

Deglacial and Holocene ~~Sea~~ ice and climate dynamics in the Bransfield Strait, at the Western-Northern Antarctic Peninsula

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Abstract

The reconstruction of past sea ice distribution in the Southern Ocean is crucial for an improved understanding of
ice-ocean-atmosphere feedbacks and the evaluation of Earth system and Antarctic ice sheet models. The ~~Western~~
Antarctic Peninsula (WAP) is experiencing ~~rapid-a~~ warming since the start of regular monitoring of the
atmospheric temperature in since the 1950ies. ~~Tand~~ the associated decrease in sea ice cover contrasts the trend of

growing sea ice extent in ~~eastern~~ East Antarctica. To reveal the long-term sea ice history at the Northern Antarctic Peninsula (NAP)WAP under changing climate conditions we examined a marine sediment core from the eastern basin of the Bransfield Strait covering the last Deglacial and the Holocene. For sea ice reconstructions, we focused on the specific sea ice biomarker lipid IPSO₂₅, a highly branched isoprenoid (HBI), and sea ice diatoms, whereas a phytoplankton-derived HBI triene (C_{25:3}) and warmer open ocean diatom assemblages reflect predominantly ice-free conditions. We further reconstruct ocean temperatures using glycerol dialkyl glycerol tetraether (GDGTs) and diatom assemblages, and compare our sea ice and temperature records with published marine sediment and ice core data. ~~Our results document a retreat of the WAP ice shelf fromat 13.89 ka BP on (before present). A~~
~~m~~Maximum sea-ice cover is observed during ~~at 12.9 ka BP indicating~~ the Antarctic Cold Reversal (13.8 ka - 13 ka BP), while, ~~seasonally ice-free conditions permitting (summer) phytoplankton productivity are reconstructed~~
~~for the late Deglacial and the early Holocene from 13 ka to 8.3 ka BP. while a still extended but variable sea ice~~
~~coverage characterized the core site during the early Holocene from 11.7 ka to 8.2 ka BP.~~ An overall decreasing sea ice trend throughout the Middle Holocene ~~is accompanied by~~ coincides with a successive summer ocean warming and increasing phytoplankton productivity. The Late Holocene is characterized by a highly variable ~~unstable~~ (winter) sea ice ~~ever~~ concentrations ~~conditions~~ and a sustained decline in ~~further~~ the duration and/or concentration of spring sea ice ~~decline until 0.5 ka BP.~~ Overall diverging trends in GDGT-based TEX₈₆L and RI-OH' SOTs are found to be linked to opposing spring and summer insolation trends, respectively.

Key Words: Bransfield Strait ~~Western Antarctic Peninsula~~, Holocene, sea ice cover, IPSO₂₅, highly branched isoprenoids, diatoms, GDGTs

1 Introduction

Sea ice significantly affects the global climate system through its impact on the atmosphere-ocean exchange of heat and gas, the physical and chemical properties of the water masses, ocean circulation, primary production and biogeochemical cycles (Chisholm, 2000; Vancoppenolle et al., 2013). Sea ice cover limits evaporation, affects precipitation and increases the reflection of solar radiation due to a high albedo (Allison et al., 1982; Butterworth and Miller, 2016; Turner et al., 2017). When sea ice forms, cold and dense brines develop, contributing to the formation of intermediate and deep waters (Nicholls et al., 2009). Importantly, the down-welling of these dense water masses can prevent warm currents from reaching the continental ~~slope-shelf where they stimulate the basal melt and stimulating basal melt~~ of Antarctic ice shelves, with implications for the stability of ice sheets and ~~eventually~~ global sea level (Cook et al., 2016; Escutia et al., 2019; Etourneau et al., 2019; Hellmer et al., 2012;

Huss and Farinotti, 2014). During the spring season, sea ice melting ~~stimulates-boosts~~ marine primary production by seeding algal cells, ~~the-release-of-releasing~~ nutrients and by promoting ocean stratification and a shallow mixed layer depth (Arrigo et al., 1997; Vernet et al., 2008). In addition, nutrient supply can be locally enhanced by ~~increasing~~ wind-driven upwelling activity along the sea ice edge, ~~thus triggering phytoplankton blooms~~ (Alexander and Niebauer, 1981). Enhanced carbon fixation through this ~~nutrient~~ sea ice-stimulated biological pump hence leads to an increase of biological material transport and organic carbon export to the ocean floor, thus ~~contributing to lower~~ lowering surface $p\text{CO}_2$ (Han et al., 2019; Kim et al., 2004; Schofield et al., 2018; Wefer et al., 1988).

Since satellite-based sea-ice data became available in 1979, fast and profound changes have been observed ~~both in the Arctic and as well as West Antarctica globally due and ascribed~~ to anthropogenic global warming (IPCC, 2021). The Western Antarctic Peninsula (WAP), in particular, is experiencing a rapid warming of the atmosphere (Carrasco et al., 2021; Vaughan et al., 2003) and the ocean (Cook et al., 2016). This ~~is~~ ~~are~~ accompanied ~~is~~ ~~accompanied~~ by rapidly retreating glaciers and ice shelves (Cook et al., 2016; Rignot et al., 2019) and by ~~significant-remarkable~~ ~~remarkably~~ loss of sea ice cover in the adjacent seas (Parkinson and Cavalieri, 2012).

For an assessment of the region's past sensitivity to climate change, the deglacial and Holocene climate history of the Antarctic Peninsula (AP) has been studied extensively. The Deglacial, the transition from the Last Glacial Maximum (LGM, Clark et al., 2012) to the Holocene, is characterized by a rapid warming punctuated by a distinct cold event, the so-called Antarctic Cold Reversal (ACR) from 14.7 ka to 13 ka BP (EPICA Community Members, 2004; Mulvaney et al., 2012; Pedro et al., 2016). This drastic cooling of both atmosphere and ocean temperatures ~~in the high Southern latitudes~~ is well reflected in ~~recorded by~~ stable isotope ~~records of~~ ~~in~~ Antarctic ice cores and ~~within~~ marine sediments (Blunier and Brook, 2001; Domack et al., 2001; Jouzel et al., 1995; Morigi et al., 2003; Stenni et al., 2001). From the Deglacial towards the Middle Holocene, the Antarctic Peninsula Ice Sheet (APIS) retreated rapidly from the outer shelf to its modern configuration with ~~heavy-high~~ melt water discharge (Bentley et al., 2014). Several ~~syntheses~~ ~~comparisons between marine and lacustrine~~ of Holocene climate ~~records~~ ~~reflected~~ ~~in reflected from marine and lake sediment cores~~ reveal that the timing of both hydrological and environmental changes ~~was is~~ highly variable ~~across~~ at the WAP (Allen et al., 2010; Ingólfsson et al., 2003; Minzoni et al., 2015; Roseby et al., 2022; Sjunneskog and Taylor, 2002; Totten et al., 2022). ~~The ice core records from James Ross Island (JRI) at the northeastern tip of the AP shows a pronounced warming between about 12 and 11 ka BP followed by a cooling trend until about 9 ka BP and stable temperatures until 2.5 ka BP. From 2.5 ka BP in the Late Holocene cooling was reversed since temperatures cooled until 0.6 ka BP (Mulvaney et al., 2012).~~ An overall consensus, ~~however~~, is that WAP ocean temperatures ~~were in the WAP was~~, in comparison to the Deglacial or the Late Holocene, warmer during the Early and Middle Holocene ~~Optimum~~, i.e. between 12 ka and 4 ka BP

91 (Shevenell et al., 2011). In contrast, ~~marine sediment records show many multiple different climate patterns for the~~
 92 Late Holocene ~~shows many different climate patterns~~ around the AP, including a continuous Neoglacial cooling
 93 (Etourneau et al., 2013). ~~whereas other records other studies resolve warmer and colder phases such as the~~
 94 ~~Medieval Climate Anomaly and/or the Little Ice Age (Bentley et al., 2009).~~
 95 Knowledge of past Southern Ocean sea ice variability is crucial ~~to for accurately~~ modelling climate feedbacks
 96 ~~impacting the Antarctic ice sheet stability since the LGM~~ (Crosta et al., 2022). For periods beyond the satellite
 97 era, ~~information on past sea-ice conditions~~ knowledge is based on proxies from marine sediments, ~~and~~ ice cores
 98 (e.g. Bracegirdle et al., 2015, 2019; Crosta et al., 2022; Escutia et al., 2019; Thomas et al., 2019), ~~and snow petrel~~
 99 ~~stomach oil deposits~~ (McClymont et al., 2022). ~~At present, most climate mModels, however, do not only~~ often fail
 100 to reproduce ~~seasonal sea ice eyes~~ observed sea ice trends of the satellite era; ~~simulated sea ice~~
 101 ~~conditions~~ reconstructions and observations of sea ice for both glacial and interglacial periods ~~and also~~ often
 102 disagree with geological proxies (Roche et al., 2012). Ice-core based sea ice reconstructions ~~for the LGM are~~
 103 primarily use based on the concentrations of sea salt sodium (WAIS Divide Project Members, 2015). However,
 104 since sea ~~salt~~ aerosols might be overprinted by the highly variable wind direction and meteorological conditions
 105 in Antarctica, ~~and thus not reflect~~ sea salt records may not sufficiently be consistent in reflecting regional sea ice
 106 conditions (Thomas et al., 2019). Although marine sediment ~~records usuallys mostly~~ have a lower temporal
 107 resolution than ice cores, ~~they marine proxy reconstructions~~ can resolve regional and ~~depending on the spatial~~
 108 ~~distribution of sediment cores - of/or~~ large-scale changes in sea ice conditions, as well as sea surface and
 109 subsurface ocean temperature, primary productivity and marine ecology (Hillaire-Marcel and de Vernal, 2007). In
 110 addition to commonly used geochemical, lithological and microfossil proxies (e.g. ice rafted debris (IRD), diatom
 111 assemblages, total organic carbon), new approaches focus on specific organic biomarkers - highly branched
 112 isoprenoids (HBIs) - as reliable proxies to distinguish between open marine and seasonally sea ice covered
 113 environments. The di-unsaturated HBI IPSO₂₅ (Ice Proxy for the Southern Ocean, C_{25:2}, Belt et al., 2016; Massé
 114 et al., 2011) that is produced by sea ice algae and deposited on the ocean floor after the sea ice melt in spring has
 115 already been applied ~~for in~~ Antarctic sea ice reconstructions (e.g. Barbara et al., 2013; Denis et al., 2010; Etourneau
 116 et al., 2013). Following the phytoplankton-PIP₂₅-sea-ice index (-PIP₂₅) approach for the Arctic (Müller et al.,
 117 2011), IPSO₂₅ has been combined with phytoplankton-derived HBI trienes and/or sterols phytoplankton to
 118 determine the phytoplankton-IPSO₂₅ sea ice index ~~called~~ PIPSO₂₅ (Vorrath et al., 2019), which has been
 119 successfully evaluated with recent Antarctic spring sea ice concentrations (Lamping et al., 2021). ~~Other studies~~
 120 applied PIPSO₂₅ and examined its potential for sea ice reconstructions over periods of the industrial era (Vorrath
 121 et al., 2020) and over-deglacial and Holocene time intervals in has been used in paleo-sea ice studies from the

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Amundsen Sea (Lamping et al., 2020). ~~Hence, the combination to~~ Combining these new molecular proxies with the classical diatom assemblage approach and/or geochemical ice core proxies ~~provides~~ offers a thorough assessment of ~~unique opportunity to robustly reconstruct past sea ice conditions at the WAP...~~

Here, we present a marine sediment record covering the past 13.89 ka BP ~~and to~~ reconstruct Deglacial and Holocene environmental conditions ~~in the eastern northern Bransfield Strait at the NAP~~ at the northernmost position of the WAP. Our study is based on a multiproxy approach focusing on the sea ice biomarker IPSO₂₅, an open ocean marine phytoplankton biomarker (HBI triene), and on glycerol dialkyl glycerol tetraether lipids (GDGTs) for subsurface ocean temperatures (SOT). Additional ~~estimates~~ information of primary productivity, about the probability of winter sea ice coverage (WSI) and summer sea surface temperature (SSST) comes from bulk sediment organic carbon and biogenic silica contents and diatom assemblages using transfer functions, respectively. ~~In an intercomparison, we evaluate the different approaches to reconstruct sea ice conditions and ocean temperatures.~~ We discuss ~~We compare~~ discuss and compare our proxy results in regard of ~~with~~ other marine sediment and ice core records ~~spanning the Holocene~~ providing further insight into the environmental dynamics at the Antarctic Peninsula across the Deglacial and the Holocene.

2 Material and Methods

2.1 Study Area

The Bransfield Strait is located between the NWAP and the South Shetland Islands (SSI) (Fig. 1a), ~~comprising a trough (> 2000 m) lying between a narrow shelf to the north (SSI) and a broad shelf area to the south (AP).~~ Within this area, a shallow shelf and deeper depressions characterize the Bransfield Basin with water depths exceeding 2000 m (Fig. 1b). The shelf areas ~~were~~ as affected by intense ice sheet dynamics during the last glaciation (Canals and Amblas, 2016b; Ingólfsson et al., 2003) leaving ice sheet grounding lines and glacial troughs on the sea-floor (Canals et al., 2016; Canals and Amblas, 2016a).

The modern Bransfield Basin is influenced by complex oceanic current systems, ~~which are not fully constrained because three different water masses enter the basin from the east and west (Moffat and Meredith, 2018; Sangrà et al., 2011) and their mixing is not well understood.~~ The Ceold (< 0 °C) and relatively salty Weddell Sea Water (WSW) enters from the east, flows alongshore the peninsula and fills the Bransfield Strait basins below 150 m water depth ~~surface~~. The WSW is also observed ~~at greater depths (200-600 m) north of the SSI (outer shelf) and at Elephant Island due to wind-driven modulation (Meijers et al., 2016).~~ In the western part of the Bransfield Strait, the WSW mixes with warmer ~~a second water mass, the~~ Bellingshausen Sea Water (BSW; 0 - 50 m water depth) and Circumpolar Deep Water (CDR; 200 - 550 m water depth; Collares et al., 2018; Sangrà

et al., 2011, 2017), which ~~are~~ transported in a branch of the Antarctic Circumpolar Current (ACC) over the
Anvers Shelf. It conveys well-stratified, fresh and warmer ($> 0^{\circ}\text{C}$) surface water to a depth of about 50 m (Sangrà
et al., 2011). A third water mass ~~o~~ Also originating from the ACC is a third, deeper water mass. Originating from
the Circumpolar Deep Water (CDW), that is present between 200 m and 550 m (Sangrà et al., 2017). BSW and
CDW flow eastward along the SSI, turn around and flow westward at the northern tip of the islands (Sangrà et al.,
2014). BSW and WSW forms the subsurface Bransfield front with the CDW at depth and the surface Peninsula
Front (PF) with the WSW, that runs parallel to the Antarctic mainland (Sangrà et al., 2011, 2017). The interplay
of currents leads to a stratification of the water column of pronounced pycnocline within the upper 20 m of the
water column in summer, with accompanied by a steep temperature gradient in the first upper 100 m, as below
sea surface. This ~~can be~~ observed in CTD hydrographic profiles from the Bransfield Basin that show a dominance
of WSW below 200 m (see Fig. 1c and Sangrà et al., 2011). The eddy system at the Peninsula Front is assumed to
play a key role for mixing and upwelling of the different surface and subsurface water masses (Sangrà et al., 2011;
Zhou et al., 2002), while several glaciers from the WAP influence coastal surface water due to meltwater discharge
~~and also transport dense bottom waters to the Bransfield Basin (Meredith et al., 2018).~~
Modern sea ice conditions at the core site in the eastern Bransfield Strait are characterized by a mean winter sea
ice concentration of ca. 50%, which declines to 18% and less than 2% sea ice concentration during spring and
summer, respectively (cf. Vorrath et al., 2019). ~~Modern sea ice conditions follow a declining trend in all seasons~~
with a nearly sea ice free summers (Hobbs et al., 2016; Vorrath et al., 2020). ~~While atmospheric temperatures show~~
a rising trend since the 1950ies ocean temperatures (Carrasco et al., 2021), ocean temperatures are increasingly
influenced by warm water intrusions and higher sea surface temperatures (Martinson and McKee, 2012; Meredith
and King, 2005). At the core site, mean annual sea surface temperatures are -0.6°C with up to 0.8°C during
summer (WOA 18; Boyer et al., 2018; Locarnini et al., 2018).
Primary production in the Bransfield Strait is mainly driven by mixing of water masses at the fronts (Gonçalves-
Araujo et al., 2015), mixed layer depth and upwelling (Sangrà et al., 2011), sea ice dynamics (Vernet et al., 2008)
and iron availability (Klunder et al., 2014). High concentrations of chlorophyll *a* and diatoms are distributed north
of the ~~Peninsula Front~~ PF and at the SSI, while lower production and communities of ~~nanoplanktonic plankton~~
~~nanoflagellates~~ are found between the Peninsula Front and the WAP (Gonçalves-Araujo et al., 2015). Further,
changes in coastal primary production are driven by upwelling, elevated iron distribution availability, as well as
the nutrient release and surface water stratification generated by melting sea ice in the austral spring and the retreat
of sea ice cover in spring releasing nutrients and stabilizing the water column (Vernet et al., 2008). A ~~close robust~~
link between marine primary production at the surface in surface waters and the sediment composition at the

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183 underlying ocean floor is reflected in high concentrations of total organic carbon (TOC), pigments, sterols and
184 diatoms (Cárdenas et al., 2019), and supported by studies confirming high fluxes of sinking particles (Kim et al.,
185 2004; Wefer et al., 1988). In the study area, particle flux is highly variable with seasonal peaks occurring in late
186 spring, which accounts for 85% of the total flux (Ducklow et al., 2008). Lithologically, the sediments consist
187 mainly of ~~terrestrial-terri~~terrestrial-terrigenous silt and clay with varying amounts of diatom mud and ooze, and sand (Cádiz
188 Hernández, 2019; Lamy, 2016; Wu et al., 2019).

190 2.2 Sediment samples and age model

191 Piston core PS97/072-1 (62° 0.39' S, 56° 3.86' W, 1993 m water depth, 1583 cm in length) was recovered in the
192 eastern Bransfield Strait Basin during R/V *Polarstern* cruise PS97 (Lamy, 2016) (Fig. 1). The ~~sedimenteore~~sediment is
193 dominated by silt with thin layers of sand, clay, and traces of volcanic ash. Single pebbles are present below 630
194 cm. ~~The core is disturbed~~Since we found disturbed sediments below 1015 cm depth ~~and~~we only considered
195 samples from above this level for our analyses. ~~After an XRF scan the core sampling for different analytical~~
196 ~~approaches~~was done at the Alfred Wegener Institute (AWI) where the the samples were stored frozen in glass
197 vials (for biomarker analysis) and at 4 °C in plastic bags (for micropaleontology).

198 The age model of core PS97/072-1 is based on ¹⁴C-radiocarbon dating of eight ~~ealeite-benthic foraminiferal and~~
199 ~~mollusk fragments~~samples with the mini carbon dating system (MICADAS) available at AWI (Mollenhauer et
200 al., 2021). From the conventional ¹⁴C age we subtracted a reservoir age based on modelling by Butzin et al. (2017)
201 and also subtracted an estimated ventilation age of 1200 years to account for the considerable water depth of our
202 site (see table supplement section 1), before we calibrated the ages with the calibration curve ~~SHIntCal20~~(Reimer
203 et al., 2020)~~(Hogg et al., 2020)~~to calendar years before present (cal BP) with Calib 7.1 (Stuiver et al., 2018). To
204 estimate the top-age of the core top, TOC and biogenic opal data of the piston core were matched with data from
205 a multicore from the same sampling site that has been previously dated via ²¹⁰Pb (Vorrath et al., 2020; supplement
206 section 2). Ages of sediments below the oldest radiocarbon date (868.5 cm; 12.04 ka BP) were extrainterpolated
207 assuming a constant sedimentation rate. AThe downcore ages between the lowest radiocarbon dates sample and
208 the core bottom was interpolated based on previous sedimentation rates. We applied the Bayesian age modelling
209 tool *hummingage*, a freely available tool developed at AWI; that has been successfully applied in previous studies
210 (e.g. Ronge et al., 2021). As the lack of age constraints between 12 ka and 6 ka BP may introduce chronological
211 uncertainties, we only focus on overall trends reflected in our data and refrain from detailed allocations of known
212 climatic events in this older time period.

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2.3 Organic geochemical analyses of piston core PS97/072-1

For the analyses of ~~the bulk~~ several organic ~~geochemical composition~~ components and biomarkers, ~~the~~ ~~334~~ ~~sediments~~ ~~samples~~ were freeze-dried and homogenized in an agate mortar. ~~Prior to sediment homogenization,~~ ~~coarse grains were separated using a sieve (5 µm mesh size).~~ Total carbon (C) and nitrogen (N) were measured with a CNS analyzer (Elementar Vario EL III, error of standards and duplicates < 5%). TOC was measured on 0.1 g of acidified samples (500 µl HCl) and determined in a carbon-sulphur determinator (CS-800, ELTRA, standard error < 0.6%). To identify the source of TOC, measurements of stable carbon isotopes of bulk organic matter were done at Universität Hamburg (UHH), Germany, and at Washington State University (WSU), USA. At UHH, the samples were acidified three times with 100 µl 1 N HCl and dried on a hotplate. High-temperature combustion was done in an Elementar CHNOS Vario isotope elemental analyser at 950 °C and the analysis was conducted with an Elementar IsoPrime 100 isotope ratio mass spectrometer. We calibrated the pure tank CO₂ with the International Atomic Energy Agency reference standards IAEA-CH6 and IAEA-CH7. These and two other standards (IVA Sediment and Sucrose) acted as internal standards in the measurement. The error of continuous standard duplicates was < 0.2‰ and < 0.06‰ for sample duplicates. At WSU, 100 mg of freeze-dried sediment samples were used. An elemental analyzer coupled with an Isoprime isotope ratio mass spectrometer (IRMS) was used, with a precision of 0.1‰. The running standard was a protein hydrolysate calibrated against NIST standards. Isotope ratios are expressed in units per mil (‰). δ¹³C values are expressed in ‰ against Vienna Pee Dee Belemnite (VPDB).

Biogenic opal was estimated ~~on 327 samples~~ following the alkaline extraction procedure described by Mortlock and Froelich (1989), but using 0.5M NaOH as a digestion solution (Müller and Schneider, 1993). Extraction and analysis by molybdate-blue spectrophotometry were conducted at the University of Concepción, Chile. Values are expressed as biogenic opal by multiplying the Si (%) by 2.4 (Mortlock and Froelich, 1989). ~~Opal values could be somewhat overestimated by 2 - 2.5% since we~~ We did not correct for the release of extractable Si from coexisting clay minerals; ~~and thus biogenic opal values could be slightly overestimated~~ (Schlüter and Rickert, 1998). Instrumental precision was ±0.5%; error of duplicates ≤ 3%. Details on the methodology used can be found in Cárdenas et al. (2019).

The extraction, purification and identification of ~~137 samples to identify~~ HBIs followed the analytical protocol published e.g. in Belt et al. (2014) and Vorrath et al. (2019). ~~Prior to extraction, 40 µl 7-hexylnonadecane (7-HND; 0.0019 µg/µl) and 100 µl C₄₆ (0.0098 µg/µl) were added~~ served as internal standards. Lipids were extracted using ultra sonication and a mixture of CH₂Cl₂:MeOH (v/v 2:1; 6 ml). HBIs and GDGTs were separated by means of open column chromatography using SiO₂ as the stationary phase and hexane, and CH₂Cl₂:MeOH (v/v 1:1) as

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244 eluents. HBIs were analyzed by means of an Agilent 7890B gas chromatograph (30 m DB-1MS column, 0.25 mm
 245 diameter, 0.250 µm film thickness) coupled to an Agilent 5977B mass spectrometer (MSD, 70 eV constant
 246 ionization potential, ion source temperature 230 °C). The initial oven temperature of 60 °C was held for 3 min,
 247 ramped to 325 °C within 23 min, and was held at 325 °C for 16 min. HBIs were identified *via* comparison of
 248 their retention times (IPSO₂₅ and HBI triene with RI 2084DB-1MS and 2046DB-1MS, respectively) and mass
 249 spectra with published mass spectra (Belt, 2018) and quantified using the ratio of peak areas of individual HBIs
 250 (*m/z* 346; *m/z* 348) and the 7-HND (*m/z* 266)- standard and consideration of instrumental response factors. The
 251 error of duplicates was <1.4% for IPSO₂₅, <2.6% for HBI trienes. The phytoplankton-IPSO₂₅ index (PIPSO₂₅) was
 252 calculated after Vorrath et al. (2019) as:

$$253 \quad PIPSO_{25} = \frac{IPSO_{25}}{IPSO_{25} + (c \times \text{phytoplankton marker})} \quad (1)$$

254 The concentrations of the phytoplankton-derived HBI HBI z-triene are ~~was is considered as a phytoplankton~~
 255 ~~biomarker and, since the concentrations in these samples are were on at~~ the same level as IPSO₂₅, and the c-factor
 256 was ~~hence~~ set to 1 (Vorrath et al., 2019). To confirm the sea-ice origin of IPSO₂₅, the stable carbon isotope
 257 composition of IPSO₂₅ was examined in 8 samples (with minimum 50 ng carbon) via GC-irm-MS at the GFZ
 258 Potsdam, Germany. The GC (7890N Agilent) equipped with ~~an~~ Ultra1 column (50 m x 0.2 mm diameter, 0.33 µm
 259 film thickness) was connected to a DeltaVPlus isotope ratio mass spectrometer through a modified GC-Isolink
 260 interface. Each sample was separated chromatographically ~~using with~~ a temperature program that started with an
 261 oven temperature of 80 °C, which was held for 3 min, ramped to 250 °C with 3 °C per min and then ramped to
 262 320 °C with 5 °C per min and finally reached temperature of 325 °C with a ramp of 1 °C per min and held for
 263 15 min. The organic substances of the GC effluent stream were oxidized to CO₂ in the combustion furnace held at
 264 940 °C on a CuO/Ni/Pt catalyst. Samples were measured in duplicate and the standard deviation was ≤0.5 %. The
 265 quality of the isotope measurements was checked regularly (~~for each analysis~~) by measuring different *n*-alkane
 266 standards with known isotopic composition of *n*-C15, *n*-C20, *n*-C25 (in equal concentration) and *n*-C16 to *n*-C30
 267 (in various concentrations) ~~–~~ provided by Campro Scientific, Germany and Arndt Schimmelmann, Indiana
 268 University, USA).

269 GDGTs were re-dissolved in 120 µl hexane:isopropanol (v/v 99:1) and filtered through polytetrafluoroethylene
 270 filters (0.45 µm in diameter) and analyzed using high performance liquid chromatography (HPLC, Agilent 1200
 271 series HPLC system) coupled to a single quadrupole mass spectrometer (MS, Agilent 6120 MSD) *via* an
 272 atmospheric pressure chemical ionization (APCI) interface. The individual GDGTs were separated at 30 °C on a
 273 Prevail Cyano column (150 mm x 2.1 mm, 3µm). After injection of the sample (20 µl) it passed a 5 min isocratic
 274 elution with mobile phase A (hexane/2-propanol/chloroform; 98:1:1, flow rate 0.2 ml/min). The mobile phase B

(hexane/2-propanol/chloroform; 89:10:1) was increased to 100% in two steps: a linear increase to 10% over 20 min followed by an increase to 100% within 10 min. During the measurement, the column was cleaned after 7 min via backflush (5 min, flow 0.6 ml/min) and re-equilibrated with solvent A (10 min, flow 0.2 ml/min). The conditions of the APCI were a nebulizer pressure of 50 psi, vaporizer temperature and N₂ drying gas temperature 350 °C, flow 5 l/min, capillary voltage 4 kV, and corona current 5 µA. Following Liu et al. (2020), iGDGTs and branched GDGTs were detected by selective ion monitoring (SIM) of (M+H)⁺ ions (dwell time 76 ms) using their molecular ions (GDGTs-I (m/z 1300), GDGTs-2 (m/z 1298), GDGTs-3 (m/z 1296), crenarchaeol (m/z 1292) and GDGTs-Ia (m/z 1022), GDGTs-IIa (m/z 1036), GDGTs-IIIa (m/z 1050)) and quantified. In relation to the internal standard C₄₆ (m/z 744), 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) were quantified. Also, the branched GDGTs-Ia (m/z 1022), GDGTs-IIa (m/z 1036), GDGTs-IIIa (m/z 1050) were quantified. The hydroxylated GDGTs OH-GDGT-0 (m/z 1318), OH-GDGT-1 (m/z 1316), and OH-GDGT-2 (m/z 1314) were quantified in the scans of their related GDGTs (Fietz et al., 2013). The standard deviation was 0.01 units of TEX₈₆^L.

Kalanetra et al. (2009) showed that GDGT-producing Thaumarchaeota are abundant in subsurface marine waters in both Arctic and Antarctic regions. As Thaumarchaeota were found between 50 m and 200 m water depth in Antarctica (Kim et al., 2012), temperatures based on GDGTs are suggested to reflect sub-surface waters (Etourneau et al., 2013, 2019). Similarly, also RI-OH' based temperatures in Prydz Bay have been interpreted to reflect subsurface water temperatures (Liu et al., 2020). We therefore consider our results to reflect subsurface ocean temperatures (SOTs). We calculated TEX₈₆^L after Kim et al. (2012) with the m/z 1296 (GDGT-3), m/z 1298 (GDGT-2), m/z 1300 (GDGT-1):

$$TEX_{86}^L = \log \log \left(\frac{[GDGT-2]}{[GDGT-1] + [GDGT-2] + [GDGT-3]} \right) \quad (2)$$

and calibrated with SOT = 50.8 * TEX₈₆^L + 36.1 (Kim et al., 2012). (3)

For the calculation of temperatures based on hydroxylated GDGTs we followed the approach of Lü et al. (2015)

$$RI - OH' = \frac{[OH-GDGT-1] + 2 \times [OH-GDGT-2]}{[OH-GDGT-0] + [OH-GDGT-1] + [OH-GDGT-2]} \quad (4)$$

and calibrated it with SOT = (RI-OH' - 0.1) / 0.0382. (5)

For the branched and isoprenoid tetraether (BIT) index for indicating terrestrial organic matter (Hopmans et al., 2004) we used crenarchaeol (m/z 1292) and the branched GDGTs and calculated it as:

$$BIT = \frac{[GDGT-Ia] + [GDGT-IIa] + [GDGT-IIIa]}{[Crenarchaeol] + [GDGT-Ia] + [GDGT-IIa] + [GDGT-IIIa]} \quad (6)$$

2.4 Diatom analyses

We selected a set of 76 samples for the analysis of diatom assemblages. ~~At first, sampling resolution was every 40-50 cm; thereafter, and based on the biogenic opal results, resolution was increased (every 8 cm) at intervals with high variability. and then was increased~~ Freeze-dried samples (20-120 mg) were treated with hydrogen peroxide and sodium pyrophosphate to remove organic matter and clays, respectively, washed several times with DI water until reaching neutral pH. The treated samples were then settled for six hours in B-Ker2 settling chambers to promote an even distribution of settled particles (Scherer, 1994; Schrader and Gersonde, 1978; Warnock and Scherer, 2015). Once the samples were dry, the quantitative slides were mounted with Norland mounting medium (refraction index=1.56). Diatom valves per slide were counted across traverses (at least 400 valves per slide) using an Axioscop 2 Plus and Olympus BX60 at a magnification of $\times 1000$. The counting procedure and definition of counting units followed those of Schrader and Gersonde (1978). We performed two sets of counts, with and without *Chaetoceros* resting spores. Diatoms were identified to species or species group level and, if applicable, to variety or form level following the taxonomy described by e.g., Gersonde and Zielinski (2000), Armand and Zielinski (2001), Esper et al. (2010), Esper and Gersonde (2014a, 2014b). Diatom ~~studies analyses~~ were done ~~by the same investigator~~ at the University of Concepción, Chile, and at Colgate University, USA.

~~Because diatom distribution in the Southern Ocean is directly associated with the temperature zonation and the frontal systems of the ACC (Cárdenas et al., 2019; Esper et al., 2010; Esper and Gersonde, 2014a, 2014b; Zielinski and Gersonde, 1997), diatom species were grouped into ecological assemblages reflecting i) seasonal sea ice – associated with temperatures -1.8 to 0°C; ii) cold open ocean – associated with the maximum sea-ice extent in winter and temperatures between 1 and 4°C; iii) warmer open ocean – with temperatures between 4 and 14°C, and iv) benthic-epiphytic habitats (Buffen et al., 2007; Cárdenas et al., 2019). Additionally, a group of reworked diatoms was identified (supplement section 6). Diatom species were grouped into ecological assemblages reflecting i) seasonal sea ice, ii) cold open ocean, iii) warmer open ocean, and iv) benthic-epiphytic diatoms environments (Buffen et al., 2007; Cárdenas et al., 2019; Esper et al., 2010) (specific group composition is described in detail in supplement section 3). Additionally, a group of reworked diatoms was identified.~~ A Spearman principal component analysis (PCA) was applied to the diatom assemblages to differentiate their temporal distribution.

For estimation of winter sea ice (WSI) concentrations, we applied the transfer function MAT-D274/28/4an ~~to the total diatom counts (including Chaetoceros resting spores). The transfer function which~~ comprises 274 reference samples with 28 diatom taxa/taxa groups and considers an average of 4 analogues (Esper and Gersonde, 2014a). The analogues refer to surface sediments from the Atlantic, Pacific and western Indian sector of the Southern Ocean. ~~There are 10 analogues from the immediate vicinity of the Antarctic Peninsula.~~ The WSI renders sea ice

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concentrations in a 1° by 1° grid for the September average of the period 1981 to 2010 (Reynolds et al., 2002, 2007). The threshold ~~of an~~between the open ocean ~~and the~~ sea ice covered area is set at 15% of sea ice concentration (Zwally et al., 2002) and the average sea ice edge is defined at 40% (Gersonde et al., 2005; Gloersen et al., 1993). ~~The qualitative estimation of sea ice concentration was derived from the abundance pattern of diatom sea-ice indicators (Gersonde and Zielinski, 2000).~~ The estimation of summer sea surface temperature (SSST) came from the transfer function IKM-D336/29/3q comprising 336 reference samples (Pacific, Atlantic and Indian Southern Ocean) with 29 diatom taxa and three factors (Esper and Gersonde, 2014b). The calculations ~~for WSI~~ were done with the software R (R Core Team, 2012) using the packages Vegan (Oksanen et al., 2012) and Analogue (Simpson and Oksanen, 2012).

3 Results

Based on our age model, the sediment core PS97/072-1 covers the last 13.89 ka BP with a mean sedimentation rate of 67 cm/ka and a temporal resolution ranging between 50 and 150 years per sample interval. We note a higher sedimentation rate of 95 cm/ka between 5.5 ka and 3 ka BP and few short-term intervals of ~~significantly~~ ~~particularly~~ lowered (19 cm/ka) and ~~higher~~enhanced (190 cm/ka) sedimentation (Fig. 2).

Organic geochemical bulk parameters (TOC, biogenic opal), concentrations of HBIs (IPSO₂₅, C_{25:3} HBI triene) and diatom species ~~of warmer open ocean conditions and sea ice~~ assemblages of piston core PS97/072-1 are summarized in Figure 3 (additional data can be found in the supplement section 34). TOC increases from very low values of 0.1 wt% at 13.7 ka BP to an average concentration of ~0.8 wt% between 9.9 ka BP and the top of the core with recurring short-lived minima down to 0.03 wt% during the Middle and Late Holocene (Fig. 3f). Some of these TOC minima ~~may be associated with~~occur within thin sandy layers of volcanic ash. Biogenic opal shows a similar pattern with minimum values in the lower part of the record (3.2 wt% at 13.0 ka BP) and increases throughout the Deglacial to Holocene with average values of 30 wt% and a maximum of 54.4 wt% at 5.3 ka BP (Fig. 3e).

Between 13.89 ka and 13.4 ka BP, both IPSO₂₅ and HBI triene concentrations are close to or below the detection limit (0.1 µg g⁻¹ OC). ~~Throughout the record, the~~The IPSO₂₅ concentration ranges between 0.1 to 31.5 µg g⁻¹ TOC, while the concentration of the HBI triene ranges between 0.1 and 6.6 µg g⁻¹ TOC (Fig. 3). IPSO₂₅ is absent before 13.5 ka BP and rises rapidly to maximum values of 31.5 µg g⁻¹ TOC at 12.89 ka BP. Subsequently, concentrations decrease steadily until 8.5 ka BP and then remain ~~at~~an average level of ~4 µg g⁻¹ TOC with a slightly decreasing trend to 1 µg g⁻¹ TOC towards the present and smaller peaks of 10 µg g⁻¹ TOC at 6.0 and 3.0 ka BP. ~~Only traces of the HBI triene occur at very low concentrations is largely absent until 13.0 ka BP, while~~

its concentration and increases to shows high elevated concentrations up to $6.6 \mu\text{g g}^{-1}$ TOC after 8.5 ka BP with large fluctuations of more than $5 \mu\text{g g}^{-1}$ TOC in the Middle Holocene and from 3.4 ka BP to the present. The diatom composition has two contrasting groups indicating open ocean conditions, a cold water assemblage and a warmer water assemblage, and a seasonal sea ice assemblage (Fig. 3; see supplement section 3). The diatom composition has two contrasting groups indicating warm open ocean conditions (Fig. 3a) and seasonal sea ice (Fig. 3c). Although the group reflecting seasonal sea ice is also present throughout the core (mostly >20%), the highest contributions are seen before 13.2 ka BP and between 10.8 and 9.9 ka BP and around 3 ka BP. The contribution of the warmer open ocean assemblage is very low in the Deglacial and Early Holocene, and rises to highest values in the Middle Holocene and remains around 10% in the Late Holocene. A biplot of a principal component analysis (PCA) shows the relationship of the ecological groups along the sediment core for three time intervals with clear dominance of seasonal sea ice before 13.3 ka BP and warmer open ocean conditions after 8.5 ka BP (supplement section 5 and 64).

Sea ice concentration estimates based on diatom assemblages (WSI) and the PIPSO₂₅ index as well as the content of IRD in PS97/072-1 are summarized in figure 4 (a-c). Reconstructed winter sea ice concentrations (% WSI) derived from the MAT transfer function results from the diatom assemblages range from 80% to 90% during the ACR and the Deglacial (13.89 ka – 11 ka BP) and exhibit an overall decreasing trend over the Middle Holocene with distinct fluctuations reaching minimum sea ice concentrations of ca. 65% during the Middle and Late Holocene (Fig. 4a). PIPSO₂₅ values show a similar trend indicating higher sea ice cover during the ACR, the Deglacial and the Early Holocene (PIPISO₂₅ > 0.8) and a successive decline to 0.5 on average throughout the Middle and Late Holocene with a distinct minimum at 0.5 ka BP (Fig. 4b). IRD (lithic particles and pebbles > 5 μm) occurs frequently between 13.89 ka and 9 ka BP and is virtually absent in the younger part of the sediment core (Fig. 4c).

Figure 5 provides ocean temperature anomalies reconstructions based on diatom assemblages (SSST) and GDGT-derived RI-OH¹ and TEX₈₆^L SOTs in core PS97/072-1 (Fig. 5 b-d). Diatom-derived SSST estimates derived from diatom data generally depict have lower minimum temperatures of -1.5°C to 0°C during the Deglacial and Early Holocene, accompanied by and a shift to ca. 1°C warming temperatures trend (to $>0^\circ\text{C}$) in the Middle and Late Holocene with a distinct cold event at 3.1 ka BP (Fig. 5b). A short cold event with a SSST decrease of ca. 1.5°C occurred around 3.1 ka BP. Similar to SSSTs, also RI-OH¹-derived SOTs likewise reflect generally lower temperatures during the Deglacial and Early Holocene, and between -1.9 to -1.2°C and a similar trend of rising 0.4°C warmer temperatures in the Middle and Late Holocene to -1.2°C until 4.2 ka BP followed by a subtle cooling to -1.4°C (Fig. 5c). TEX₈₆^L-derived SOTs data from GDGTs cover a temperature range of 0.7 to 3.8°C

397 and display an opposite trend to both SSST and RI-OH' SOT with peak temperatures decreasing temperatures to
398 0.7 °C since from during the Deglacial and an overall Holocene cooling towards present (Fig. 5ed).

399

400 4 Discussion

401 4.1 The late Deglacial (13.814 ka to 11.7 ka BP)

402 In the oldest part of our sediment record, covering the later part of the last Deglacial from 13.814 ka until 11.7 ka
403 BP, we observe a remarkable environmental change indicated by significant-large shifts in the TOC, biomarker
404 and diatom records (Fig. 3). Before 13.4 ka BP, the very low concentrations of HBI biomarkers (Fig. 3b and d),
405 TOC (Fig. 3f), and biogenic opal (Fig. 3e) between 13.8 ka and 13.5 ka BP suggest that primary production of
406 phytoplankton associated with open marine conditions and also sea ice algae synthesizing IPSO₂₅ settings was
407 diminished, while sea ice related diatom species show the highest contribution of 73% (Fig. 3c), albeit with very
408 low concentrations (supplement section see online ressource5). Highest WSI concentrations values of winter sea
409 ice Highest (WSI, Fig. 4a) and PIPSO₂₅ values spring sea ice (PIPSO₂₅, Fig. 4a, b) indicators and WSI values are
410 pointing towards a maximum sea ice cover that lasted until summer in both seasons and are. Lowest and lowest
411 ocean temperatures reflected in the RI-OH' derived SOTs are well in line with peak ssNa concentrations and
412 minimum $\delta^{18}\text{O}$ values in the EDML and WAIS and JRI ice core records, referring to an extended sea ice cover
413 until 13 ka BP and lowered atmospheric temperatures (Fig. 4; EPICA Community Members, 2006; Fischer et al.,
414 2007; WAIS Divide Project Members, 2015). We note that for the interpretation of PIPSO₂₅ values, changes in
415 both IPSO₂₅ and HBI triene concentrations need to be evaluated carefully to reliably deduce information on sea
416 ice conditions. High PIPSO₂₅ values may refer to an extended sea ice cover that lasts until summer (thus hampering
417 phytoplankton productivity/HBI triene synthesis), whereas low PIPSO₂₅ values point to a reduced sea ice cover in
418 terms of duration (in spring) and/or sea ice concentration. In agreement with the biogenic opal and the near
419 absence of IPSO₂₅, the HBI triene and warm open ocean diatom species as well as minimum contents in TOC
420 and biogenic opal between 13.89 ka and 13.5 ka BP evidences a very thick or permanent, potentially perennial sea
421 ice cover or at least sea ice that was too thick to allow photosynthesis of sea ice algae inhabiting at the sea ice
422 bottom. Similarly, Lamping et al. (2020) related the absence of IPSO₂₅ and a phytoplankton-derived dinosterol
423 biomarker in sediments in the western Amundsen Sea to the re-advance of a floating ice shelf canopy during the
424 ACR. At the PS97/072-1 core site in the eastern Bransfield Strait, both the presence of perennial sea ice, or an ice
425 shelf tongue extending from the APIS, could explain the lack of indicators of phytoplankton productivity and
426 IPSO₂₅ synthesizing ice algae. We hence assume that the very low absolute concentrations of sea ice associated

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diatoms result from lateral transport underneath the ice or reworking of sediments older than 13.5 ka BP. The abrupt increase in IPSO₂₅ concentrations at 13.5 ka BP, however, may indicate the retreat or thinning of such an ice-shelf cover canopy, from the core site permitting sea ice algae growth during spring and a subsequent increase in primary production reflected in rapidly rising HBI triene concentrations since 13 ka BP (Fig. 3b, d). Such a transition from a perennial floating ice canopy to conditions characterized by (seasonal) sea ice cover is also reported by Milliken et al. (2009) for the nearby Maxwell Bay (King George Island; SSI) between 14 ka and 10 ka BP. Interestingly, a significant prominent decrease in sea ice associated diatoms between 13 ka and 12 ka BP (Fig. 3c), however, is not mirrored by the still high WSI concentrations. This discrepancy could relate to a weaker preservation potential of certain diatoms reflecting seasonal sea ice (e.g. *Synedropsis* sp., *Nitzschia stellata*) that are not considered within the transfer function to estimate WSI, which highlights the need to examine silica dissolution effects for the interpretation of diatom records. We note that traces of biomarkers and diatoms (supplement section 4 and 65) deposited in sediments older than 13.5 ka BP may reflect sub-ice shelf lateral advection and reworking (Smith et al., 2019).

With regard to the ocean temperatures recorded at core site PS97/072-1, we note that the overall cool deglacial temperatures derived from diatom data (SSST) and hydroxylated GDGTs (RI-OH') seem to be linked to the lowered summer insolation (Fig. 5a), whereas higher TEX₈₆^L temperatures seem to be associated with a higher spring insolation (Fig. 5d). While the impact of seasonality on GDGT-based ocean temperature estimates is still under debate and would require further improvements in on-regional calibration, the observation of maximum abundances of thaumarchaeota species (producing isoGDGTs applied to determine TEX₈₆^L) in Antarctic coastal waters during spring (Kalanetra et al., 2009; Murray et al., 1998) seems to support our interpretation and also helps to explain the divergent trends in TEX₈₆^L and RI-OH' derived SOT estimates, as the latter proxy might be also sourced by other archaea species that probably grow mostly during the summer season.

While the ACR lasts from 14.7 ka to 13 ka BP (Pedro et al., 2016) as indicated by e.g. the WAIS Divide ice core records from JRI (Fig. 5b, Mulvaney et al., 2012) and WAIS Divide (Fig. 5i, WAIS Divide Project Members, 2013), our sediment record shows that cold conditions with an extended sea ice cover, limiting summer phytoplankton productivity (Fig. 4a, b) and reduced summer ocean temperatures in the eastern Bransfield Strait, lasted until ca. 11 ka BP (Figs. 4 and 5). Further, the Deglacial and Early Holocene (Fig. 4e) IRD content (Fig. 4c, including the presence of single large pebbles) in core PS97/072-1 points to the frequent occurrence of icebergs during the Deglacial and the Early Holocene (Fig. 4e), which relates related to evidencing the overall ice sheet disintegration along the WAP that occurred around 14 ka BP at the SSI South Shetland Islands and promoted seasonally open-marine conditions at Anvers-Hugo Trough at 13.6 ka BP (middle WAP shelf) and at 12.3 ka BP.

ka BP in at Palmer Deep at the southern (inner WAP shelf), respectively AP (Domack et al., 2001; Domack, 2002; Jones et al., 2022; Milliken et al., 2009; Roseby et al., 2022). At our core site, rising RI-OH' SOTs and a slight decrease in PIPSO₂₅ values and rising RI-OH' SOTs characterize the late Deglacial between 13 ka and 11.7 ka BP (Fig. 4b, 5c). A prominent decline in large-scale sea ice cover is also reflected in the decreasing ssNA concentrations in the EDML and WAIS ice cores between 13 ka and 11.7 ka BP (Fig. 4e, f) and is likely related to a distinct atmospheric warming, as reflected in ice core stable water isotopes (Fig. 5h). The ACR cooling and the subsequent Late Deglacial This subsurface ocean warming may relate to inter-hemispheric teleconnections through a global reorganization of atmospheric and ocean circulation that is associated with related to the bipolar seesaw pattern of opposite climate trends between the northern and southern hemisphere (Anderson et al., 2009; Broecker, 1998; EPICA Community Members, 2006; Pedro et al., 2016). While a northward shift of the southern westerlies during the ACR (Fletcher et al., 2021) promoted Antarctic sea ice expansion and glacier readvance (potentially affecting causing an ice cover over the PS97/072-1 core site), a With-cooling of the northern hemisphere and with a southward shift of the Intertropical Convergence Zone and the southern hemisphere westerlies (Lamy et al., 2007) resulted in intensified wind stress in the Drake Passage (Timmermann et al., 2007), and This pattern would have increased upwelling that may have driven the continued ocean warming and sea ice retreat in Antarctica towards the Holocene (Anderson et al., 2009).

4.2 Early Holocene warming from 11.7 ka to 8.2 ka BP

The Early Holocene from 11.7 ka to 8.2 ka BP is characterized by a progressively decreasing spring sea ice cover inferred from shown by declining PIPSO₂₅ values (Fig. 4b), as well as though highly variable winter and spring sea ice cover with prominent as shown by further declining WSI shifts in sea ice concentration (from 90% to 65%; and PIPSO₂₅ values (Fig. 4a and b). These WSI fluctuations are not reflected in the sea ice diatom assemblage, which, similar to the biogenic opal content, follows an increasing trend until 10.5 ka BP (Fig. 3c, e). Increased Improved accumulation of biogenic opal and a better preservation of (thin-walled) sea ice-related diatoms that are not used for the transfer function may explain the mismatch between the WSI record and sea ice diatom assemblage. The increase in While biogenic opal is further accompanied by a rising and TOC contents exhibit increasing trends, while concentrations of the HBI triene and warm open ocean diatoms remain low and, only an significant increase after 9 ka BP, signal signalling suggests higher phytoplankton productivity (Fig. 3a, b). Diatom-derived SSSTs exhibit marked fluctuations but remain relatively low until 8.2 ka BP (Fig. 5b). RI-OH' and TEX₈₆^L SOTs display diverging trends following the summer and spring insolation, respectively (Fig. 5).

Ocean temperatures based on warming is indicated by RI-OH¹-based SOT, while TEX₈₆¹-SOT and diatom-derived SSST show fluctuating temperatures without a clear trend (Fig. 5b, c and d). While PIPSO₂₅ values display a rather gradual decrease in sea ice coverage, the WSI record suggests a highly variable sea ice cover, with several few distinct sea ice minima between 11 ka and 10 ka BP and around 9 ka BP (Fig. 4a and b). These sea ice minima may have resulted from punctuated warming events, e.g. around 10 ka BP, when SSST shows a short temperature peak, which might have led to a delayed sea ice formation in autumn and winter (Fig. 5b). Another WSI minimum at 9 ka BP coincides with a major, final (and final) peak in IRD deposition at the core site (Fig. 4), evidencing iceberg discharge during episodes of peak AP ice-sheet loss-retreat and enhanced calving at the WAP (Jones et al., 2022). As sea ice melting may have been an important driver of the ocean stratification, we suggest warmer, stratified surface waters with moderate production in summer, supported by increasing summer insolation in December (Fig. 5a). Ameliorating climate conditions, ice-shelf retreat along the NAP and the establishment of modern-like ocean conditions after 9 ka BP have also been proposed for the western Bransfield Strait by (Heroy et al. (2008) and are well in line with the rising concentrations contribution of warm open ocean diatoms and the phytoplankton-derived HBI triene at our core site after 9 ka BP (Fig. 3). The general decrease in spring sea ice cover (reflected in declining PIPSO₂₅ values) Our marine records of decreasing sea ice may have been fostered by a maximum spring and rising summer insolation (Fig. 5a, d), and subsurface ocean temperatures shortening the duration of sea ice cover. Rising RI-OH¹ temperatures are which are consistent with the overall slight warming trend recorded in the WAIS Divide ice core (Fig. 5h), which has been shown to be mainly driven by increasing summer temperatures (Jones et al., 2022). ... Interestingly, neither this rise in RI-OH¹-derived SOTs nor the highly variable The decreasing TEX₈₆¹-SOT temperature trends at core site PS97/072-1 corresponds to the declining TEX₈₆ temperatures reported for ODP site 1098 in at Palmer Deep (Fig. 5g; Shevenell et al., 2011) though the latter displays a more pronounced temperature drop (of ca. 6 °C) between 11.7 ka and 8.2 ka BP, or the declining δD values recorded in the JRI ice core (Fig. 5; Mulvaney et al., 2012). These regional differences may relate to changing ocean circulation patterns, and associated shifts in water mass distribution along the WAP and EAP, and the local post-glacial environmental development during the Early Holocene. Deposition of laminated diatom oozes in the Anvers-Hugo Trough at the WAP middle shelf during the early Holocene since 11.5 ka BP, for example, documents episodes of extremely high productivity in response to a southward shift of the southern hemisphere westerlies and the advection of warm and nutrient-rich CDW (Roseby et al., 2022). We propose that the eastern Bransfield Strait remained mainly "inaccessible" for CDW and BSW until further ice recession between 10 ka and 5 ka BP (Ó Cofaigh et al., 2014 and references therein) permitted advection of these water masses into the Bransfield Strait. We further note that the partly opposing trends

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in RI-OH⁺ and TEX₈₆⁺ temperatures at our core site could indicate that the respective GDGT-producing archaea thrive in different water depths or during different seasons.

4.3 Middle Holocene from 8.2 ka until 4.2 ka BP

The Middle Holocene from 8.2 ka to 4.2 ka BP was a period of significant sea ice retreat and minimum iceberg flux-activity records at the core site indicated by decreasing WSI and PIPSO₂₅ values and, virtually absent IRD (Fig. 4), and an oceanic warming reflected in SSST and RI-OH⁺ SOT (Fig. 4 and 5). For the whole period, diatoms associated with warmer open ocean conditions, peak HBI triene concentrations and maximum TOC and as well as biogenic opal contents (Fig. 3) indicate a high export production during the Middle Holocene (Abelmann et al., 2006; Smetacek et al., 2004). These higher primary productivity export productivity production can be linked to a decrease in both winter and spring sea ice and potentially ice-free summers indicated by WSI and PIPSO₂₅ minima, respectively (Fig. 4a, b), and elevated SSSTs and (summer) SOTs (Fig. 5b, c) promoting ice-free summer ocean conditions favorable for phytoplankton productivity. These Middle Holocene sea-ice conditions compare well with the modern situation at the core site characterized by a seasonal decrease in sea ice concentration from 50% during winter to mainly ice-free summers (NSIDC; Cavalieri et al., 1996), like it was observed for modern sea ice conditions in this region (Vorrath et al., 2020). The continued retreat of the previously grounded APISAP ice sheet adjacent to over the Bransfield Strait between 10 ka and 5 ka BP finally opened the passage for ACC surface waters to enter the Bransfield Strait from the west (Bentley et al., 2014; Ó Cofaigh et al., 2014). As a result, we suggest that sea ice conditions at our core site were predominantly influenced by branches incursions of warmer oceanic waters carried associated with of the ACC (i.e. the BSW and CDW) leading to a shorter sea ice season and/or less intensive sea ice cover, while and cold water inflow and sea ice advection from the Weddell Sea was diminished due to the still grounded ice sheet at the tip of the AP (Ó Cofaigh et al., 2014), leading to a shorter sea ice season in the eastern Bransfield Strait. This shift towards a warmer, less ice-covered ocean setting in the eastern Bransfield Strait is well in line with reflected in the transition from proximal to distal glacial marine conditions in Maxwell Bay (Milliken et al., 2009) and may be associated with the Mid-Holocene climatic optimum. This timing contrasts the notation of Heroy et al. (2008), who, based on diatom assemblage analyses of a sediment core in the western Bransfield Strait, confined the Mid-Holocene climatic optimum to a shorter time interval between 6.8 ka and 5.9 ka BP based on diatom assemblage analyses of a sediment core in the western Bransfield Strait. We propose that this temporal offset may relate to regionally different responses, to glacial retreat patterns impacting oceanic pathways and the position of frontal systems controlling primary productivity within the Bransfield Strait. The generally decreasing WSI and variable

PIPSO₂₅ values further depict different trends than PIPSO₂₅ values determined for the JPC10 in Palmer Deep (Fig. 4d; Etourneau et al., 2013), which suggest an overall increase in spring sea ice along the WAP until 4.2 ka BP. Though minima in spring sea ice at 7.5 ka, 6.5 ka and 5.4 ka BP at core site PS97/072-1 may be related compare to PIPSO₂₅ minima observed for JPC10, the lack of Middle Holocene age ~~constraint~~ tie points in our core from the Bransfield Strait ~~detersprevents~~ us from concluding on a common driver ~~causingfor~~ these sea ice reductions. ~~minima in spring sea ice at 6.5 ka and 5.4 ka BP~~ The weak influence from the Weddell Sea limited the export of cold waters and supported was weak and opposite sea ice conditions were reconstructed for in the eastern AP where HBI biomarker and diatom assemblages record ~~regionally~~ extended sea ice cover between 7 ka and 4.5 ka BP (Fig. 4c, Barbara et al., 2016a; Minzoni et al., 2015).

Regarding ocean temperatures, we observe a sustained warming in RI-OH' SOT, punctuated by a cooling at 5.5 ka BP (Fig. 5c), while TEX₈₆^L temperatures depict a subtle cooling of ca. 0.5 to 0.9 °C between 8.2 ka and 7 ka BP, followed by a warm reversal ~~of up to 3.1 °C~~ until 6 ka BP, and a further cooling until 4.2 ka BP (Fig. 5e). This A Middle Holocene slight cooling trend is ~~also~~ has also been observed in the TEX₈₆^L records at from the core sites ~~core sites at in~~ Palmer Deep at the WAP (Fig. 4 and 5f, g; Etourneau et al., 2013; Shevenell et al., 2011). The similarity between these records encourages us to assume that these TEX₈₆-derived temperatures from along the WAP and NAP are driven by spring insolation rather than ~~reflecting~~ being a reflection of annual mean ocean temperature conditions ~~(see above)~~, and contrasts a rapid warming observed in JPC38 from the eastern AP between 8 ka and 6.5 ka BP (Fig. 1 and 5, Barbara et al., 2016; Etourneau et al., 2019). Here, the near-coastal marine sediment core close to JRI (Fig. 5g, Barbara et al., 2016) records the transition from cold and heavily sea ice covered conditions at 8.2 ka BP to a warmer ~~water~~ environment with reduced sea ice cover permitting more phytoplankton growth between 6.5 ka and 4.2 ka BP (Barbara et al., 2016). Since stable temperatures are inferred from the JRI ice core during the entire Middle Holocene (Mulvaney et al., 2012), we suggest that the environmental changes recorded in JPC38 reflect ocean-driven rather than atmospheric processes.

4.4 Late Holocene and Neoglacial from 4.2 ka BP until today

The Late Holocene covering the past 4.2 ka BP is characterized by a highly variable winter sea ice and decreasing spring sea ice cover at core site PS97/072-1, as indicated ~~reflected~~ in the MAT-derived WSI and a decline in PIPSO₂₅ values over the past 2 ka (Fig. 4a, b). Rather constant ~~relatively stable environmental conditions at our~~ core site ~~reflected in constant biogenic opal and TOC contents~~ (Fig. 3e, f), however, suggest that primary productivity remained relatively unaffected by this reduction in spring sea ice cover. ~~low~~ While decreasing IPISO₂₅ concentrations between 2.5 ka BP and the core top (Fig. 3d) suggest a reduced productivity of the sea ice diatom

species synthesizing this molecule, no significant changes are observed in the sea ice diatom assemblage (Fig. 3c), which supports the assumption that only a restricted group of diatoms - at least *Berkeleya adeliensis* - produce IPSO₂₅ (Belt et al., 2016). The warm open ocean diatom assemblage follows an overall declining trend throughout the Late Holocene, which is not reflected in the highly variable and slightly increasing HBI triene concentrations (Fig. 3a, b), and a prominent decrease in HBI triene concentrations occurs only at 1 ka BP, which display a slight increase until it decline and still variable but elevated HBI triene concentrations. A gradual decline in PIPSO₂₅ values between 4.2 ka and 1.5 ka BP contrasts the highly variable WSI concentrations (Fig. 4). ... While the observation of cooler sea surface temperatures, and a diminished spring sea ice cover indicated by the joint decrease in the warm open ocean diatom assemblage and PIPSO₂₅ values since 2 ka BP may seem counterintuitive, Milliken et al. (2009) report a similar development in Maxwell Bay since 2.6 ka BP. Interestingly, records of diatom and radiolarian assemblages of a sediment core (Gebra-2) collected in very close vicinity to PS97/072-1 document an overall increase in sea-ice taxa over the past 3 ka BP with distinct Neoglacial events characterized by higher (denser and longer) sea ice cover (Bárcena et al., 1998). The lower sampling resolution and missing age control for the past 3 ka BP in PS97/072-1, however, hamper a more detailed comparison of diatom species in our core with those investigated for Gebra-2. The Neoglacial increase in (spring) sea ice cover is also indicated by a prominent rise of PIPSO₂₅ values determined for JPC10 in Palmer Deep (-Fig. 4d; Etourneau et al., 2013). Similarly, deposition of ssNa in the EDML ice core (Fischer et al., 2007) increases since 2 ka BP. Minimum PS97/072-1 PIPSO₂₅ values at 0.5 ka BP result from are due related to the significantly-notably reduced IPSO₂₅ and HBI triene concentrations (Fig. 3b, d). While Similar to our observation for the Deglacial, this pattern of minimum-low HBI triene and minimum-lowest-IPSO₂₅ concentrations is similar to the period between 13.8 ka and 13.5 ka BP, which was characterized by -may point to perennial-cold conditions and a heavy-pronounced - potentially perennial - ice cover, the elevated TOC and biogenic opal values, as well as the presence of diatoms associated with warm open ocean conditions at 0.5 ka BP, point to favorable ocean conditions. We hence relate this drop in HBI concentrations to a shift in the diatom community rather than to an abrupt readvance of an ice cover. Late Holocene ocean temperature reconstructions for core PS97/072-1 display different patterns. Generally increasing diatom-derived SSTs are only punctuated by a cooling event at 3.1 ka BP, while RI-OH' SOT remains relatively constant with a very subtle cooling of ca. 0.2 °C between 1.5 ka and the present, which could be linked to the slight decrease in summer insolation (Fig. 5a, b, c). The decrease in TEX₈₆^L SOT by about 1 °C between 4 ka and 3.3 ka BP in eastern Bransfield Strait is also depicted in the TEX₈₆^L data from the Palmer Deep core JPC10 (-Fig. 5e, f; Etourneau et al., 2013). The following warming reflected in PS97/072-1 TEX₈₆^L SOT until ca. 2 ka

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BP may relate to the establishment of open marine conditions fostering primary productivity at the Perseverance Drift north of Joinville Island (northern tip of the AP) as a result of warm water intrusions (Kyrmanidou et al., 2018). This warming is reversed by another cooling at about 2 ka BP - coincident with an abrupt temperature increase of ca. 4 °C depicted in the ODP1089 TEX₈₆ SOT record in Palmer Deep (Fig. 5g; Shevenell et al., 2011). The latterThis warming is not displayed in the TEX₈₆^L data of the nearby JPC10 and we relate this contrast to the different approaches used to determine SOT (*i.e.*, TEX₈₆ vs. TEX₈₆^L omitting the crenarchaeol regio-isomer, which seems to be less important for membrane adaptation in polar waters; Kim et al., 2010). Evidently, temperature trends at the AP in the Late Holocene are highly variable between different areas (Allen et al., 2010; Barbara et al., 2016; Bárcena et al., 1998; Bentley et al., 2009; Etourneau et al., 2013; Mulvaney et al., 2012; Shevenell et al., 2011) and this is likely associated with the complex oceanographic and atmospheric settings. This heterogeneous pattern, however, contrasts with the currently observed large-scale ocean warming along the AP driven by intrusions of ACC-derived warm CDW onto the continental shelf of the WAP (Couto et al., 2017) and the NAP (Ruiz Barlett et al., 2018), as well as the overall loss of sea ice (Parkinson and Cavalieri, 2012), which supports the assumption that the changes impacting the AP already exceed natural variability. conditions and the establishment of thick and/or compacted sea ice limiting the productivity of both phytoplankton and also sea ice diatoms. This short period of sea ice growth may be related to the Little Ice Age (LIA), when cooler conditions also triggered glacial readvance at the Antarctic Peninsula 500 years ago (*e.g.* Simms et al., 2021). While a significant large pulse in sea ice export from the Arctic Ocean is proposed to have caused the LIA cooling (Miles et al., 2020), knowledge about LIA sea ice conditions in the Southern Ocean is scarce and hence inconclusive (Parkinson, 1990). The Neoglacial cooling as found in the JRI ice core, for example, is clearly reflected in an increased sea ice cover at Palmer Deep since 2 ka BP (Fig. 4d, Etourneau et al., 2013) but this record, however, contains no clear evidence for a further expansion of sea ice in response to the LIA. We conclude that a comprehensive assessment of how Antarctic sea ice conditions changed during the LIA requires more studies of well dated and ideally higher resolved sediment records. Similar to our sea ice signals, also the Late Holocene ocean temperature reconstructions display different patterns. While RI-OH⁺ SOT remains relatively stable, TEX₈₆^L indicates a cooling around 3 ka BP followed by a warming until 1.5 ka BP and another cooling towards the top of the core. Diatom-derived SSST also point to a cold period around 3 ka BP immediately followed by peak a warming peak at ca. 2.5 ka BP. Evidently, temperature trends at the WAP in the Late Holocene are highly variable between different areas (Allen et al., 2010; Barbara et al., 2016; Bárcena et al., 1998; Bentley et al., 2009; Etourneau et al., 2013; Mulvaney et al., 2012; Shevenell et al., 2011) and this may relate to the complex oceanographic and atmospheric settings. With regard to the diverging

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temperature trends observed in sediment core PS97/072-1, we note that also inconsistencies between different analytical approaches to reconstruct ocean temperatures need to be acknowledged and examined. As previously stated, more information on the applicability and significance of GDGT-derived ocean temperatures in polar latitudes is needed.

5 Conclusions

We reconstructed the sea ice and climate development at the Northwest-AP since the last Deglacial using the sediment core PS97/072-1 from the eastern Bransfield Strait. Pursuing a multi-proxy approach that focuses on organic geochemical bulk and biomarker analyses, diatom assemblage studies and transfer functions as well as IRD data, we identified different Deglacial and Holocene environmental conditions impacted by sea ice and ocean temperature changes. In our multiproxy study we focused on the sea ice biomarker IPSO₂₅, the HBI-z triene representing open marine environments, and GDGTs for ocean temperature reconstructions. Diatom ecological groups characteristic of sea ice or cold/warmer open ocean conditions were used, as well as diatom transfer functions to reconstruct winter sea ice and summer sea surface temperature. Additional information was derived from sedimentological records such as IRD and biogenic opal. Our results reveal the retreat of a perennial ice cover floating ice shelf canopy after the ACR and an overall sea ice reduction/retreat and summer ocean warming during the Holocene. The late Deglacial from 13.89 ka to 11.7 ka BP was a highly dynamic period: until 13.4 ka BP primary productivity/the sedimentation of organic proxies was diminished due to a permanent ice cover during the ACR. The ACR terminated with a shift to slightly warming conditions at 13 ka BP along with a reduction/retreat in the length of the spring-sea ice season, which permitted phytoplankton productivity at least during summer. The Early Holocene from 11.7 ka to 8.2 ka BP was characterized by increasing summer ocean temperatures/warming, further slightly decreasing (in terms of duration and/or sea ice concentration) spring-sea ice cover in terms of duration and/or sea ice concentration and highly variable winter sea ice cover. In the Middle Holocene from 8.2 ka to 4.2 ka BP, increased advection of BSW and CDW led to a shortened sea ice season (confined to winter and spring) sea ice coverage confined to winter and spring season stable environmental conditions prevailed with elevated and rising summer ocean temperatures fostering primary production, indicating and this period may be associated with the Middle Holocene Climatic Optimum due to intervals of lower sea ice cover. In general, sea ice seasons were short and sea ice cover was significantly greatly reduced to a minimum around 5.5 ka BP, even though high seasonal amplitudes and short-term, centennial changes in sea ice conditions occurred. During the Late Holocene, the core site experienced a distinct fluctuations in variable WSI with concentrations shifting between 90% and 60% concentration, while PIPSO₂₅ values declined

continuously suggesting a less intensive or shorter spring sea ice coverspring sea ice declined continuously. and
a short-term SSST cooling at 3 ka BP. Phytoplankton biomarkers as well as sea ice proxies (IPSO₂₅, PIPSO₂₅,
WSD) were lowest during the period coincident with the Little Ice Age which we relate to the establishment of a
~~multi-year sea ice cover~~. We note that GDGT-based TEX₈₆^L and RI-OH' SOTs correspond to spring and summer
insolation, respectively, which may explain the divergent trends displayed by both SOT proxies. Clearly, while
this observation may help with the interpretation of other Southern Ocean GDGT-based temperature estimates and
the reconstruction of seasonal SOT variability, more investigations into the mechanisms driving GDGT synthesis
in polar waters ~~are~~is needed.

Data Availability

All data mentioned in this paper will be available at the open access repository www.pangaea.de (<https://doi.pangaea.de/10.1594/PANGAEA.952279>).

Author contributions

The study was conceived by MV and JM. Data collections and experimental investigations were done by MV together with CBL (core description, sampling, diatoms, biogenic opal, age model), PC (diatoms), AL (age model, diatoms), OE (diatom transfer function), GM (GDGTs [PS97/072-1](#), ^{14}C dating), AVH ($\delta^{13}\text{C}$ IPSO²⁵), NL ($\delta^{13}\text{C}$ TOC), LLJ (foraminifera, age model), SMS (age model, humming age), CBL (core description, sampling, diatoms, biogenic opal, age model), PC (diatoms), AL (age model, diatoms), OE (diatom transfer function), GM (GDGTs [PS97/072-1](#), ^{14}C dating), AVH ($\delta^{13}\text{C}$ IPSO₂₅), NL ($\delta^{13}\text{C}$ TOC), J.E., DE and CE provided temperature and salinity profiles near the study site. MV drafted the manuscript. All authors contributed to the interpretation and discussion of the data and the finalization of this manuscript.

Competing interests

None of the authors have a conflict of interest.

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Figures

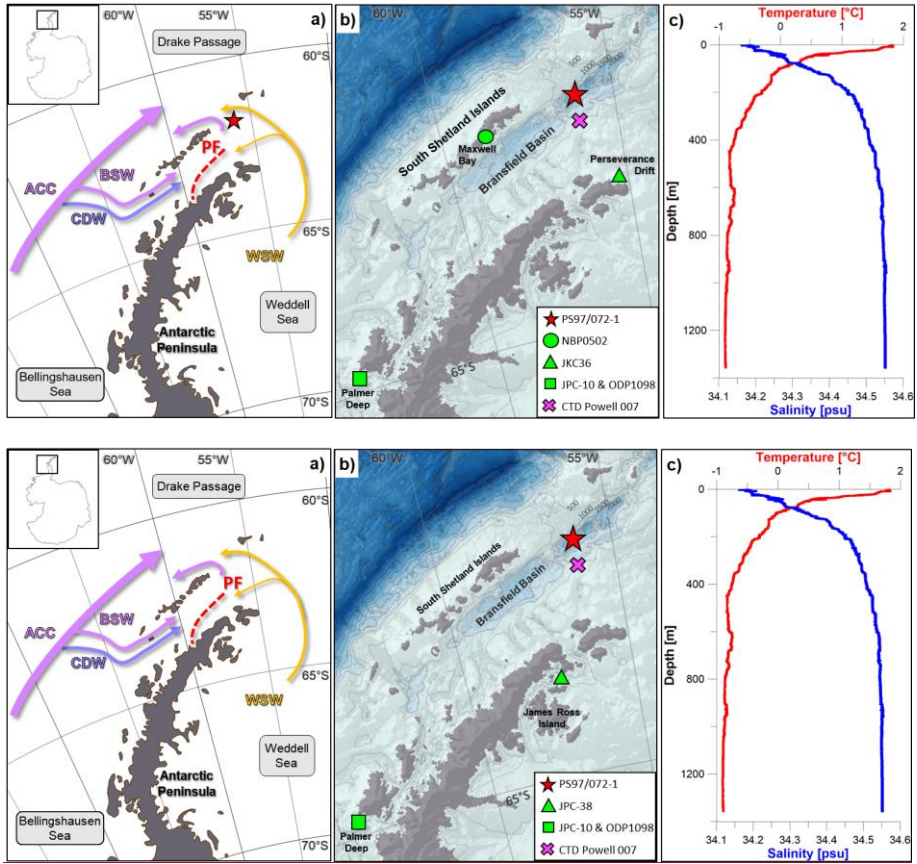


Figure 1: a) Overview map with modern oceanography in the study area (Hofmann et al., 1996; Sangrà et al., 2011). ACC = Antarctic Circumpolar Current, BSW = Bellingshausen Sea Water, CDW = Circumpolar Deep Water, WSW = Weddell Sea Water, and PF = Peninsula Front. b) Bathymetric features in the Bransfield Strait with the location of sediment core PS97/072-1 (red star) and other sediment records discussed in the text (green), and the CTD station (purple cross) where c) the vertical profile of ocean temperature and salinity (cruise POWELL2020, CTD 007 (62°09.075°S, 56°37.09°W) from 27.01.2020) shows a clear stratification of the upper 100 m of the water column. It indicates that surface waters are dominated by the BSW, while the basin is filled with WSW water. Maps were done with QGIS 3.0 (QGIS, 2018) and the bathymetry was taken from GEBCO_14 from 2015.

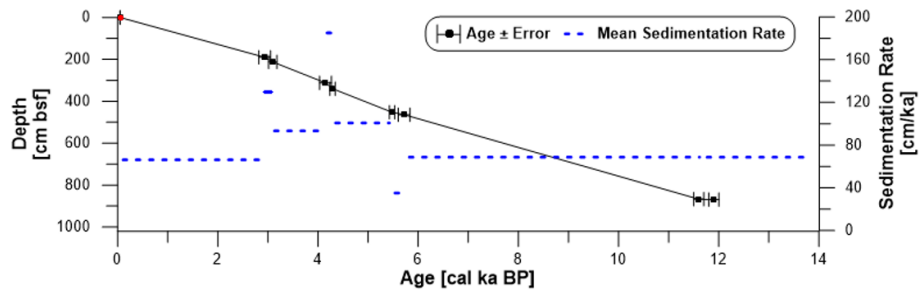
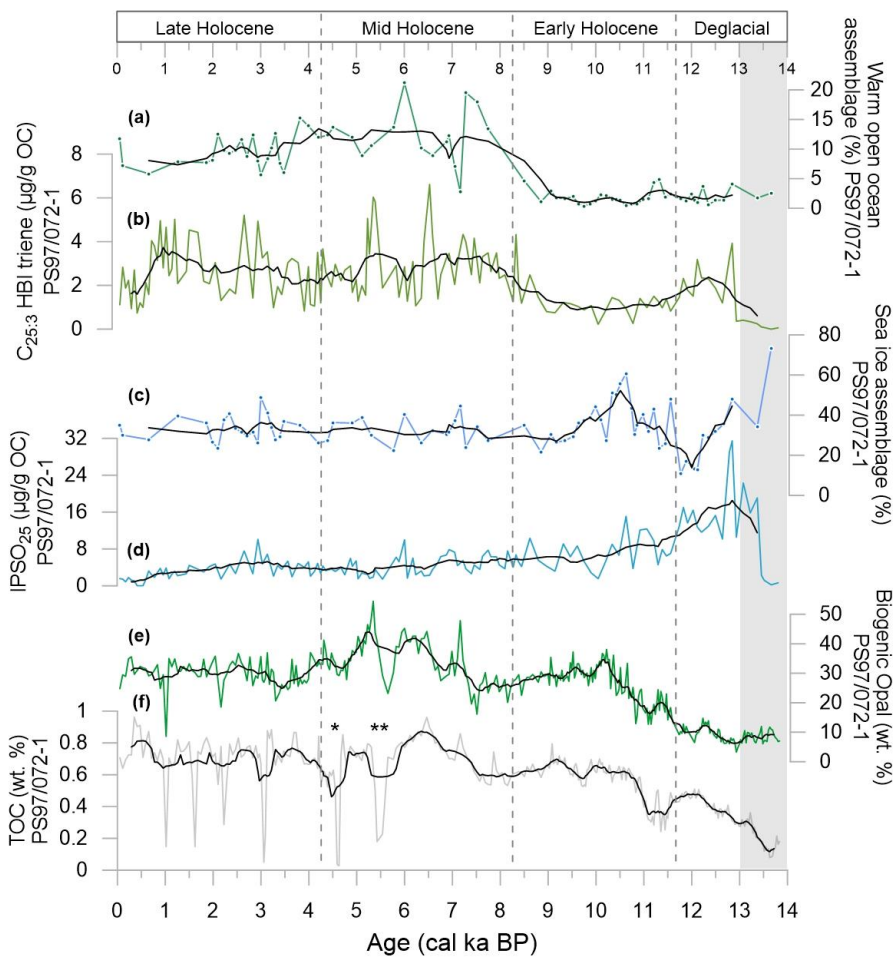


Figure 2: Age-depth model for sediment core PS97/072-1 based on eight ^{14}C dated calcite samples (black) with error bars and mean sedimentation rates (cm/ka, dashed blue line). The core top age (red) was estimated as 0.05 ka BP from matching with the ^{210}Pb -dated multicore PS97/072-2 (Vorrath et al., 2020; see supplement section 2).



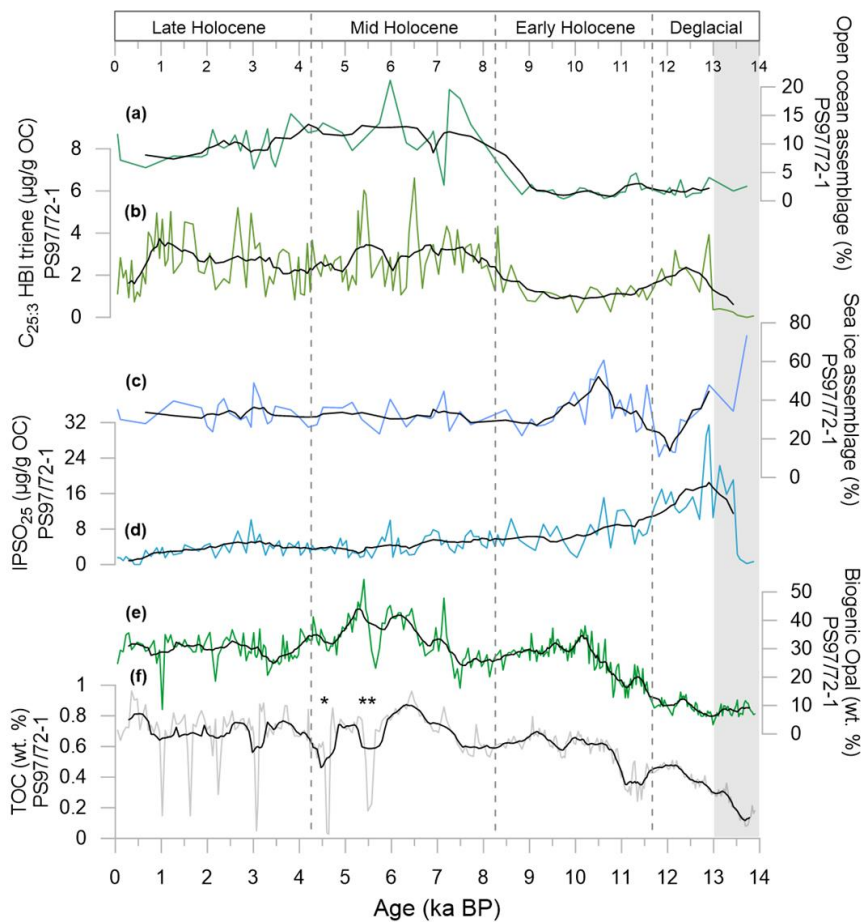
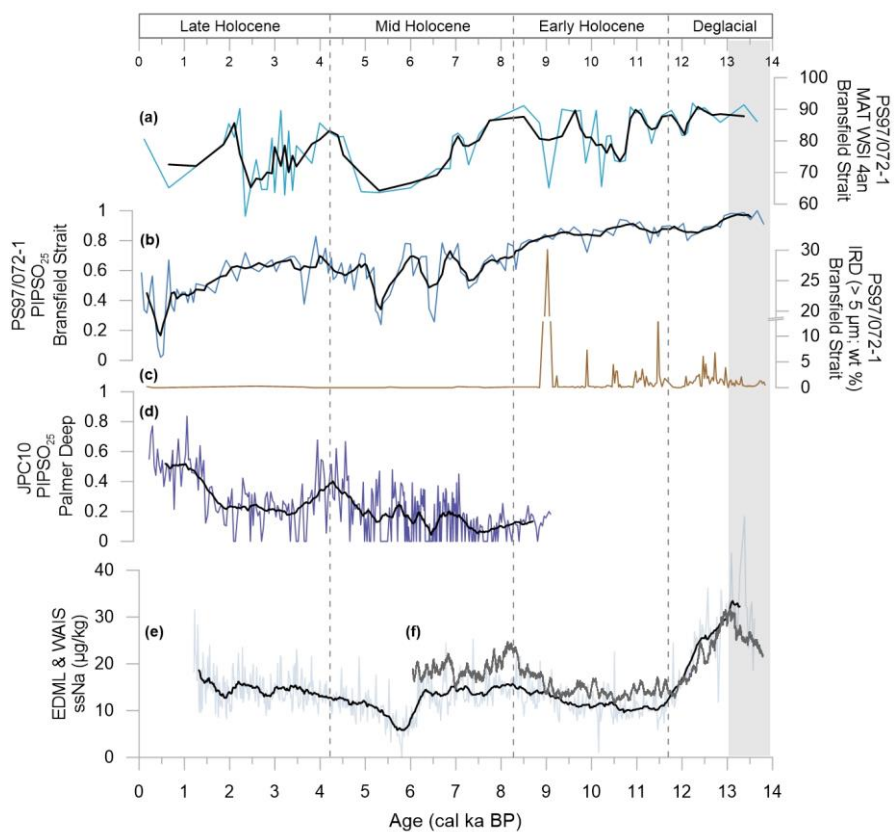


Figure 3: Overview of organic geochemical parameters and main diatom assemblages determined in sediment core PS97/72-1 used to characterize the environmental setting over the past 14 ka BP. a) warm open ocean diatom assemblage, b) C_{25:3} HBI triene, c) sea ice diatom assemblage, d) IPSO₂₅, e) biogenic opal and f) TOC contents. Asterisks in f) mark layers of volcanic ash, where ** can be linked to a tephra layer in a sediment core from the Bransfield Strait at 5.5 ka BP (Heroy et al., 2008). Black lines display running averages. Grey shaded interval refers to the Antarctic Cold Reversal.



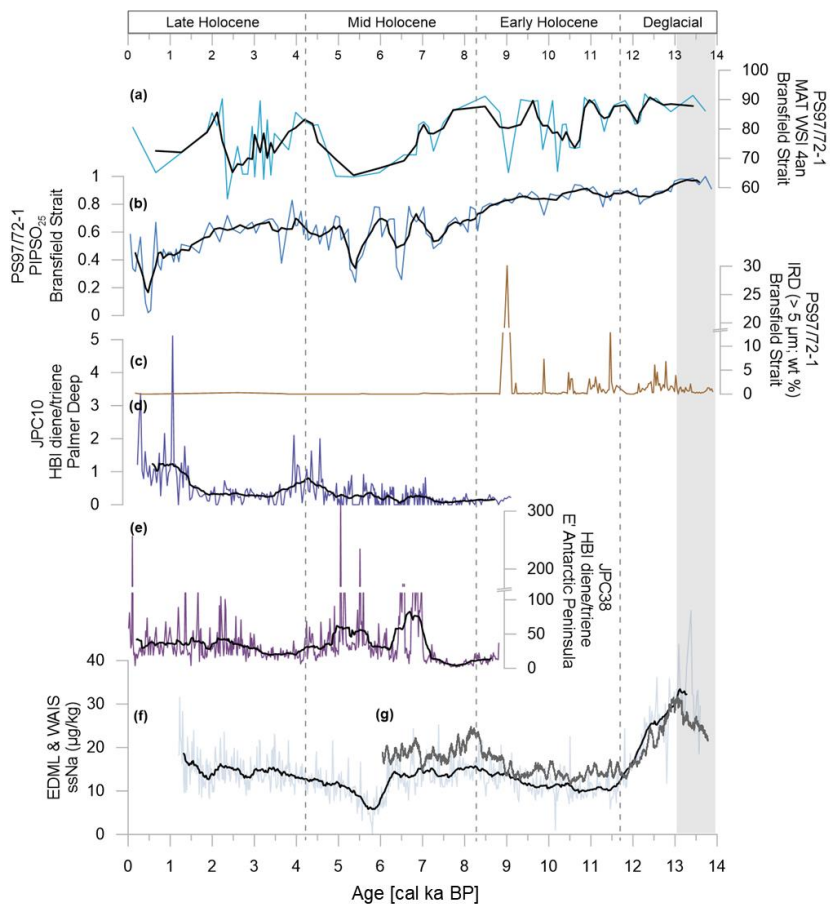
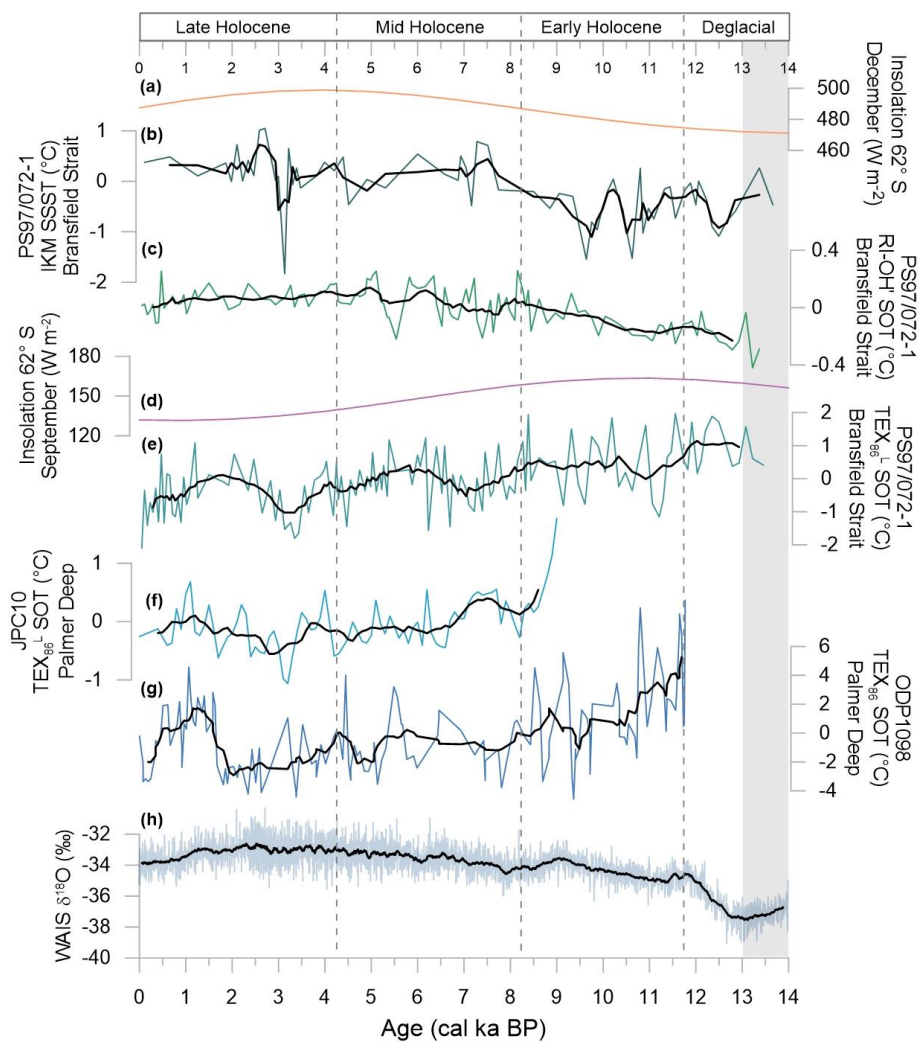


Figure 4: Sea ice related proxies in sediment core PS97/072-1 with a) the diatom based WSI, b) the sea ice index PIPSO₂₅, and c) ice rafted debris (IRD). For comparison: PIPSO₂₅ values the HBI diene/triene ratio of sediment core d) JPC10 from the Palmer Deep station (Etourneau et al., 2013) and e) JPC38 at the East Antarctic Peninsula (Barbara et al., 2016). ssNa records of f) the EDML ice core (Fischer et al., 2007) and g) the WAIS ice core (WAIS Divide Project Members, 2015). Black lines display running averages. Grey shaded interval refers to the Antarctic Cold Reversal.



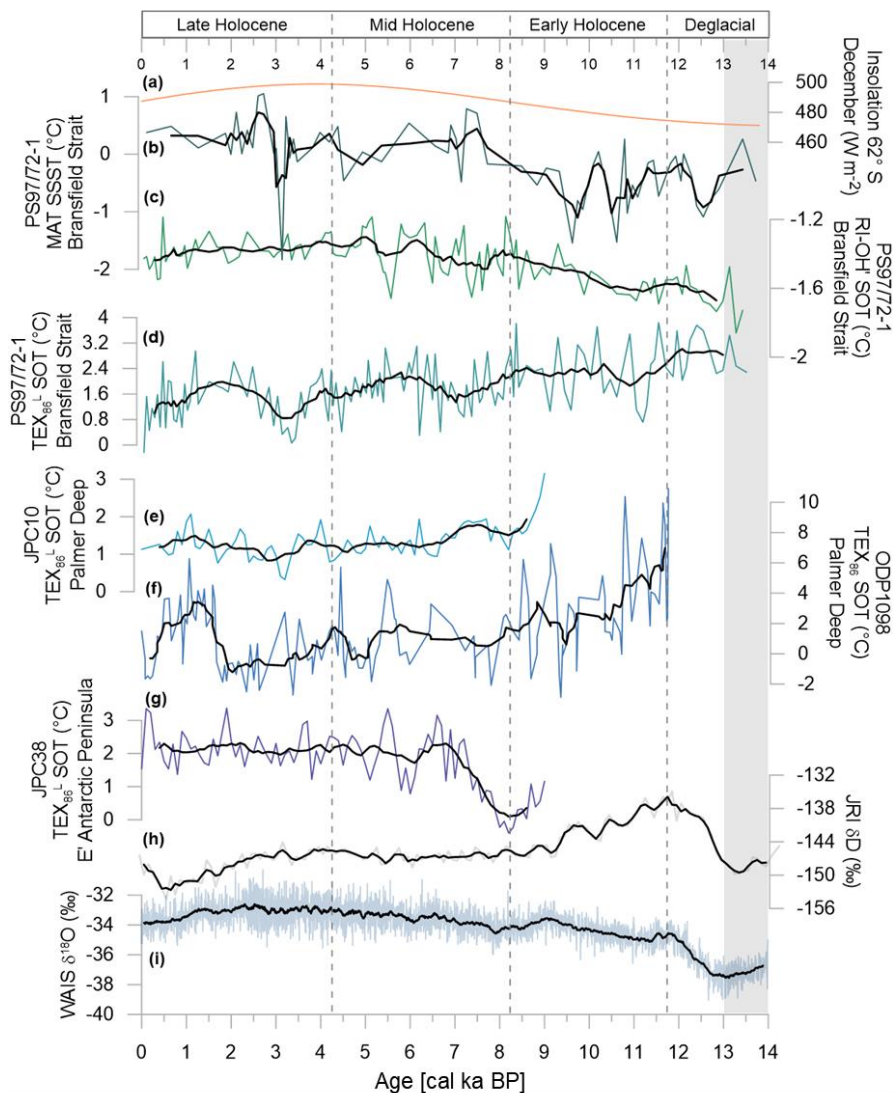


Figure 5: A comparison of a) December insolation (Laskar et al., 2004), b) diatom-based SSST, c) RI-OH⁺-derived SOT, d) September Spring insolation (Laskar et al., 2004), e) TEX₈₆¹-SOT of sediment core PS97/772-1, and temperature reconstructions f) TEX₈₆¹ from JPC10, Palmer Deep (Etourneau et al., 2013), g) TEX₈₆ from ODP1098, Palmer Deep (Shevenell et al., 2011), h) TEX₈₆¹ from JPC38, East Antarctic Peninsula, and i) ice core stable isotope records of h) JRI (Mulvaney et al., 2012) and j) WAIS Divide (WAIS Divide Project Members, 2013). Ocean temperatures are displayed as anomalies with respect to the mean of the individual SOT and SSST

1179 values of the entire record. Black lines display running averages. Grey shaded area refers to the Antarctic Cold
1180 Reversal.
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