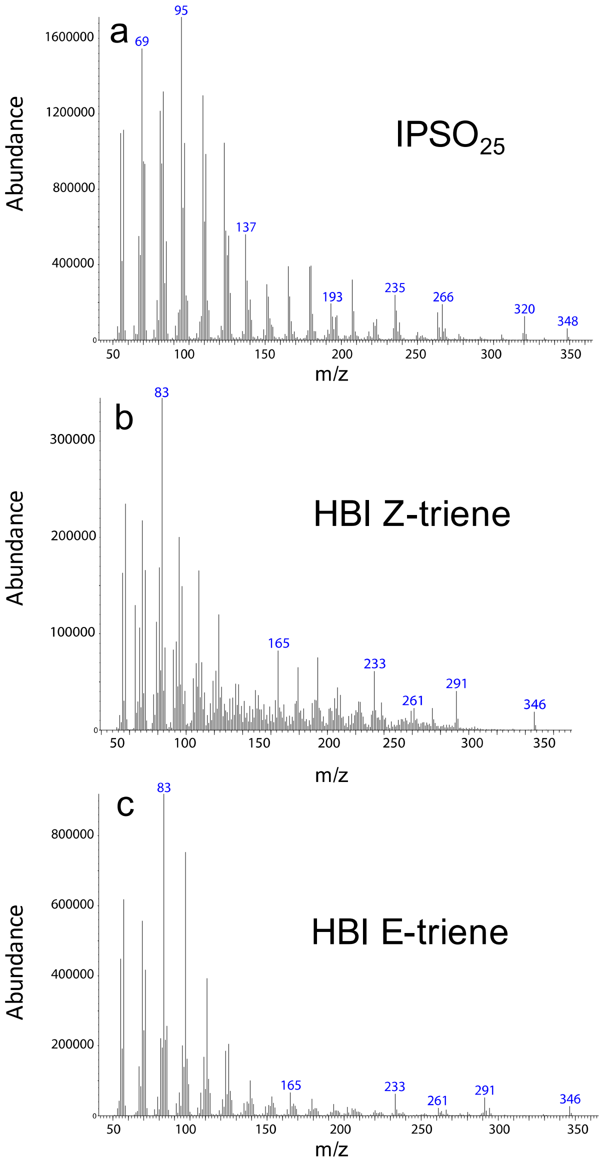
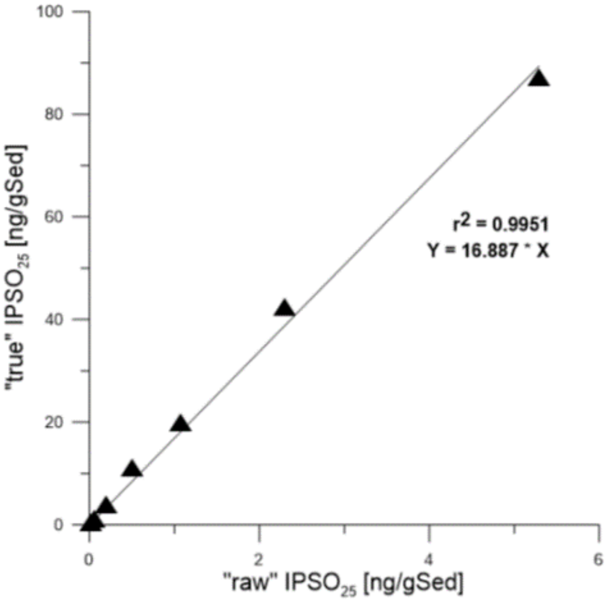
10. APPENDIX



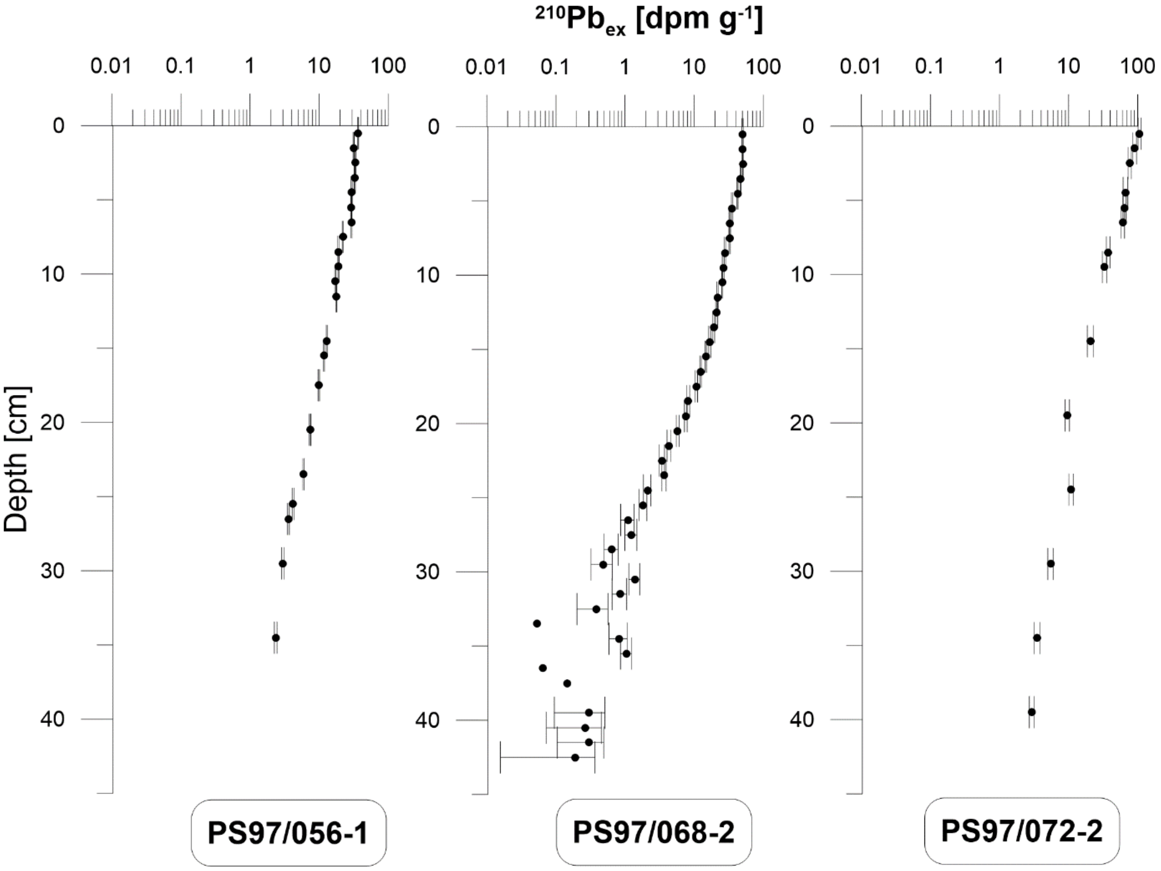
Appendix 1 Examples of mass spectra of IPSO$_{25}$ (m/z 348), HBI Z-triene and E-triene (both m/z 346) obtained from surface sediments in the study area.

APPENDIX

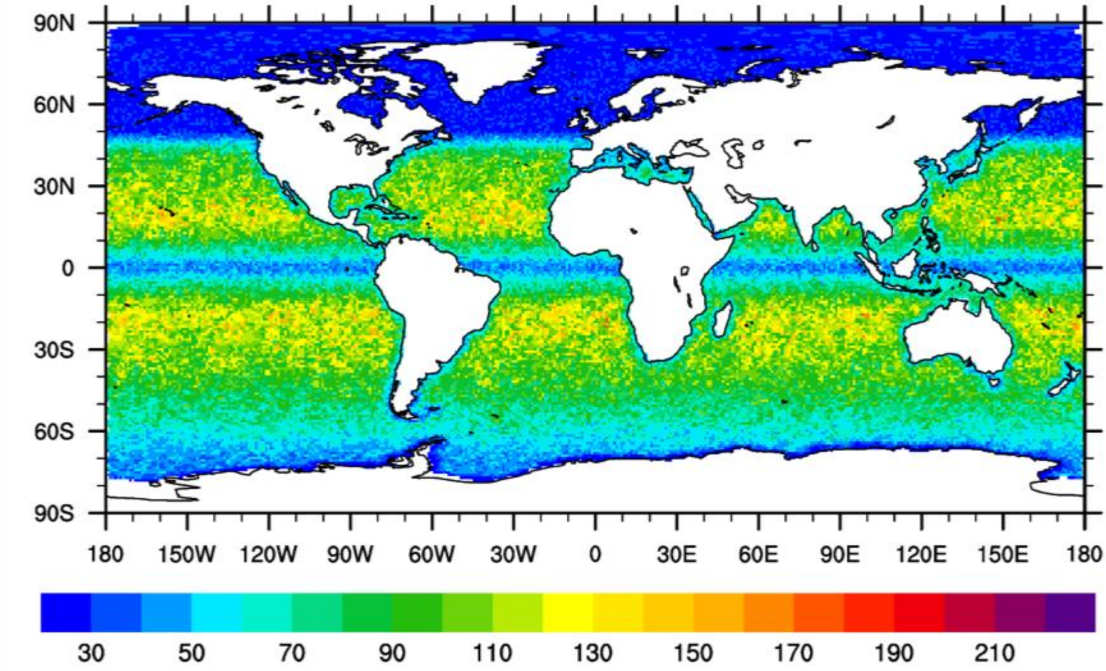


Appendix 2 Example calibration curve for the quantification of $IPSO_{25}$. Different (true) $IPSO_{25}$ concentrations determined via gas chromatography-flame ionization are plotted against (raw) $IPSO_{25}$ concentrations determined via gas chromatography-mass spectrometry using selected ion monitoring (*m/z* 348). The instrumental response factor is obtained from the regression line.

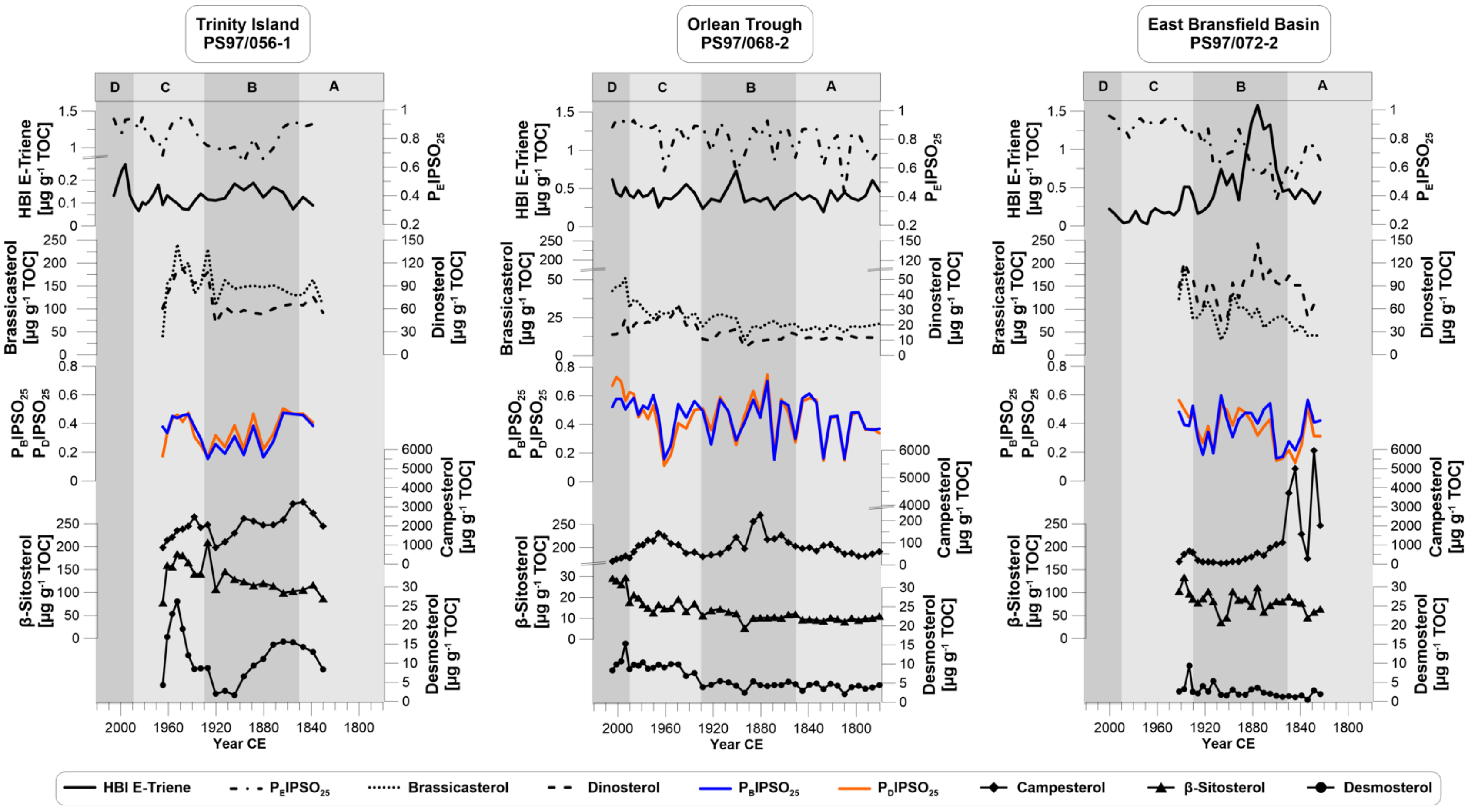
Appendix 3 Excess ^{210}Pb activity from the sediment cores with depth in dpm (disintegration per minute) per gram with error bars (1 σ).



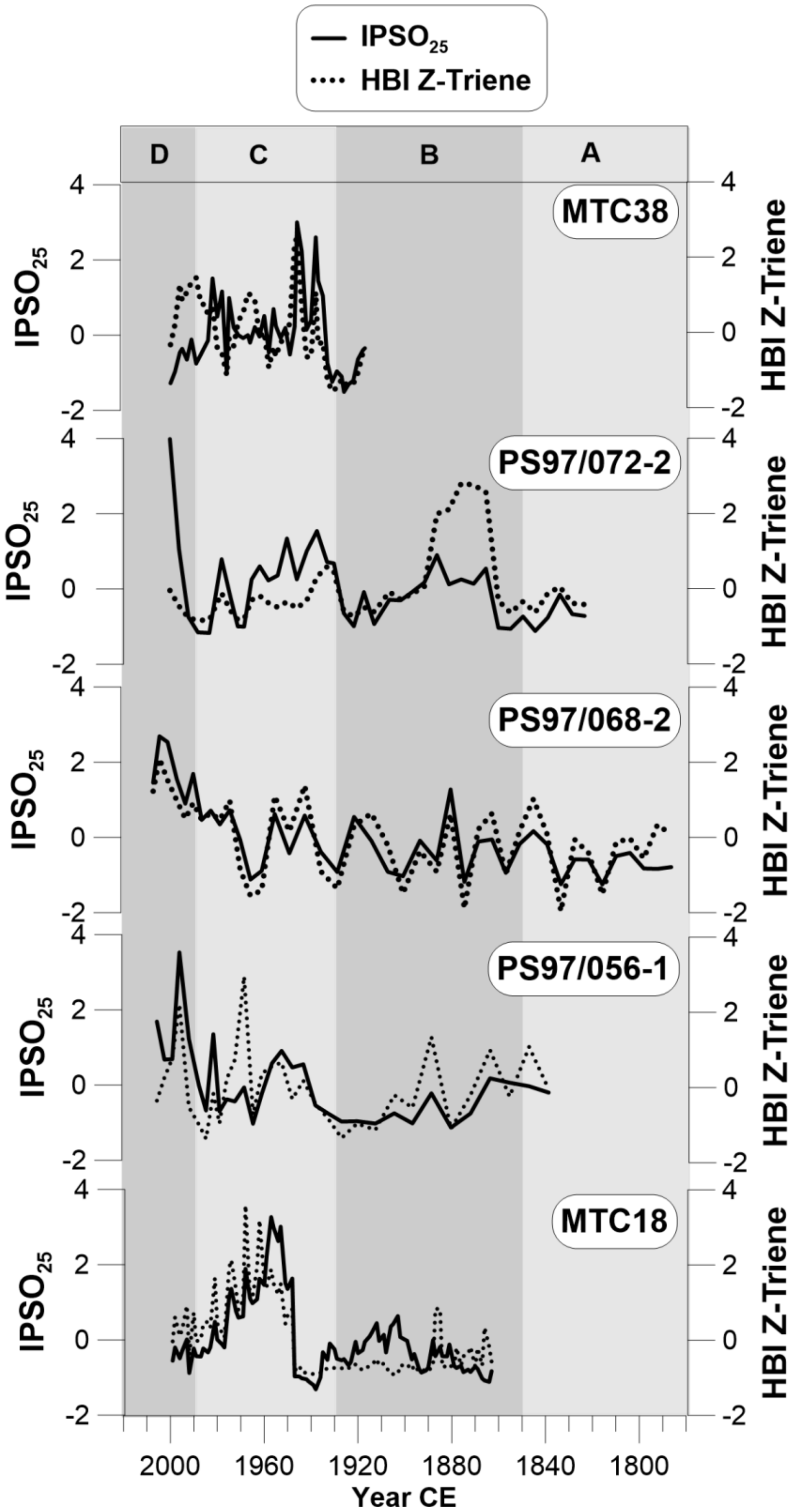
Appendix 4 The resolution of the ocean model in AWI-ESM2.



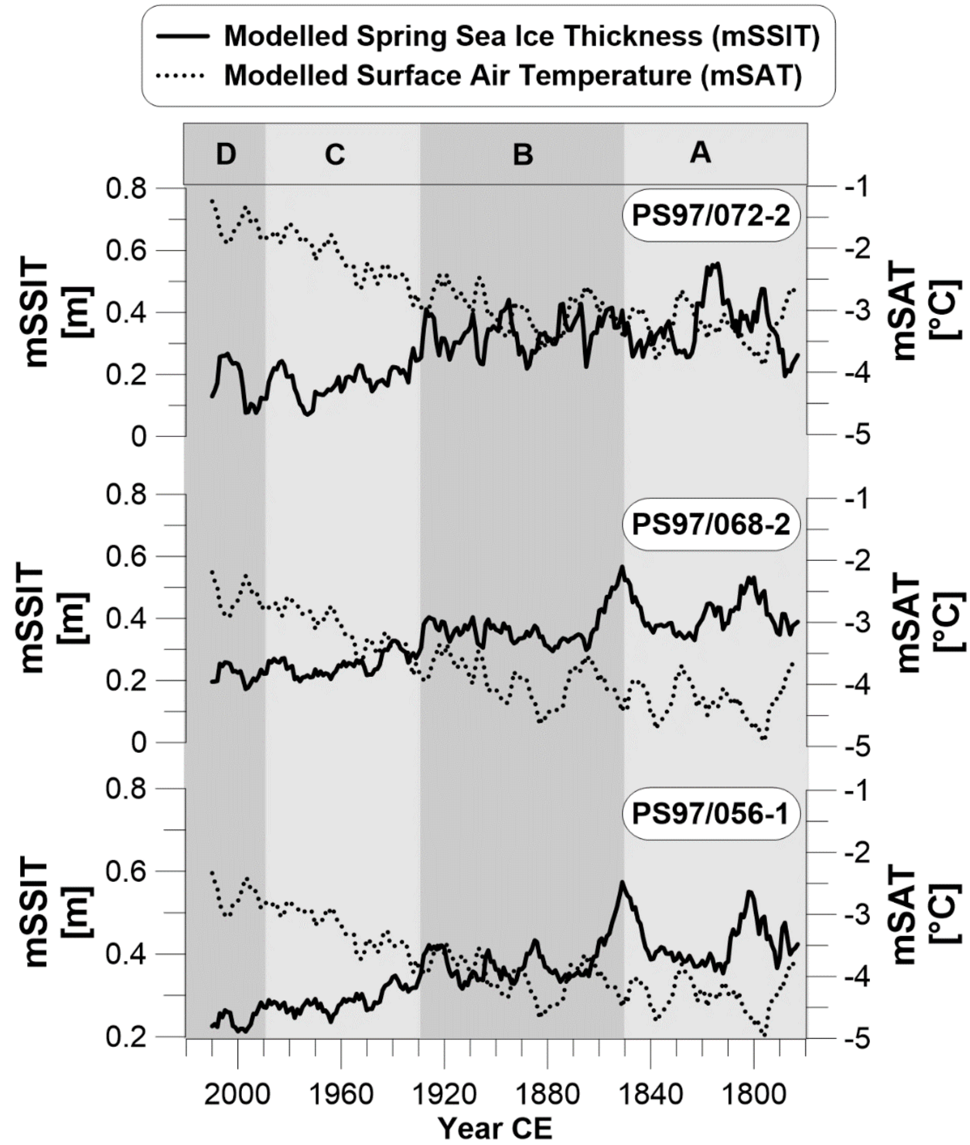
Appendix 5 Additional analytical biomarker results from all three core sites including (from top to bottom) HBI E-trienes, the sea ice index P_EIPSO_{25}, brassicasterol and dinosterol (Kanazawa et al., 1971; Volkman, 2003) with their according sea ice indices P_BIPSO_{25} and P_DIPSO_{25}, respectively. The terrestrial biomarkers campesterol and ß-sitosterol (Volkman, 1986) were not used for sea ice estimations. Desmosterol is suspected to be related to sea ice (Cárdenas et al., 2019) but was not considered in our discussion as well. Vertical grey bars denote the stratigraphic units A to D.



Appendix 6 The normalized biomarker $IPSO_{25}$ and HBI Z-triene from eastern AP (MTC38A) and western AP (MTC18A) (Barbara et al., 2013) compared to biomarker records from this study. High biomarker concentrations are evident in all records since 1930, or later, pointing to a shift towards an environment with dynamic sea ice seasons supporting higher primary production. Vertical grey bars denote the stratigraphic units A to D.



Appendix 7 Additional numerical model data from spring sea ice thickness (mSSIT, 10 year running mean) and surface air temperature (mSAT, 10 year running mean) from all three core sites. Vertical grey bars denote the stratigraphic units A to D.



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