



1 Late Eocene to early Oligocene productivity events in the proto-

- 2 Southern Ocean as drivers of global cooling and Antarctica
- 3 glaciation
- Gabrielle Rodrigues de Faria^{1, 2}, David Lazarus¹, Johan Renaudie¹, Jessica Stammeier³, Volkan
 Özen^{1,2}, Ulrich Struck^{1,2}

¹Museum für Naturkunde, Leibniz Institute for Evolution and Biodiversity Science, Invalidenstraße, 43, Berlin, 10115,
 Germany

- 8 ²Freie Universität Berlin, Institute for Geological Sciences, Malteserstraße 74-100, Berlin, 12249, Germany
- 9 ³GFZ German Research Centre for Geosciences, Telegrafenberg, Potsdam, 14473, Germany
- 10 Correspondence to: Gabrielle Rodrigues de Faria (gabrielle.faria@mfn.berlin)

11 Abstract. The Eocene-Oligocene transition (ca 40-33 Ma) marks a transformation from an ice free to an ice-house 12 climate mode that is well recorded by oxygen stable isotopes and sea surface temperature proxies. Opening of the 13 Southern Ocean gateways and decline in atmospheric carbon dioxide have been hypothesised as possible triggers of the 14 major climate shift during the Cenozoic. However, the identification of the driving mechanisms remains controversial 15 and it depends on a better understanding of how the different environmental changes correlate to each other. In this 16 study, we investigate the spatio-temporal variation in export productivity using biogenic Ba (bio-Ba) from different 17 Ocean Drilling Program (ODP) Sites in the Southern Ocean, focusing on possible mechanisms that controlled them as 18 well as correlation of export productivity changes to changes in the global carbon cycle. We document two significant 19 SO region high export productivity late-Eocene events (ca. 37 and 33.5 Ma) that are correlated to pronounced changes 20 in global atmospheric pCO_2 . We propose that paleoceanographic changes that followed Southern Ocean gateway 21 openings, along with more variable increases in circulation driven by episodic expansion and decline of the Antarctic 22 ice sheet, drove enhanced SO export production in the late Eocene through basal Oligocene. These factors may have 23 driven the episodic reduction of atmospheric carbon dioxide and contributed to Antarctic glaciation during the Eocene-24 Oligocene transition.

25 1 Introduction

26 1.1 The late Eocene Events as Precursor to Antarctic Eocene/Oligocene Boundary Glaciation

The Eocene-Oligocene transition (EOT, \sim 40-33 Ma) is the most important climatic interval of the Cenozoic era 27 28 (Kennett, 1977; Miller et al., 2009). This interval involves profound transformations in environmental conditions 29 including the onset of continental-scale Antarctica glaciation at the Eocene-Oligocene boundary (Shackleton & Kennett, 30 1975, Zachos et al., 1996, Coxall et al., 2005), sea-level fall (Houben et al., 2012) and global cooling (Prothero and 31 Berggren, 1992; Liu et al., 2009; Bohaty et al., 2012; Hutchinson et al., 2021) as evidenced by a global shift in oxygen 32 isotope records from biogenic calcium carbonate (>1‰; Zachos et al. 2001; Coxall et al. 2005; Bohaty et al., 2012; 33 Westerhold et al., 2020). A positive deep-sea carbon isotope excursion of up to 1‰ (Zachos et al., 2001, Coxall et al,. 34 2005; Coxall and Wilson, 2011; Westerhold et al., 2020) and a change from a shallow (~3.5 km) to a deeper (~4.5 km) 35 calcite compensation depth (CCD) (Coxall et al., 2005; Rea and Lyle, 2005; Pälike et al., 2012; Dutkiewicz and Müller, 36 2021; Taylor et al., 2023) have also been observed and indicate that the carbon cycle played an important role in the





changes observed during the transition, although the mechanisms that caused the carbon cycle perturbation are stillunsolved.

39 Carbon cycling acts through a variety of feedback mechanisms. Even though it is well recognized that changes in

40 atmospheric carbon dioxide (CO₂) impact the Earth's climate because of its large effect on temperature (Arrhenius,

41 1896; IPCC, 2021), the mechanisms controlling CO₂ over long timescales are still a matter of debate. The carbon cycle

42 perturbation at the EOT provides an opportunity to understand climate-carbon cycle feedback (Zachos and Kump,

43 2005). The mechanisms proposed to explain such perturbations are processes operating gradually over long timescales,

44 and thus likely to have had their origins around the middle to late Eocene.

45 Preceding the abrupt change at the E/O boundary, the late Eocene was a period of gradual cooling and progressive CO₂ 46 decrease (Lauretano et al., 2021). The events associated with this time period may have had substantial importance to 47 trigger the major climatic shift at the E/O boundary. The potential main drivers for the initiation of this global cooling 48 and ice build-up in Antarctica are actively debated. Declining global atmospheric carbon dioxide concentrations, and the 49 opening of Southern Hemisphere oceanic gateways, namely the Drake Passage (DP) and the Tasmanian Gateway (TG), 50 are the two main proposed hypotheses to explain this transition (Coxall and Pearson, 2007; DeConto et al. 2008). The 51 decline of carbon dioxide levels are an important factor in driving cooler temperatures, and have been suggested as the 52 crucial factor in the EOT cooling and subsequent build-up of continental glaciers on Antarctica (DeConto and Pollard, 53 2003; Huber and Nof, 2006; Pagani et al., 2011). Atmospheric CO₂ partial pressure (pCO₂) decline has observational 54 support during the E/O boundary by independent proxies, showing levels falling below 800 ppm (Pearson, 2009; Pagani 55 et al. 2011; Zhang et al., 2013; Anagnostou et al. 2016), although data is sparse and thus details of the magnitude and 56 timing are still unclear. Atmospheric pCO_2 has shown to decline through the Eocene, from ca 2000 ppm in the Middle 57 Eocene (Bijl et al., 2010) to ca. 1000 ppm in the latest Eocene (Pearson et al., 2009). While pCO_2 reconstructions have 58 advanced, there is marked variation between different proxies and the absence of tighter constraints on causative 59 mechanisms requires further investigation of the carbon-climate interactions.

60 The tectonic opening of the Southern Ocean gateways is considered a trigger mechanism of the climatic shift because it 61 allows the initiation of the Antarctic Circumpolar Current (ACC) (Kennett, 1977; Barker, 2001; Scher and Martin, 62 2006; Toumoulin et al. 2020). This intense eastward flowing current is proposed in this hypothesis to impact the 63 regional and global climate by preventing tropical heat of low latitudes from reaching Antarctica, promoting the thermal 64 isolation of Antarctica (Kennett and Shackleton, 1976). Numerous ocean circulation model studies of this hypothesis 65 have yielded conflicting results (De Conto & Pollard, 2003; Goldner et al., 2014; Inglis et al., 2015; Ladant et al., 2014; 66 Mikolajewicz et al., 1993; Najjar et al., 2002; Sijp et al., 2009) but most of these earlier works were limited by 67 unrealistic boundary conditions or other issues (Tournoulin et al., 2020, Hutchinson et al., 2021). Recent modelling 68 circulation studies (e.g. Toumoulin et al., 2020; Sauermilch, et al. 2021) demonstrate the importance of the Southern 69 gateway openings and the proto-ACC on ocean cooling in the Southern Hemisphere. Additionally, glaciation has itself a 70 strong influence both on the circulation of the Southern Ocean and on global climate, via increased albedo, colder 71 temperatures and increased latitudinal temperature gradients, and stronger zonal winds (Goldner et al., 2014). There is 72 increasing evidence for at least partial, if transient Antarctic continental glaciation within the late Eocene (Scher and 73 Martin, 2014), and thus this also needs to be considered in understanding how climate and ocean change developed 74 within this period.

75 Moreover, the ACC is associated with the development of fronts that contribute to upwelling-induced biological

76 productivity (Chapman et al., 2020). Considering that the changes in the Southern Ocean circulation have the potential





77 to affect export productivity and the role of export productivity in removing pCO_2 from the ocean-atmosphere system, 78 the 'CO2' hypothesis and the 'tectonic' hypothesis may be linked, via the influence that gateways may have had on 79 Southern Ocean circulation, increasing export productivity enough to affect global pCO_2 Therefore, evaluating export 80 productivity patterns in the Southern Ocean across the Eocene-Oligocene and its relationship with circulation and 81 decline of atmospheric carbon dioxide during this time period provide important information about the climate feedback 82 in this prominent climatic transition. 83 Many studies have shown variations in biological productivity at this time interval (Diester-Haass, 1995; Diester-Haass 84 and Zahn, 1996; 2001, Salamy and Zachos, 1999; Diester-Haass and Zachos, 2003; Schumacher and Lazarus, 2004; 85 Anderson and Delaney, 2005; Villa et al., 2014), pointing towards a productivity increase associated with ocean 86 circulation changes that increased surface water nutrient availability (Diester-Haass 1992; Zachos et al 1996). However, 87 existing studies have mostly focused on a single site, whose paleoceanographic history may reflect local rather than

regional developments. A much broader spatial investigation is particularly important for understanding the influence of large-scale ocean circulation on this process. Moreover, the timing of productivity changes differs among the studies

90 and different proxies, limiting our understanding of cause-and-effect relationship, therefore, highlighting the importance

91 of constrained age models and consistent paleoproductivity proxy.

92 Here, we reconstruct the changes in export productivity across the late Eocene and early Oligocene, and evaluate how 93 the changes observed may be linked to ocean circulation changes and contributed to the climate changes observed at 94 this interval. We utilize biogenic barium (bio-Ba) accumulation rates to measure marine export productivity. Bio-Ba is 95 defined as the fraction of total barium that not associated with terrigenous sources, sometimes referred as excess-Ba 96 (Dymond et al., 1992), it has been applied in several studies in the Paleogene (eg. Nielsen et al., 2003; Anderson and 97 Delaney, 2005; Faul and Delaney, 2010), and is considered a relatively reliable proxy to estimate changes in 98 paleoproductivity in the Southern Ocean. Newly generated carbon and oxygen stable isotope records from the same 99 samples of our bio-Ba data constrain the question of the causative mechanisms for the climatic shift at the EOT. We 100 compare our export productivity proxy results to indicators of ocean circulation change, including how these changes 101 correspond with gateways opening, paleoceanographic changes, ice sheet history, and their influence on marine 102 biological productivity. We also compare our productivity records to proxies for the global carbon cycle, specifically 103 pCO_2 and $\partial^{13}C$ of benthic deep sea foraminifera. Advancing our understanding of the cause of this event is crucial in 104 identifying the mechanisms governing global climate change.

Although much of our understanding of the Eocene-Oligocene transition has been achieved through modelling studiesas they provide means to compare several possible scenarios, this paper focuses on proxy evidence of the changes that

107 occurred in this time interval. Our multiproxy approach and wide coverage allow us to test the hypotheses:

108 H1: Changes in ocean circulation patterns that took place during the late Eocene and early Oligocene (eg. development

109 of ACC and strengthening of AMOC) contributed to the increase in biological productivity in the Southern Ocean.

110 H2: The magnitude of the export productivity increase during a time period that preceded the EOT may have been an

111 important contribution to the drawdown of pCO₂.

112 First, we investigate the export productivity changes across the late Eocene to early Oligocene in two different regions

113 in the Southern Ocean. Then we compare our results to the paleo-circulation changes that occurred at the same time

114 period. We conclude by summarising the implications of the changes in ocean circulation and the possible climate

115 driving mechanisms that led to the cooling of Earth.

116 **1.2. Paleoceanographic Setting**





117 The Southern Ocean (SO) today is an important part of the global ocean circulation and climate system, interconnecting 118 the Atlantic, Pacific and Indian Ocean basins, providing and thus inter-basin exchange of ocean properties and heat. 119 There are strong latitudinal gradients and seasonal changes in ocean properties which affect surface water and export 120 productivity, and thus this region's role in global carbon capture and sequestration. Low light levels and, in higher 121 latitudes, extensive sea ice limit productivity during the winter months. Deep surface mixed layers over the large areas 122 of the Southern Ocean, beyond the shallow stratification effects of meltwater near the sea ice edge, also tend to limit 123 productivity in spring through fall as plankton is mixed below critical thresholds of light availability. The relationship 124 between mixed layer thickness and productivity however is complex (Nelson and Smith, 1991; Li et al. 2021). Southern 125 Ocean productivity is thus concentrated near the Antarctic Circumpolar Current (ACC), the dominant current in the 126 region. This current is the longest and strongest ocean current on Earth. This complex circulation system is driven 127 mainly by westerly winds, resulting in Ekman transport and favouring deep water upwelling. This flow pattern is 128 possible in the absence of land barriers and is balanced by bottom topography friction (Rintoul et al., 2001; Carter et al., 129 2008), while the strength of the current is driven by the strength and location of the westerly winds, and thus, among 130 other factors, the global latitudinal thermal gradient. The ACC is a key component of the 'ocean conveyor belt', playing 131 a role in the global transport of heat (Katz, et al. 2011). Moreover, this circumpolar current influences the strength of 132 meridional overturning circulation and several authors have proposed that this current is one of the main drivers of the 133 Atlantic meridional overturning circulation (AMOC) (Toggweiler and Samuels, 1995; Toggweiler and Bjornsson, 2000; 134 Scher and Martin, 2006, Kuhlbrodt et al., 2007, Scher et al., 2015, Sarkar et al., 2019). The ACC is structured of multiple hydrological fronts, associated with specific water mass properties such as 135 136 temperature and salinity (Sokolov and Rintoul, 2009). Orsi et al., 1995 were the first to propose the traditional view of 137 Southern Ocean fronts. It consists of the Subantarctic Front (SAF), the Antarctic Polar Front (APF) and the Southern 138 ACC Front (SACCF). Besides these main fronts, a Subtropical Frontal Zone (STFZ) can be found north of the ACC 139 (Orsi et al., 1995; Palter et al. 2013; Chapman 2020). This frontal structure is fundamental to different processes that 140 occur in the region, such as the distribution of important nutrients through the exchange between deep and surface 141 ocean, and the exchange of tracers (Palter et al., 2013). Upwelling of Circumpolar Deep Water (CDW) brings nutrient-142 rich waters to the surface towards the Polar Front Zone (PFZ) where Antarctic Surface Waters (AASW) sink to form 143 Antarctic Intermediate Water (AAIW), thereafter it extends into the Subantarctic Zone (SAZ) (Sarmiento et al., 2004) 144 (Figure 1). 145 Wind-driven upwelling, that occurs within the Southern Ocean fronts, enhance biological productivity in these regions 146 (De Baar et al., 1995; Moore et al., 1999). More recently, upwelling related to ACC bathymetry has been found as an 147 important mechanism for establishing phytoplankton blooms in the SO (Sokolov and Rintoul, 2007). This complex

148 structure involving ACC fronts, westerlies and the bottom topography, makes the Southern Ocean a highly productive

region. Iron remobilisation has also been shown to occur due to latitudinal variations of the ACC (Kim et al., 2009),

150 hence inducing a massive increase in productivity.

During the Cenozoic, the ACC structure began to develop with the opening of the pathways between South America and Antarctica and the following formation of the Drake Passage (DP) and, also between Australia and Antarctica that

153 allows the Tasmanian Gateway (TG) opening. Removing these geographic barriers permitted the gradual development

154 of circumpolar flow (Toggweiler and Bjornsoon, 2000). The TG opening to intermediate and deep waters occurred in

the late Eocene, ca 35.5 Ma (Stickley et al., 2004). Tectonic reconstructions for the Drake Passage timing opening

remain controversial, ranging from the late Eocene (ca 41 Ma; Scher and Martin, 2004, 2006) to the early Miocene (ca





157 23 Ma, Barker 2001). Even if the timing of the deepening of the Drake Passage is less well constrained, a "proto-ACC" 158 has been proposed as an earlier expression of the ACC and it is defined as a shallow-depth circumpolar current (Scher 159 et al., 2015, Sarkar, et al., 2019). Cramer et al. 2009 suggested that "proto-ACC" would have played an important role 160 in the ocean circulation changes that occurred in the Eocene. 161

- Many climate model studies have contributed with insights into the ocean structure and circulation of the late Eocene
- 162 (e.g. Huber et al. 2004, Huber & Not 2006, Sipj et al., 2011, Sijp et al., 2016, Elsworth et al., 2017, Baasten et al, 2020, 163
- Toumoulin, et al., 2020). Although some of these experiments have shown that opening of gateways was not sufficient 164 to have caused the global cooling recorded by proxies (DeConto & Pollard, 2003, Huber et al. 2004, Huber & Not 2006,
- 165 Sipj et al., 2011, Baasten et al., 2020), they acknowledge that the circulation patterns have changed during the Eocene.
- 166 A recent model circulation experiment has demonstrated the impact of the DP opening and its effects on ocean structure
- 167 and dynamics even for shallow depths (Toumoulin et al., 2020).
- 168 The organisation of Southern Ocean proto-oceanic fronts may have occurred during the Eocene and formed poleward
- 169 (proto-PF: <~70-60°S; proto-STF: 65-50°S) of their present-day positions, progressing to lower latitudes during the
- 170 Oligocene and Miocene (Lazarus and Caulet, 1994; Nelson and Cooke, 2001; Cooke et al, 2002). This frontal zone
- 171 migration likely played a role in major changes at that time period, including higher ocean productivity.
- 172 Evidence of significant events during the late Eocene highlights the importance of this period that preceded the
- 173 permanent glaciation in Antarctica. Increasingly heavy global benthic oxygen isotope values in the late Eocene, at ca 37
- 174 Ma have been interpreted to reflect pre-EOT glaciation and cooling, this episode is referenced as PrOM event
- 175 (Priabonian Oxygen isotope Maximum, Scher et al., 2014). Additional evidence for a prominent cooling episode has
- 176 been found during this time period (Anderson et al., 2011, Douglas et al., 2014). Despite uncertainties about the nature
- 177 and extent of the earliest ice in Antarctica, these changes imply that paleogeographic reconfiguration has affected the 178 late Eocene Antarctic climate. It is clear that some combined processes favoured the development of permanent
- 179 glaciation in Antarctica.
- 180 Given the importance of changes during the Eocene-Oligocene time interval, especially the ACC development and its
- 181 frontal structure to the climate system and ecosystems, it is crucial to investigate the timing and magnitude of late
- 182 Eocene paleoceanographic changes in the Southern Ocean, and equally important to expand our understanding of the
- 183 implications of such changes on paleoproductivity and how these mechanisms are linked to a changing climate.

2 Materials and Methods 184

185 2.1 Site Descriptions

186 We investigated sediment samples from 3 Ocean Drilling Program (ODP) Sites in the Southern Ocean (Table 1). ODP

187 Leg 177 Site 1090 on the southern flank of the Agulhas Ridge in the Southern Atlantic Ocean (42°54.8'S, 8°53.9'E,

- 188 water depth 3,702m), ODP Leg 133 Site 689 on Maud Rise in the Southern Atlantic Ocean (64°31'S, 3°6'E, water
- 189 depth 2,253m) and ODP Leg 120 Site 748 on Kerguelen Plateau in the Southern Indian Ocean (58°26.45'S, 78°58.89'E,
- 190 water depth 1,290.9m). We selected samples from the middle Eocene through the E-O boundary, depending on the
- 191 sample availability.
- 192 Currently, the sites studied are located in the Southern Ocean through the ACC. Sites 689 and 748 are located in the
- 193 south of the Polar Front zone (PFZ) and Site 1090 in the Subantarctic zone, between the Subtropical front (STF) and the
- 194 Subantarctic Front (SAF) (Figure 1). Across the Eocene-Oligocene transition, the sites were shallower (Table 1). Sites





689 and 748 locations were similar to today and site 1090 was as much as 5° farther to the south (Gersonde et al., 1999)(Table 1).

The major lithology from the lower Eocene to the upper Oligocene at the Maud Rise is composed of calcareous and silicious oozes (Barker et al., 1988). Kerguelen Plateau site is composed mainly of nannofossil ooze and chert (Barron et al., 1989). Agulhas Ridge is predominantly composed of diatoms and nannofossil ooze, with CaCO₃ wt% highly variable, ranging from non-detectable to 69% of sediment throughout the study interval. (Gersonde et al., 1999) with rare occurrences and barren intervals of planktic and benthic foraminifera making it difficult to establish stable isotope records on this site.

203 Table 1. Position of the ODP Sites studied in the present-day and in the late-Eocene (~ 37 Ma). Paleocoordinates

Site	Geographic Setting	Latitude	Longitude	Water depth (m)	Paleodepths (m)	Paleo- latitude	Paleo- longitude
1090	Agulhas Ridge	42°54.8'S	8°53.9'E	3 702	ca. 3,000-3,300 (Pusz et al. 2011)	ca 47°33'S	ca 1°46.8' E
689	Maud Rise	64°31'S	3°6'E	2 253	ca. 1500 (Diester-Haass and Zahn, 1996)	ca 64°19.2'S	ca 2°43.2' E
748	Kerguelen Plateau	58°26.45'S	78°58.89'E	1 290.9	ca. 1200 (Wright et al., 2018)	ca 56°48.6'S	ca 75°36' E

204 calculated based on Seton et al. (2012) rotation model.

205 2.2 Age Models, Linear Sedimentation Rates

Revised age models for the ODP Site 1090, ODP Site 689 and ODP Site 748 in this study were based on all
magnetostratigraphic and biostratigraphic data available on the Neptune database via NSB system (Renaudie et al.,
2020) (Figures S1-S4). All ages in our study are given in the Gradstein et al. (2012) GPTS scale, or have been remapped
to this scale from prior studies.

ODP Site 177 1090 has an age model constructed from shipboard magnetostratigraphic data "U-channel", the records fit the geomagnetic polarity timescale (GPTS) (Channell et al., 2003). Nannofossil biostratigraphy has confirmed the Chron ages (Marino and Flores, 2002), as well as foraminiferal biostratigraphy (Galeotti et al. 2002), strontium isotopes (Channell et al., 2003) and oxygen and carbon isotope data from benthic foraminifera (Zachos et al., 2001, Billups et al., 2002). This integration of several age indicators and their consistency makes this a robust and very well constrained age model.

216 Magnetostratigraphic data for ODP 113 Site 689 is partially reinterpreted from the measurements originally made by 217 Spiess, 1990. A new high-resolution study of Eocene-Oligocene "U-channel" samples from this site presents high 218 correlation with the GPTS (Florindo and Roberts, 2005). Ocean calcareous nannofossil datums (Wei and Wise, 1992;

219 Wei, 1992, Persico and Villa, 2002, 2004), planktonic foraminiferal datums (Kennett and Sott, 1990; Thomas, 1990;

Berggren et al., 1995) and Argon-argon (⁴⁰Ar/³⁹Ar) dating (Glass et al., 1986; Vonhof et al., 2000) is used to re-calibrate
 ages for this site.

A high-resolution magnetostratigraphic study from ODP Site 748B was carried out by Roberts et al. 2003 in continuous

223 "U-channel" samples, revising the shipboard analysis from Inokuchi and Heider, 1992. Calcareous nannofossils





biostratigraphy (Aubry 1992), planktonic foraminiferal biostratigraphic datums (Berggren et al., 1995), diatom datums
(Baldauf and Barron, 1991, Roberts et al., 2003) and strontium isotopes ages (Zachos et al., 1999; Roberts et al., 2003)
were re-evaluated for a better age model.

Accumulation rate fluxes are obtained by calculating the product of linear sedimentation rates (LSR) and shipboard measured dry bulk densities (DBD), thus a robust age model is crucial for this calculation because it determines the linear sedimentation rates. We present data using a straightforward LSR calculation between age-depth control points based on magnetostratigraphic data, stable isotopes and biostratigraphic data. Mass accumulation rates (MARs, mol cm⁻ ² kyr⁻¹) were calculated using LSR based on the above age models multiplied by DBD.

233 Since bio-Ba AR is a direct function of LSR, it is essential to evaluate any possible influence. Figure S5 shows a 234 comparison of linear sedimentation rates and bio-Ba AR. This comparison showed a high amplitude peak at ODP Site 235 1090, with LSR of 4.11 cm kyr⁻¹ at the late Eocene, this high rate is based on a very constrained model. The LSRs for 236 ODP Site 689 varies from 0.1 cm kyr⁻¹ during early Oligocene to up to 1.3 cm kyr⁻¹ in the late Eocene, whereas ODP 237 Site 748 has more uniform values during late Eocene. Small adjustments to LSRs may result in large changes in MARs, 238 emphasising the importance of very well constrained age models. The available age data for our sites allow some 239 variation in the placement of the line of correlation, and thus the precise timing and magnitude of sedimentation rate 240 changes on the scale of \pm ca.5 m.y. are not well constrained, patterns and calculated values over longer time scales are 241 thought to be robust.

242 2.3 Stable Isotope Analyses

243 Stable isotopes of carbon and oxygen were measured both on the bulk fine fraction ($<45\mu$ m) and benthic foraminifera. 244 Bulk sediments were oven-dried and washed through different sieve sizes (125 and 45µm). Smear slides observations 245 indicate that the main carbonate composition of the fine fraction is coccoliths, therefore stable isotopic compositions of 246 bulk fine fraction (<45 µm) reflect primary nannofossil isotope signals. Contamination by non-coccolith carbonate such 247 as fragments of foraminifera shells is minimal (Figure S5). Fifteen to twenty tests of benthic foraminifera (Cibicidoides 248 spp.) were picked from the >125-µm-size fraction. Foraminiferal tests were ultrasonically cleaned using ethanol and 249 oven-dried. Stable isotopic analyses were carried out at the Stable Isotope Laboratory of the Museum für Naturkunde 250 (Berlin, Germany) on a Thermo Isotope Ratio Mass Spectrometer. All values are reported in the δ -notation in parts per 251 mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB). In this study, we applied an adjustment of +0.64‰ 252 (Shackleton and Opdyke, 1973; Shackleton et al., 1984) to all δ^{18} O values of the benthic foraminifera *Cibicidoides* to 253 account for disequilibrium effects.

254 2.4 Barium Analyses and Biogenic Barium as a Paleoproductivity Proxy

Barium (Ba) and aluminum (Al) were analysed by ICP OES, performed at the ElMiE Lab at the German Centre for Geosciences (GFZ, Potsdam, Germany) using a 5110 spectrometer (Agilent, USA). The analytical precision and repeatability were generally better than 2% and it is regularly tested by certified reference material and in-house standards. For preparation, 2g of each sample were grounded and dissolved with ultra-pure HCL. Intensity calibration was performed by external calibration using the same batch of solvent to ensure matrix matching. The analytical blank was negligible compared to the sample concentration. Using barium as a paleoproductivity proxy requires some adjustments because other biogenic sources may contribute to

the barium content in the sediment. Detrital aluminosilicate may affect the barium signal in Southern Ocean sediments.





In order to solve this issue and reveal aluminosilicate contributions, the Biogenic Barium calculation was proposed byDymond et al., 1992, following Eq (1):

265 Biogenic Barium (Bio Ba) = (Ba total) sample - (Ba/Al) bulk continental crust x Al sample (1)

266 This assumes that the aluminum (Al) concentration and the average continental crust abundance are representative of

the detrital Ba component. The Ba/Al crust ratio of 0.0075 is the global average value from sedimentary rocks as

268 suggested by Dymond et al. (1992). This value is based on various compilations of elemental abundances in crustal

269 rocks. This normative calculation potentially introduces uncertainty in samples with high and variable detrital barium,

- 270 but considering that clay assemblages and weathering regimes were relatively constant during the early Paleogene in the
- 271 Southern Ocean, therefore, the crustal ratio probably did not vary much (Robert et al. 2002).
- 272 2.5 Data Compilation

273 2.5.1 Neodymium Isotope Data

274 Neodymium isotopes in seawater reflect the different weathering sources of neodymium that affects each water mass. 275 The isotope values act as conservative elements during ocean mixing. They are therefore a robust water mass tracer, and 276 further are faithfully archived in sediments (Piepgras and Wasserburg, 1982; Martin and Haley, 2000). Their behaviour 277 in seawater and the conservation of the signal in sediments make them a valuable proxy for paleoceanographic studies 278 and past ocean circulation reconstruction. Fossilised fish teeth is commonly used and are considered robust archives to 279 extract Nd isotopic signature because they incorporate and preserve their Nd signature during very early diagenesis 280 (Martin and Scher, 2004), and they can be found in deep-sea sediment samples all over the world and in many geologic 281 time intervals. The Nd signal is given in ε Nd, where ε Nd is the ratio ¹⁴³Nd/¹⁴⁴Nd of a sample relative to the same of the 282 bulk Earth, in parts per 10,000.

In this study, we compiled published Nd isotope data from fossil fish teeth, from the same Ocean Drilling Program (ODP) sites that we investigated in the Southern Ocean (ODP Site 1090 Agulhas Ridge, ODP Site 689 Maud Rise and ODP Site 748 Kerguelen Plateau) and explore the Nd isotope variability to examine the intrusion of waters from the Pacific to the Atlantic sector of the Southern Ocean. We then used these data and our records to explore the evolution of the Southern Ocean circulation and significant circulation changes across the Eocene-Oligocene transition. Sources of Nd isotope data are given in Table S1.

289 2.5.2 pCO₂ Data

290 A variety of geological proxies have been applied to reconstruct the partial pressure of atmospheric CO_2 (pCO_2) during 291 the Cenozoic Era (Pearson & Palmer, 2000; Pagani et al., 2005; Beerling & Royer 2011). Given the low sampling 292 density through the critical Eocene-Oligocene interval, we compiled published pCO_2 data from marine and terrestrial 293 proxies that have been identified as reliable for reconstructing pCO_2 in the Cenozoic. The marine geochemical proxies 294 include alkenone-based estimations, carbon and boron isotope ($\delta^{11}B$) composition of well-preserved planktonic 295 foraminifera calcite. Proxies from the terrestrial reservoir include paleosol carbon and stomatal density. Our 296 atmospheric CO₂ compilation (Table S2) consists to our knowledge all the currently available proxy data on most recent 297 Eocene and Oligocene pCO_2 records. Such compilations are commonly used to estimate past pCO_2 , although it is 298 known that there are limitations and variation among them (IPCC, 2021). Zhang et al. (2013) specifically argued that





compositing limited, short time interval data from different proxies, and different localities may introduce substantial bias into the resulting fitted curve, and instead generated a 40 My long history of Cenozoic pCO_2 from a single section (Site 925 in the equatorial Atlantic). We consider this study's results to be the best single source of information on the history of atmospheric pCO_2 . However, precisely because of the substantial amounts of between proxies and between locality variation, data using a single proxy, from a single site is also potentially not representative of global pCO_2 history. We thus use both the single site results of Zhang et al. (2013) and the full, multi-site and multi-proxy compilation (Supplementary material) in evaluating our own study's results.

306 3 Results

307 3.1 Biogenic Barium

308 Biogenic Barium accumulation rate (bio-Ba AR) records (Figure 2) show a pronounced rise in the late Eocene when the 309 values were up to twice as high as in previous periods for all sites studied. At Kerguelen Plateau ODP Site 748, we also 310 observe a previous and smaller increase around the middle Eocene Climatic Optimum (MECO, ca 40 Ma). At Maud 311 Rise the increase began at ca 38.3 Ma and persisted for around 1.5 Myr. bio-Ba ARs show high value in the Agulhas 312 Ridge at ca 36.8 Ma that is induced by a high sedimentation rate (Figure S5a). Although export productivity was higher 313 (maximum values to about 16.8 µmol bio-Ba cm⁻² ky⁻¹) at Maud Rise compared to the other sites -the Kerguelen Plateau 314 reached maximum values of about 14.3 µmol cm⁻² ky⁻¹ and the Agulhas Ridge site 13.74 µmol cm⁻² ky⁻¹, the records 315 show a high degree of temporal correspondence in the late Eocene peak (ca 36.8 Ma). Bio-Ba values were low at all 316 sites between ca 36 and 34.5 Ma. Between ca 34.5 Ma and ca 33.3 Ma, which includes the EOT interval, bio-Ba AR 317 increased in both sites of the Atlantic Sector, but these increases were not very concurrent between the sites 318 investigated. On the Agulhas Ridge, ODP Site 1090, the rise in bio-Ba (from 7.37 to 20.46 µmol cm-2 kyr⁻¹) is observed 319 in the very latest Eocene (ca 34.3), just before the Oi-1 event. At Maud Rise, ODP Site 689, the increase is not observed 320 until ca 1 Myr after, in the early Oligocene (maximum value 16.25 µmol cm⁻² kyr⁻¹ at ca 33.3 Ma). On the Kerguelen 321 Plateau, ODP Site 748, the increase in export productivity registered by bio-Ba during the Oligocene is notably smaller 322 than in the Atlantic sites, with values not higher than the low values observed during the Eocene.

323 Our bio-Ba results are in general concordant with the temporally more limited data obtained by prior studies of 324 Southern Ocean sites (Anderson and Delaney, 2005, Site 1090; Diester-Haass and Faul 2019, Site 689) (Figure 2). 325 However our results for Kerguelen Plateau Site 748 differ from those of Faul and Delaney, 2010 for nearby Site 738, 326 where the latter estimate bio-Ba accumulation rates up to twice those obtained in our study of Site 748. The differences 327 may be due to the different locations of the two sites, Site 738 is located several degrees further south, and in ca 1 km 328 deeper water depth. The bio-Ba proxy is also very sensitive to sedimentation rates, and the differences may be due to 329 the poor age control for Site 738 which in our studied time interval consists only of a few rather scattered 330 biostratigraphic events (Figure S4a), which results in substantially different age models between our study, Faul and 331 Delaney (2010), and other recent studies of this site, e.g. Huber and Quillevere (2005). In these studies the location and 332 extent of hiatuses, and the uniformity of sedimentation rates varies considerably (SOM Figure S4b). The age model for 333 Site 748 by contrast (Figure S3) is very well constrained by coherent biostratigraphic events from multiple groups of 334 microfossils, Sr isotope stratigraphy and paleomagnetic stratigraphy, and we therefore accept the results from Site 748 335 as being more reliable.





When the data for individual sites is composited together, the behaviour of the Southern Ocean region can be roughly estimated, even though our geographic coverage (lacking data from the Pacific/New Zealand sector) is incomplete and thus may not be entirely representative of the Southern Ocean as a whole. A lowess curve fit to the composited bio-Ba data shows that the key patterns noted in individual records are retained in the composite signal, and thus that Southern Ocean productivity can be characterised as having had two intervals of high values at around 37 and 34 Ma.

341 3.2 Oxygen and Carbon Isotopes

342 Our new oxygen (Figure 3C and E) and carbon (Figure 3D and F) stable isotope data allow us to identify previously 343 noted trends and distinct events during the period studied. Benthic δ^{18} O values exhibit an overall increasing trend during the late Eocene indicating the overall decrease of oceanic bottom water temperatures. A sharp increase occurs at the 344 345 Eocene-Oligocene transition (between 33.9 and 33.3 Ma) in both sites examined. This rapid shift has been observed in 346 several sites in the Southern Ocean (e.g., Muza et al., 1983; Miller et al., 1987; Mackensen and Ehrmann, 1992; Zachos 347 et al., 1996; Billups et al., 2002; Pusz et al., 2011) and it is well established as a global signal (Zachos et al., 2001). It is 348 generally interpreted as a combination of deep ocean water cooling and major ice growth on the Antarctic continent 349 (Zachos et al., 2001). At Site 689, the planktic δ^{18} O curve almost mimics the benthic one. The δ^{18} O values measured on 350 fine fraction reveal a heavier trend more pronounced at ODP Site 748 (Kerguelen Plateau) compared to ODP Site 689 351 (Maud Rise). During the Eocene, heavier values are observed around 37 Ma in both Atlantic and Indian Sectors of SO. 352 Both benthic and planktic foraminifera δ^{13} C records show fluctuations across the period studied, with low values across 353 the Eocene-Oligocene boundary, followed by an increase that accompanied the δ^{18} O increase and low values again in 354 the upper Oligocene. The benthic trend is also observed by previous data from the same sites (Mackensen and Ehrmann, 355 2002; Diester-Haass and Zahn, 1996; Bohaty et al., 2003). The fine fraction records show elevated δ^{13} C values between 356 Late Eocene to Early Oligocene, followed by a decreasing trend during the Oligocene (from ca 33.2Ma). At Site 748, 357 the fine fraction $\delta^{13}C$ curve shows less fluctuation than the benthic curves during the middle Late Eocene. A 358 synchronous δ^{13} C increase (ca 0.6% shift) is observed at 36.5 Ma. Elevated fine fraction δ^{13} C values are observed from 359 the late Eocene until the early Oligocene, coherent with previous studies (Bohaty et al., 2003), while the benthic values 360 stay low during the same period (Figure 3D and F).

361 3.3 pCO₂ Proxies

As noted above, given the complexities and potential biases of compiling data from different proxies and different time intervals, we prefer to use the single site single proxy time series of pCO_2 from Zhang et al. (2013). This data (Figure 4) shows two peaks in the late Eocene, with a maximum for the entire study interval at ca 37 Ma and a smaller peak at ca 34.5 Ma, and a rapid drop of over 200 ppm from nearly 1000 to ca 750 ppm in the earliest Oligocene (ca 33.5 Ma). Despite the limitations of multi-proxy, multi-site compilations, the compiled data (Table S2; Figure S7) shows the same basic features, nor does the result appear to be sensitive to the precise choice of data to include in the analysis.

368 4 Discussion

369 4.1 Late Eocene Productivity Event and its Potential Impact





370 The noticeable bio-Ba AR peak at ~ 36.8 Ma (Figure 2), suggests an important, ca 1 my long event of approximate 371 doubling of export productivity during the late Eocene, preceding the significant cooling and the first formation of large 372 Antarctic ice sheets at the Eocene-Oligocene boundary. The temporal synchronicity among different site locations in the 373 Southern Ocean suggests that the process driving this enhanced export productivity in the late Eocene occurred 374 throughout the Southern Ocean, requiring a mechanism that increased the delivery of nutrients to the surface ocean. 375 Our findings corroborate previous, more limited paleoproductivity studies that indicate an increase in export 376 productivity in the Atlantic Sector of the Southern Ocean during this time period. Anderson and Delaney (2005) found 377 several peaks in productivity indicators at the Agulhas Ridge during the same time interval, and benthic foraminiferal 378 accumulation rates show an increase in paleo-primary productivity on Maud Rise (Diester-Haass & Faul, 2019) (Figure 379 2). A pronounced opal abundance peak is also documented by Diekman et al. (2004) between 37.5 and 33.5 Ma at the 380 ODP Site 1090. The Kerguelen productivity record from Site 744 data shows a substantial peak around 37 Ma and an 381 earlier one near 40 Ma. Our results thus show that the 37 Ma event extended at least as far as the Kerguelen Plateau in 382 the Indian Ocean sector, thus affecting most of the Southern Ocean region. 383 The potential significance of this event for the development of late Eocene global climate depends on the extent to 384 which the enhanced productivity contributed to enhanced carbon sequestration, and the magnitude of sequestration over 385 the ca 1 my interval of enhancement. Our ability to estimate the impact of higher productivity on carbon sequestration is 386 limited, as many of the factors that affect this in the modern ocean are poorly understood for Eocene oceans (export 387 efficiency to the subsurface waters, rates of transport and degradation in the water column and upper sediment layers, 388 organic carbon content of Southern Ocean Eocene pelagic sediments; as well as transport of organic carbon by 389 subsurface water layers in the late Eocene oceans to lower latitude areas of productivity and sequestration). For 390 simplicity we thus use values for the modern Southern Ocean, but conservatively ignore the (in the modern oceans) 391 substantial transport of nutrients in the modern ocean to lower latitudes by Antarctic Intermediate Water (Sarmiento et 392 al., 2004). The purpose of such a calculation is simply estimating if the magnitude of enhanced productivity, could, 393 within the region studied, and over the 1 my interval of the event, at least potentially have sequestered a climatically 394 significant amount of carbon. Using Hayes et al. (2021) data on the composition and flux of seafloor sediments in the 395 Global Ocean, we compute the mean total organic carbon (TOC) exported to deep-sea sediments per cm2 per year in the 396 Southern Ocean (SO, area below the polar front and above the Antarctic continent), the Polar Frontal Zone (PFZ, based 397 on Park et al. 2019 coordinates for the subantarctic and polar fronts) and, as a subset of the SO total, just the Atlantic 398 sector of the Southern Ocean. We thus estimate the total amount of organic carbon currently exported to the deep sea 399 per year in these areas. Finally, given the approximate doubling of productivity during the 1 my interval, we compute 400 the amount of excess exported carbon over 1 Myr, and translate it into the corresponding amount of atmospheric CO₂ in 401 ppm (using Clark 1982 equivalency) to roughly estimate the order of magnitude of how much carbon the biological 402 carbon pump could have buried in the sediments of the area of interest. The results (Table 2) suggest that enhanced 403 carbon sequestration in the late Eocene SO, even if restricted only to the Atlantic sector, could have indeed been 404 sufficient to have affected global pCO_2 (hypothesis 2 as stated in the introduction). If the enhanced productivity affected 405 most, or all of the circumpolar region, and if indirect carbon sequestration via intermediate water transport also played a 406 role the impact could have been dramatic.

407 Table 2. Potential impact of doubling modern Southern Ocean export productivity/carbon sequestration for a 1 my time408 interval. See text for definitions of areas and calculations.





Region	Area (km2)	Mean TOC (gC cm²yr¹)	Exported carbon (PgC Myr¹)	Equivalent <i>p</i> CO₂ (ppm)
Southern Ocean	35 882 985	0.004882	1 751.856	882.5
PFZ	10 290 123	0.004326	445.108	209.0
Atlantic Sector of SO	11 561 803	0.005047	583.518	274.0

409 4.2 Surface Water Changes in Physical Conditions in the Late Eocene

410 The late Eocene is generally accepted as a time interval of gradual cooling of Southern Ocean waters. Indeed, 411 biomarker-based temperature estimates reveal substantial (3-5 °C) high latitude sea surface temperatures (SST) cooling 412 within the late Eocene (Liu et al., 2009, O'Brien et al., 2020). Our fine fraction stable oxygen isotopes confirm this 413 cooling trend following MECO, with a distinct peak at 37 Ma during the Eocene, matching the peak cooling reported by 414 O'Brien et al. (2020). This interval of maximum δ^{18} O values occurred during the same interval in which export 415 productivity increased (Figure 2). In this interval the difference in the $\delta^{18}O$ gradient between benthic foraminifera and 416 fine fraction (nannofossil) carbonate is less pronounced. This increase in similarity can either be caused by a decrease in 417 water column stratification or by enhanced vertical mixing. In other words, either the (temperature) conditions during 418 deposition were identical across larger areas and depths, or water masses were mixed more frequently.

419 This change in export productivity in the late Eocene is coeval with a change towards increasing variability carbon 420 stable isotopes (δ^{13} C) of benthic foraminifera (Figure 4). Benthic foraminiferal δ^{13} C provides a powerful tracer for the 421 reconstruction of bottom water circulation patterns, nonetheless, should be carefully interpreted because the signal can 422 be overprinted by multiple effects such as the global carbon cycle or local dissolved nutrient contents. Comparing our 423 local stable carbon isotope records to a global compilation shows that the local $\delta^{13}C$ curves fit reasonably well within 424 the global records (Figure 3B, D and F). In the global context, a shift towards more positive values in the δ^{13} C at 37 Ma 425 demonstrates a carbon cycle perturbation. The subsequent decrease towards more positive values in the late-Eocene is 426 coeval with the global trend and also coincides with the productivity changes. One possible explanation is that the 427 marine organic carbon burial is increased, preferentially scavenging the light 12C from the carbon pool.

428 This adds evidence to an event of high productivity during the late-Eocene. However, in the Indian Sector and 429 afterwards in the Atlantic Sector of the Southern paleo Ocean, the local δ^{13} C does not follow the secular trend. This 430 argues that ocean circulation also changes along with productivity.

431 **4.3 Oceanographic Circulation Drivers of the Late Eocene Productivity Change**

We propose that the main cause for the productivity increase observed in the late Eocene is upwelling of nutrient-rich deep waters. Understanding however the physical oceanographic mechanisms that led to increased upwelling throughout the Southern Ocean requires examining links between the different processes that occurred at that time period. Changes in paleoceanography during the Paleogene were significantly mediated through tectonic reorganisation, such as the Southern Ocean gateways opening (i.e., the Drake Passage and the Tasman Gateway), changes in the Atlantic-Arctic gateway and in the Tethys Seaway. In this context, the Southern Ocean circulation during this time period is still debated due to uncertainties concerning

In this context, the Southern Ocean circulation during this time period is still debated due to uncertainties concerningthe opening of the gateways that led to the development of the Antarctic Circumpolar Current (ACC). Estimates for the

440 onset of the modern-like ACC have not reached a consensus yet and vary from as early as middle Eocene (ca 41 Ma,





441 Scher & Martin, 2006; ca 35.5 Ma, Stickley et al. 2004) to middle Oligocene (ca 23Ma; Pfuhl and McCave, 2005). This 442 inconsistency suggests that the onset of ACC could have been a gradual or an intermittent change. Further, local proxy 443 records cannot distinguish between regionally developed fronts and true circumpolar, i.e. ACC flow.

In addition to δ^{18} O and δ^{13} C, ϵ Nd has been used to identify circulation changes and water masses exchange through the Eocene (Scher and Martin, 2004, 2008; Scher et al., 2014; Huck et al., 2017; Wright et al., 2018). Nd isotopes are one of the most robust tracers of water mass origin (Frank, 2002). The residence time of Nd in oceans is much shorter (300 -1000 years) than ocean mixing time and is thus distinct at a given location. Further, the isotope composition of the Nd ocean budget is solely determined by terrigenous contribution. The latter is balanced by Nd sinks that remove Nd quantitatively, yet this only influences the net budget and thus the magnitude and/or swiftness of changes to the ϵ Nd composition. However, mixing of water masses, e.g. through lateral or vertical mixing, can also cause changes as long

451 as they occur more rapidly than the residence times.

452 In the late Eocene, starting at 37 Ma, Scher and Martin (2004) found a dramatic positive shift in ε-Nd values in the 453 Atlantic sector of the SO that they interpreted as the influx of Pacific deep waters, due to its characteristic of more 454 radiogenic (positive) waters, not previously observed in the Atlantic Ocean. Recently published Nd isotope records from 455 the Kerguelen Plateau (Wright et al., 2018) revealed a long-term negative trend during the late Eocene, which also 456 suggests that the water mass mixing between the Pacific and Atlantic preceded 36 Ma. ENd (t) records from the 457 Kerguelen Plateau in fact showed values comparable to modern CDW during the Oligocene, inferring water mass 458 composition similar to the present day. Thus, Nd isotope data support at least partial opening of Drake Passage by the 459 late Eocene (before 36 Ma), consistent with plate tectonic reconstructions (Livermore et al., 2005, 2007). Regardless of 460 the depth, Neodymium isotope evidence for late Eocene opening of the Drake Passage suggests that increased fetch for 461 surface flow and changing deep water composition could have had changes in the surface water conditions in the South 462 Atlantic sector of the late Eocene Southern Ocean.

463 This has been explicitly demonstrated in a recent modelling study conducted by Toumoulin et al. (2020). They 464 demonstrate that the Drake Passage opening, even at shallow depth, notably connects prior regional frontal systems 465 together, thereby allowing the formation of a proto-ACC; and has a strong effect on the Southern Ocean Eocene water 466 mass structure, inducing ocean cooling in most of the Southern Hemisphere. These temperature changes are not linear 467 and differ from one region to another, with DP opening causing changes in the mixed layer depths and provoking 468 different responses in the Atlantic and Indian Sectors of the SO. In the Atlantic and Indian Ocean sectors in particular, 469 very deep seasonal mixing (several hundred meters) over broad areas of the entire region is replaced by more moderate 470 levels of mixing (generally ca 200 m or less), except near the proto-polar front region, where seasonal mixing of 300-471 400 m still occurs. Vila et al. 2014 have found nannofossil assemblages characteristic of cool sea surface waters in the 472 late-Eocene in Kerguelen Plateau samples Cooler temperatures are coeval with the paleoceanographic re-organization 473 and intensified upwelling that we infer for this time period, while differences in the depth of the mixed layers between 474 ocean basins may explain the different magnitude of export productivity observed in the Atlantic and Indian sectors of 475 the SO.

The wind-driven eastward flow and the characteristic fronts of the modern ACC support the upwelling of nutrient-rich water to the surface and consequently high levels of productivity. On the balance of evidence, it seems that the export productivity seen in our data in the late Eocene is likely to have occurred in response to a proto-ACC front's development and its associated upwelling. The inferred onset of a proto-ACC in the late Eocene and our finding of increased upwelling fits the hypothesis that ACC type circulation itself helps drive the AMOC circulation (Toggweiler





and Bjornsson, 2000; Katz et al., 2011; Sarkar et al., 2019). A proto-ACC causes SO upwelling, and thus provides support for increasing AMOC-like circulation in the late Eocene as an additional cause of increased upwelling as a causative mechanism of the export productivity event. Temperature asymmetry between Northern and Southern Hemisphere and comparisons between benthic δ^{13} C records provide evidence for the strengthening of the AMOC in the late Eocene (Elsworth et al., 2017).

486 4.4 Eocene-Oligocene Boundary Productivity Changes

487 The earliest Oligocene, following the EOT, has been suggested as a period of a significant rise in biological productivity 488 in high southern latitudes (Diester-Haass, 1995, 1996; Diester-Haass and Zahn, 1996, 2001). However, in contrast to the 489 late Eocene event, the export productivity changes across the Eocene-Oligocene boundary observed in our study were 490 not always concurrent between the sites investigated (Figure 2). In the Atlantic sites, export productivity increases and 491 decreases several times from the late Eocene to early Oligocene. We thus argue that the fluctuations in export 492 productivity that occurred in the Southern Ocean during this global climatic re-organization are more strongly 493 modulated by local parameters, whereas the late Eocene productivity event is more uniform and reflects the global re-494 organization of ocean circulation. If the trends observed in export productivity across the EOT were regulated only by 495 global, or at least regional temperature and circulation changes, then we would observe significant changes also in the 496 Indian sector of the Southern Ocean. It seems however that productivity increase was more pronounced in the Atlantic 497 sector of the Southern Ocean.

498 Today, the Southern Ocean (SO) has a frontal system that strongly impacts circulation, primary productivity and the 499 entire climate system (Chapman et al., 2020). The Antarctic Polar Front (APF) is particularly important for controlling 500 nutrient distribution. Latitudinal variations of the APF for example have been shown to alter regional productivity over 501 the glacial cycles (Kim et al., 2014, Thole et al., 2019). The causes of the lack of significant export productivity changes 502 in the Indian sector of the Southern Ocean during the early Oligocene after the Eocene-Oligocene boundary are unclear. 503 The Kerguelen Plateau may not have been located in a position favourable to nutrient-rich upwelling. In addition, the 504 regional frontal migration may have been more intense in the Atlantic sector compared to the Indian sector of the SO.

505 4.5 A Scenario for Southern Ocean Productivity and Circulation Change in the Late Eocene

The patterns of productivity change seen in our study can be placed in an (admittedly speculative) scenario, which is at least compatible with prior studies and modelling of conditions in the late Eocene austral ocean region and Antarctica. In the earliest interval covered in our study (ca 40-38 Ma) productivity was in most sites fairly low (Figure 5a). At this time there is little evidence for significant influx of Pacific waters into the Atlantic, and the Drake Passage is thus assumed to be effectively closed to ocean circulation. During the 38-36 Ma interval, evidence summarised by Scher et al. (2014) suggests that a significant, if transient, glaciation event occurred on the Antarctic continent - the Priabonian oxygen maximum, or PriOM. If sufficient in

512 gluention event occurred on the Antarche continent and Antaohim oxygen maximum, or From. If surficient in 513 magnitude this would have significantly affected circulation throughout the austral ocean region, with strengthened

514 temperature gradients, stronger circumpolar circulation, and increased upwelling (Goldner et al, 2014). This would

515 account both for the substantial increase in productivity, and the broad geographic extent of the increase seen in our data

516 (Figure 5b). The cause of this glaciation event is unknown, but may be related in part to the trend in the late Eocene

- 517 towards lower atmospheric pCO_2 interacting with orbital fluctuations in polar insulation as explored in model
- 518 simulations by Van Breedam et al. (2022).





519 With the end of transient glaciation, atmospheric forcing of ocean circulation would have declined, and with it the high 520 levels of productivity seen in our data (Figure 5c). However, by this time (ca 36-34 Ma) the Nd isotope data suggests 521 that a significant influx of Pacific water was reaching the South Atlantic sector of the austral ocean (Scher and Martin, 522 2004), and consequently, the Drake Passage must have been at least partially open. This would have resulted in, if not as 523 strong as during the PriOM, nonetheless stronger circumpolar circulation in a proto-ACC, increased upwelling, and 524 increased nutrient availability from Pacific-sourced deep waters. The locus of high productivity would have become 525 however more cantered near the proto-ACC, which at that time, according to the model results of Toumoulin et al. 526 (2020) was located a few degrees north of the current location of the ACC. The high productivity and accumulation of 527 biogenic opal seen at Site 1090, fortuitously located at this time in this region can be thus be explained, as can the lower 528 relative productivity of Site 689, located much further to the south and thus outside the region primarily influenced by 529 the proto-ACC system.

530 Lastly, at the E/O boundary itself (Figure 5d), the well known major shifts in oxygen isotopes signal the formation of a

531 full continental ice-sheet, which would have in turn driven a renewed increase in circumpolar ocean circulation - a full,

532 if early form of the ACC, and dramatically increased levels of productivity, again however primarily near the ACC

533 region.

534 4.6 Possible Implications to the EOT Global Cooling

535 Our pCO₂ compilation shows that carbon dioxide levels declined gradually from ca 1200 ppm in the late Eocene to ca 536 750 ppm across the EOT (Figure 4 and Figure S7). There are different processes involved in the oceanic uptake of CO₂. 537 The solubility pump is a physic-chemical process that promotes gas transfer between atmosphere and sea water in order 538 to achieve chemical equilibrium. This process depends on temperature, in which the solubility increases as temperature 539 decreases. Evidence for cooling of surface waters observed in the Southern Ocean (Liu et al., 2009; Hutchinson et al., 540 2021) could have favoured the ability to dissolve atmospheric CO_2 , thus being an important contributor to the 541 drawdown of pCO2 during the late-Eocene. 542 Silicate weathering has been suggested to play an essential role in regulating CO₂ across the EOT (Zachos and Kump, 543 2005). On geologic time scales, chemical silicate weathering is considered to modulate atmospheric CO_2 levels through

a negative feedback mechanism (Berner et al., 1983). Weathering of silicate rocks is a source of alkalinity to the oceans
and thus a sink for atmospheric CO₂, thereby influencing global climate. Increasing silicate weathering increases
primary productivity through the delivery of nutrients to the ocean. Intensified weathering is supported by Os isotope
records, showing an anomaly before the EOT, at ca 35.5Ma (Dalai et al., 2006).

The potential effects of enhanced export productivity could have modulated these changes in CO_2 because it removes organic carbon from the surface ocean and transport it into the deep ocean, and thus via sequestration is a mechanism that contributes to the decline of atmospheric carbon dioxide and intensifies the cooling trend. Therefore, enhanced productivity in the late-Eocene and at Eocene-Oligocene transition recorded in our study is a potential candidate that may have provided important positive feedback to the pCO_2 decline. Despite some modelling studies showing that circulation changes were not the main factor in driving the cooling and

glaciation on Antarctica (e.g. Huber et al., 2004; Huber and Not 2006; Sijp et al., 2011), sea surface temperature decreased affecting the atmosphere-ocean CO_2 equilibrium. A succession of events may have contributed to the evolution of climate: thermal isolation of Antarctica, glaciers formation, increasing intensity of silicate weathering,

557 together with upwelling of nutrient rich and cold deep waters, leading to higher solubility pump and high biological





productivity, then declining pCO_2 . Moreover, because the Atlantic Meridional Overturning Circulation (AMOC) affects the distribution of tracers such as temperature, dissolved inorganic carbon (DIC), alkalinity and nutrients (Boot et al., 2021), the strengthening of AMOC could explain the further decrease in atmospheric CO_2 via biological export productivity. Elsworth et al., (2017), for example, suggest that enhanced weathering is driven by intensified AMOC in the latest Eocene due to increasing AMOC causing differential global distribution and increase of surface temperatures and precipitation over land areas. These factors together suggest that E-O changes in AMOC also may play an important role as a driver of CO_2 decline.

565 Taken together, the above processes indicate that a variety of positive feedbacks contributed to Antarctic glaciation from 566 about 37 Ma onwards. Recent evidence suggests that continental-scale Antarctic glaciation initiated in the late Eocene 567 (Scher et al., 2014; Carter et al., 2017). Our results indicate that significant changes in Southern Ocean export 568 productivity preceded the E/O boundary by approximately 3 million years. These trends are likely to be a response to 569 the combination of the intensified processes that had been in place since the late Eocene, and suggest that biological 570 productivity played an important role in the drawdown of pCO₂ levels. The CO₂ fixation by phytoplankton and carbon 571 export to the seafloor increased via biological pump may have contributed to decrease atmospheric CO2 through a 572 positive feedback and, thus boosting the cooling trend. The establishment of Antarctic glaciation may have been 573 influenced significantly by enhanced productivity. What remains unclear is the biological drivers (plankton) of this 574 productivity change and their role in the long-term evolution of global climate change.

575 4.7 Limitations and Future Directions

576 Our study has numerous limitations. Our data on paleoproductivity does not cover the full time interval in all of the sites 577 studied, and our geographic coverage is still incomplete. In particular, we have not examined sections from the Pacific 578 sector, or the influence of the Tasman gateway. Most of our interpretations are based on a single productivity proxy -579 biogenic Barium. While this proxy is well established and gives coherent results in our study, productivity proxies are 580 known to have complex behaviours, and results using different proxies might be at least somewhat different. Our 581 estimates of how much elevated late Eocene Southern Ocean productivity might have affected global carbon 582 sequestration is only a rough estimate of potential magnitude and much more detailed study of both actual sequestration values in sediment, and the impact on atmospheric pCO2 are still needed. Our interpretative scenario attributing 583 584 productivity changes to a combination of Drake Passage opening and continental scale glaciation on Antarctica are 585 purely qualitative and need further study. Despite these limitations, our study sheds new light on the late Eocene 586 oceanic precursors of the Eocene-Oligocene glaciation event - the most dramatic climate change of the Cenozoic.

587 5 Conclusions

588 Our bio-Ba data provide important records of the Southern Ocean productivity history across the EOT. These data show 589 that export productivity increased significantly in the late Eocene in the Southern Ocean and was affected by ocean 590 circulation changes. The development of a regionally varying circumpolar polar flow (proto-ACC) and the associated 591 frontal system is likely to have contributed to the enhanced productivity in the Southern Ocean through the 592 intensification of upwelling (H1). 593 Our results show that increasing Southern Ocean productivity in the late Eocene to earliest Oligocene is correlated to

 $p_{\rm CO_2}$ global changes in atmospheric $p_{\rm CO_2}$ and carbon isotope proxies for organic carbon extraction. This finding points toward a potential positive climate system feedback, involving ocean circulation changes, enhanced export productivity





and drawdown of atmospheric CO_2 . Although studies have the inclination to point to a dominant mechanism (ocean gateway opening vs pCO_2 decline) for causing the initiation of Antarctica glaciation, each mechanism plays a different role and has associated complex feedbacks. Our study points toward a climate feedback system involving ocean circulation, thermal isolation and biological productivity, where several mechanisms are interconnected and cannot be considered separately. Openings of gateways led to the development of a circumpolar flow, promoting cooling and increased upwelling that contributed to ocean carbon pumps and promotes the decline of atmospheric carbon dioxide.

601 Data Availability

- 602 The supplementary information related to this article is available in the Supplement, the raw data will be available upon
- 603 publication in an open-access database (PANGAEA: https://www.pangaea.de).

604 Author Contributions

- 605 The manuscript was designed and written by GRF in collaboration with DL. DL updated age models. GRF prepared all
- the samples for geochemical analyses. JS run barium and aluminum analyses. US generated carbon and oxygen stable
- 607 isotope data. pCO₂ data and neodymium isotopes data were compiled by GRF. Biogenic barium was calculated by GRF.
- 608 All authors contributed to editing the manuscript.

609 Competing Interests

610 The authors declare that they have no conflict of interest.

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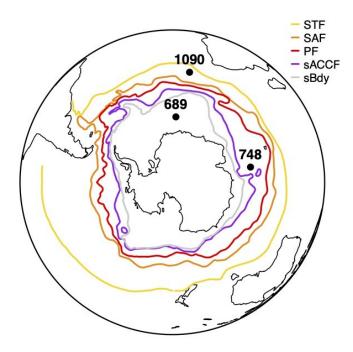


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- Figure 1: Schematic Antarctic Circumpolar Current (ACC) and Southern Ocean fronts as determined by Orsi et
 al., 1995, named from north to south, STF: Subtropical front, SAF: Subantarctic Front; PF: Polar Front and
 SACCF: Southern Antarctic Circumpolar Current Front, and sBdy: Southern Boundary front. Modern location
- of ODP sites (1090, Agulhas Ridge; 689, Maud Rise and 748, Kerguelen Plateau) used for reconstructions in this
- 997 study. ODP = Ocean Drilling Program.





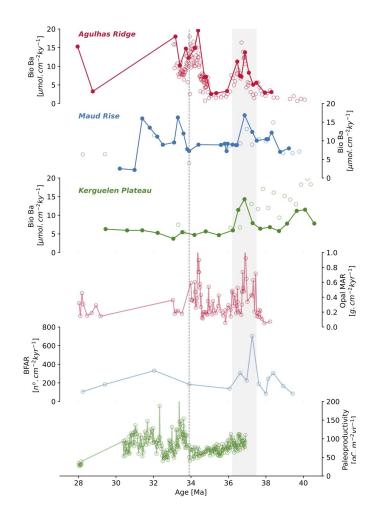
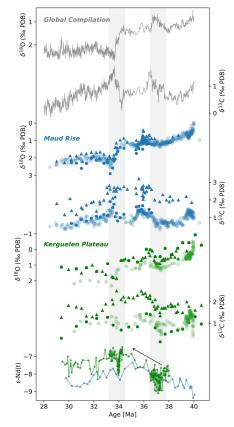


Figure 2: Paleoproductivity proxies vs Age (Ma) for Agulhas Ridge (ODP Site 1090, in red), Maud Rise (ODP Site 998 999 689, in blue) and Kerguelen Plateau (ODP Sites 748, 744 and 738, in green). Solid circles are new biogenic barium accumulation rate (bio-Ba, µmol cm⁻² kyr⁻¹) data of this study, open circles from prior literature (Agulhas 1000 Ridge data from Anderson and Delaney, 2005; Maud Rise data from Diester-Haass and Faul 2019; Kerguelen 1001 1002 Plateau data from Faul et al., 2010). Site 1090 opal MAR data are from Diekmann et al., 2004. Site 689 BFAR data are from Diester-Haass and Zahn 1996. Kerguelen Plateau Site 744 paleoproductivity data from Diester-1003 1004 Haass (1996). Vertical bar identifies the E/O boundary (at ca 33.8 Ma). Shaded area encompasses the late-Eocene 1005 productivity event.



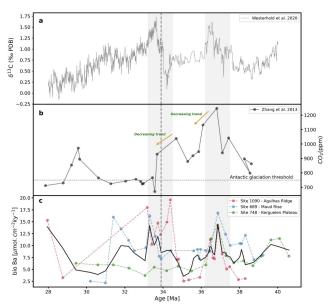




1006 Figure 3: Multiproxy records from the late Eocene and early Oligocene. Global compilation of oxygen and carbon stable isotopes (from Westerhold et al., 2020). New generated oxygen and carbon benthic foraminiferal 1007 1008 isotopes data (solid circles) and fine fraction (<45µm) (solid triangles), and previously published oxygen and 1009 carbon stable isotopes (shaded circles, from Mackensen and Ehrmann, 1992; Diester-Haass and Zahn, 1996; 1010 Bohaty et al., 2003) from Atlantic Southern Ocean (Maud Rise) ODP Site 689 (in blue) and Indian Southern 1011 Ocean (Kerguelen Plateau) ODP Site 748 (in green). PDB is PeeDee Belemnite carbonate reference. Compilation 1012 of ENd data obtained from fossil fish teeth for the Atlantic Sector of SO (Maud Rise - in blue, site 689), and for 1013 the Indian sector of SO (Kerguelen Plateau - in green, sites 738 and 748) (Scher and Martin, 2004, 2006; Scher et 1014 al., 2014; Wright et al. 2018). Shaded area identifies E/O boundary at ca 33.8 Ma and the changes in ocean 1015 circulation. Note inverted y-axis scales for oxygen and Nd isotopes.







1016 Figure 4: Comparison between (a) a global compilation of carbon stable isotopes (from Westerhold et al., 2020),

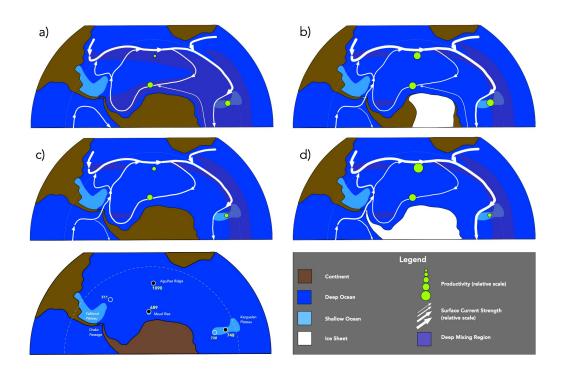
1017 (b) alkenone-based atmospheric *p*CO₂ record (from Zhang et al., 2013) and (c) biogenic Barium (bio-Ba) export

productivity proxy. Antarctic glaciation thresholds (approx. 750 ppm) (from climate model, DeConto et al. 2008)
 is marked by a dashed line. Shaded areas encompass the late-Eocene and early-Oligocene high productivity

1020 intervals.







1021Figure 5: Interpretive scenario of paleoceanographic change in the late Eocene to earliest Oligocene Southern1022Ocean. Base map, circulation patterns and extent of deep mixing regions largely after Toumoulin et al. (2020), ice1023sheet extent at 38 Ma after models in Van Breedam (2022).Productivity values based on results of this study,1024shown in relative scale. Note general trend towards higher productivity values, and within this, higher1025productivity, focussed near proto-ACC, during intervals with inferred ice sheets.