1

Enhanced terrestrial carbon export from East Antarctica during the early Eocene

Gordon N. Inglis^{1,2}, Jaime L. Toney³, Jiang Zhu⁴, Christopher J. Poulsen⁵, Ursula

2

3

Röhl⁶, Stewart S. R. Jamieson⁷, Jörg Pross⁸, Margot Cramwinckel¹, Srinath 4 Krishnan^{9,10}, Mark Pagani^{9,13}, Peter K. Bijl¹¹ and James Bendle¹² 5 6 ¹ School of Ocean and Earth Science, University of Southampton, UK 7 ²Organic Geochemistry Unit, School of Chemistry, University of Bristol, UK 8 ³ School of Geographical and Earth Sciences, University of Glasgow, UK 9 ⁴ Climate and Global Dynamics Laboratory, National Center for Atmospheric 10 Research, Boulder, Colorado, USA 11 ⁵ Department of Earth and Environmental Sciences, University of Michigan, USA 12 ⁶ MARUM – Center for Marine Environmental Sciences, University of Bremen, 13 14 Bremen, Germany ⁷ Department of Geography, Durham University, Durham, UK 15 ⁸ Institute of Earth Sciences, Heidelberg University, 69120 Heidelberg, Germany 16 ⁹ Department of Geology and Geophysics, Yale University, New Haven, CT 06511, 17 USA 18 ¹⁰ CICERO Center for International Climate and Environmental Research, Oslo, 19 20 Norway 21 ¹¹ Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Utrecht, Netherlands 22 ¹² School of Geography, Earth and Environmental Sciences, University of Birmingham, 23

24 UK

25	¹³ Deceased, November 2016
26	
27	Corresponding author: Gordon N. Inglis
28	Email: gordon.inglis@soton.ac.uk. Telephone: +44 (0)117 954 6395
29	
30	
31	
32	
33	
34	
35	
36	
37	
38	
39	
40	
41	
42	
43	
44	

45 Key points:

46	•	Terrestrial organic carbon is an important CO2 sink when transported via rivers
47		to the ocean and sequestered in coastal marine sediments.

- Biomarkers indicate enhanced terrestrial organic carbon burial during early
 Eocene this could have acted as a negative feedback mechanism
- Hydrology regulates organic carbon export from the terrestrial biosphere at this
 site
- 52

53 **Abstract:**

Terrestrial organic carbon (TerrOC) acts as an important CO₂ sink when transported 54 via rivers to the ocean and sequestered in coastal marine sediments. This mechanism 55 might help to modulate atmospheric CO_2 levels over short- and long timescales (10³) 56 to 10⁶ years), but its importance during past warm climates remains unknown. Here 57 we use terrestrial biomarkers preserved in coastal marine sediment samples from 58 Wilkes Land, East Antarctica (~67°S) to quantify TerrOC burial during the early 59 Eocene (~54.4 to 51.5 Ma). Terrestrial biomarker distributions indicate the delivery of 60 plant-, soil- and peat-derived organic carbon (OC) into the marine realm. Mass 61 accumulation rates of plant- (long-chain *n*-alkane) and soil-derived (hopane) 62 biomarkers dramatically increase between the earliest Eocene (~54 Ma) and the early 63 Eocene Climatic Optimum (EECO; ~53 Ma). This coincides with increased OC mass 64 accumulation rates and indicates enhanced TerrOC burial during the EECO. Leaf wax 65 δ^2 H values indicate that the EECO was characterised by wetter conditions relative to 66 the earliest Eocene, suggesting that hydroclimate exerts a first-order control on 67 TerrOC export. Our results indicate that TerrOC burial in coastal marine sediments 68

could have acted as an important negative feedback mechanism during the earlyEocene, but also during other warm climate intervals.

71

72 **1. Introduction**

Over long-timescales (10⁴ to 10⁶ years), the evolution of atmospheric carbon dioxide 73 (CO₂) concentrations primarily reflects the balance between CO₂ sources (e.g., solid 74 earth degassing, oxidation of rock-derived OC and sulphide minerals; Plank and 75 Manning, 2019; Hilton et al., 2014; Torres et al., 2014) and CO₂ sinks (e.g., silicate 76 weathering, organic carbon burial) (Berner 1990; Gaillardet et al., 1999; Galy et al., 77 2007). Between ~20 to 50% of total OC burial in modern marine sediments is derived 78 from the terrestrial biosphere (TerrOC; i.e. soils and vegetation) (Hilton & West 2020). 79 Consequently, TerrOC burial in marine sediments may act as an important CO₂ sink 80 over short- to long timescales (10^3 to 10^6 years) (Hilton et al 2015). 81

The erosion and subsequent burial of TerrOC in marine sediments is 82 determined by a variety of climatic and tectonic controls (Eglinton et al 2021). Steep 83 river catchments are typically characterised by enhanced TerrOC export (e.g., Hilton, 84 2017; Kao et al., 2014). However, climate also exerts a key control on TerrOC export 85 (Hilton, 2017; Galy et al 2015) and there is a close link between mean annual run-off 86 and TerrOC export in modern river systems (Hilton, 2017; Wang et al., 2020). Although 87 TerrOC export and burial may help to modulate atmospheric CO₂ over geological 88 timescales, the importance of this process in the past is unknown and the majority of 89 work has been on modern erosive systems (e.g., Hilton, 2017; Galy et al., 2015; Wang 90 91 et al., 2020).

⁹² The early Eocene Climatic Optimum (EECO; 53.3-49.1 Ma) is characterised by ⁹³ high temperatures (~10 to 16°C warmer than pre-industrial) (Inglis et al 2020), an

intensified hydrological cycle (Carmichael et al., 2016), and lacked continental-scale 94 ice sheets (Francis and Poole, 2002). As such, it can serve as a natural laboratory to 95 understand how TerrOC export and burial operates when it is significantly warmer and 96 wetter than present. Here we use samples recovered from the East Antarctic margin 97 (Integrated Ocean Drilling Program (IODP) Leg 318; IODP Site U1356; ~ 67°S 98 paleolatitude) (Escutia et al 2011b) to determine the amount of TerrOC transported 99 along the land-sea continuum during the earliest Eocene (54.3 to 51.5 Ma), including 100 one of the three DeepMIP intervals (i.e., the Early Eocene Climatic Optimum; 53.3 to 101 102 49.1 Ma) (Hollis et al 2019). A combination of bulk and molecular proxies are used to fingerprint the type of OC in the East Antarctic margin. We then apply a mixing model 103 approach to quantify TerrOC burial along the East Antarctic margin. We also develop 104 105 new leaf wax δ^2 H records and compare these alongside isotope-enabled modelling 106 simulations to determine the relationship between the hydrological cycle and TerrOC export during the early Eocene. 107

108

109 2. Methods and Materials

110 2.1. Site description

Site U1356 (modern coordinates: 63°18.6138' S, 135°59.9376' E) is located ~300 km off Wilkes Land, Antarctica, at the transition between the continental rise and the abyssal plain. Current water depth is 3992 meters (Escutia et al 2011a) (Figure 1). Samples were obtained from lithological Unit XI (~948 to 1000 mbsf) that consists of bioturbated hemipelagic early Eocene claystones. Occasional laminated siltstone and sandstone interbeds indicate sporadic gravity flows or bottom current activity reaching the site (Escutia et al 2011a). Lithological Unit XI is dated as early Eocene based upon a combination of published dinoflagellate cyst (dinocyst) biostratigraphy and
 magnetostratigraphy (Bijl et al 2013, Tauxe et al 2012).

120

121 2.2. Bulk isotope geochemistry

Total organic carbon (TOC) measurements were carried out at MARUM, University of 122 Bremen. Approximately 10 cm³ of sediment (n = 360) was freeze-dried and ground to 123 a fine powder using an agate mortar. Total carbon (TC), total organic carbon (TOC), 124 and total sulphur (TS) were measured using a LECO CS-200 Carbon-Sulphur 125 analyzer. Approximately 65 mg of the homogenized sample was weighed in a ceramic 126 cup and burnt in an induction furnace. The resultant CO₂ and SO₂ were then measured 127 with a nondispersive infrared detector to provide a measure of the sedimentary TC 128 129 and TS content. To determine the TOC content, sediments (~65 mg) were decalcified using 12.5% hydrochloric acid (HCI) to remove carbonate species, followed by a 130 subsequent rinse of the residue with de-ionized water. Samples were subsequently 131 analyzed as described above. Total inorganic carbon (TIC) was determined by 132 subtracting TOC from TC. All data are reported in weight percent (wt. %) dry sample. 133

Bulk carbon isotope analyses of the OC fraction ($\delta^{13}C_{org}$) were carried out at MARUM, University of Bremen at 2 cm resolution throughout Cores 318-U1356A-103R to -106R (n = 368). The bulk samples were decalcified with 1 N HCl solution, followed by a subsequent rinse of the residue with de-ionized water. The sample was then combusted using the oven of an HERAEUS CHN-Analyser. The δ^{13} C value was subsequently measured with a Finnigan MAT Delta E Mass-spectrometer. Measurements were calibrated using a house standard (milled and decalcified organic-rich surface sediment from the German Wadden Sea), itself calibrated to
 international standards. Repeatability of the house standard is typically ±0.15‰.

143

144 2.3. Organic geochemistry

A total of 118 sediment samples (~10-15g dry mass) from IODP Site 1356 (948.96 to 145 998.1 mbsf) were freeze-dried and extracted using Accelerated Solvent Extraction with 146 dichloromethane (DCM) and methanol (MeOH) (9:1, v/v, respectively) as the organic 147 solvent. An internal standard (5α -andostrane) with a known concentration was added 148 to each sample prior to extraction. Excess solvent was removed using rotary 149 evaporation under vacuum. The total lipid extract (TLE) was separated into 'apolar', 150 'ketone', 'ethyl acetate' (EtOAc), and 'polar' fractions over an activated alumina (Al₂O₃) 151 column using hexane:DCM (9:1, v/v; N1), hexane:DCM (1:1, v/v; N2), EtOAc:DCM 152 (1:1 v/v; N3), and DCM:MeOH (1:1, v/v; N4), respectively. Al₂O₃ was activated by 153 oven-drying for at least 4 h at 150 °C. 154

For a subset of earliest Eocene samples (n = 11), we performed urea adduction 155 on the N1 fractions to separate cyclic (i.e. non-adduct) and aliphatic (i.e. adduct) 156 hydrocarbons. To achieve this, 200µl of hexane, acetone and urea (10% in MeOH) 157 were added to the saturated hydrocarbon fraction. The sample was frozen for ca. 60 158 minutes until urea crystals formed. Solvent was then removed under a stream of N2 159 and extracted (x5) with ca. 1ml of *n*-hexane (non-adduct fraction). The urea crystals 160 were then dissolved in 500 µl of MeOH and 500 µl of water and the adduct fraction 161 was extracted (x5) with ca. 1ml of *n*-hexane. The adduction procedure was repeated 162 on the adduct fraction once more to ensure all non-adduct material was removed 163 (Inglis et al 2019). 164

165

166 2.3.1 GC and GC-MS analysis

167 N1 fractions were redissolved in hexane and analyzed using a gas chromatograph (GC; Shimadzu 2010) with a flame ionization detector (FID) and hydrogen as carrier 168 gas at constant pressure (190 kPa). Separation of the different compounds was 169 achieved using the following column: length: 60 m, diameter: 0.25 mm, film thickness: 170 0.25 µm, coating: 100% dimethyl-polysiloxane. The gas chromatograph temperature 171 program increased from 50 to 120 °C at 30 °C min⁻¹, then 120-310 °C at 5 °C min⁻¹, 172 with a final isothermal time of 20 min at 300 °C. Compound identification was 173 confirmed by GC-MS (Shimadzu QP2010-Plus Mass Spectrometer (MS) interfaced 174 with a Shimadzu 2010 GC) using the same column described above. Compounds 175 were identified using retention times and mass spectra. The abundance of *n*-alkanes 176 and hopanes are normalised to TOC. An in-house external standard comprised of 20 177 178 *n*-alkanes (ranging from C_{16} to C_{37}) was run every 10 samples to monitor analytical performance. 179

180

181 2.3.2. GC-C-IRMS analysis

Compound specific hydrogen isotopic compositions were determined for a subset of samples from the earliest Eocene (n = 11) and EECO (n = 5). We analysed long-chain (C₂₇, C₂₉) *n*-alkanes via gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) using a ThermoFisher Trace GC Ultra coupled to a ThermoFisher Scientific Delta V Isotope Ratio MS. The GC column used was a 30 m × 0.25 mm i.d. fused silica column with ZB1 stationary phase. The H₃ factor was measured daily allowing isotope values to be corrected for protonation reactions

occurring within the ion source of the mass spectrometer (Sessions et al 1999). The 189 H₃ factor was typically below 5 ppm mV⁻¹ and had a rate of change of less than 0.1 190 day⁻¹. The GC program was as follows: starting temperature 70 °C, rising at 10 °C/min 191 to 300 °C, at which point the oven temperature was held stable for 8 min, giving a total 192 analysis-time of 32 min. Triplicate runs of each sample were performed. The average 193 standard error of the mean (SEM) value for a triplicate measurement was typically 2 194 195 to 7‰. Each individual sample was co-injected with sacrificial compounds consisting of *n*-pentadecane and ethyl caprylate to condition the reactor. Measured isotope 196 197 values were normalised by comparing the instrument's response to a suite of nalkanes with a known isotopic composition (B5 mix; supplied by A. Schimmelmann, 198 Indiana University, USA) injected before and after each triplicate of sample runs. The 199 200 root mean square error determined by replicate measurements of the standard across the course of analyses was between 4 and 7 ‰. Normalised results are reported in 201 standard per mil (‰) notation as δ^2 H values relative to Vienna Standard Mean Ocean 202 Water (VSMOW) and calculated against calibrated H₂ gas, introduced directly into the 203 ion source. 204

205

206 2.4. Lipid biomarker proxies

We use biomarkers ratios to assess the source and maturity of organic matter. The average chain length (ACL) expresses the average number of carbon atoms for the long-chain odd-carbon numbered *n*-alkanes (Pancost & Boot 2004). The ACL is defined for *n*-alkanes using the following equation (Eglinton & Hamilton 1967):

211

212 ACL=
$$(25 \times C_{25}) + (27 \times C_{27}) + (29 \times C_{29}) + (31 \times C_{31}) + (33 \times C_{33}) / (25 + 27 + 29 + 31 + 33)$$
 [e.q. 1]

214

The carbon preference index (CPI) reflects the dominance of odd-carbon-numbered relative to even-carbon-numbered *n*-alkane homologues (Bray & Evans 1961). Modern sediments exhibit high CPI values (> 3 to 30) (Diefendorf & Freimuth 2017). This value decreases over time due to diagenesis, approaching values of unity (= 1) in mature rocks and oils. The CPI is defined using the following equation (Bray & Evans 1961):

221

222 CPI =
$$0.5 \times ((C_{25} + C_{27} + C_{29} + C_{31} / C_{26} + C_{28} + C_{30} + C_{32}) + (C_{27} + C_{29} + C_{31} + C_{33} / C_{26} + C_{28} + C_{30} + C_{32}))$$
 [eq. 2]

224

The hopane $\beta\beta/(\alpha\beta+\beta\beta)$ ratio is used to evaluate changes in sediment maturity. 225 Modern sediments exhibit high hopane $\beta\beta/(\alpha\beta+\beta\beta)$ ratios (up to 1) whereas thermally 226 mature rocks and oils are characterised by lower hopane $\beta\beta/(\alpha\beta+\beta\beta)$ ratios 227 (Mackenzie et al 1980), although there can be exceptions (e.g. acidic peats) (Inglis et 228 al 2018). With increasing maturation, **C**31 to C35 hopanes also 229 undergo isomerisation at the C-22 position. An increase in 22S/(22R + 22S) values is 230 characteristic of increasing thermal maturation (Mackenzie et al., 1980). 231

232

233 2.5. Mass accumulation rates

Biomarker mass accumulation rates (MARs; in ng/cm²/kyr¹) are calculated using
linear sedimentation rate (LSR; cm/kyr), dry bulk density (p; g/cm³) (Dadey et al 1992)
and biomarker abundance (ng/g dry sediment):

237

238 MAR = LSR * ρ * biomarker abundance [eq. 3]

239

Linear sedimentation rates (LSRs) are calculated between the age tie-points. To avoid age inversions (i.e., within Core 105R-1) we constructed LSRs based on a selection of tie points rather than incorporate all bio- and magnetostratigraphic datums in the age model (see Supplementary Information).

244

245 2.6. Continental shelf area calculations

We calculate continental shelf area using the Eocene-Oligocene (ca. 34 Ma) 246 paleotopography published elsewhere (Hochmuth et al 2020a, Hochmuth et al 2020b, 247 Paxman et al 2019). The same calculations are also conducted using Bedmap2 248 249 (Fretwell et al 2013) for the present day. Continental shelf area for the Eocene is defined as being from the 0 m contour (e.g. shore of an ice free Antarctica) to the -250 1000m bathymetric contour (Figure S1). We calculate continental shelf area for the 251 region directly adjacent to Wilkes basin and for the whole Antarctic continent 252 (Appendix) in order to understand potential (Terr)OC sequestration. 253

254

255 2.7. Modelling simulations

 $\delta^2 H_{wax}$ is usually employed as a proxy for the isotopic composition of precipitation 256 $(\delta^2 H_w)$. However, this integrates a combination of climatic changes including 257 temperature, rainfall amount and characteristics, and atmospheric vapour transport. 258 Here we use modelled $\delta^2 H_w$ obtained via the isotope-enabled Community Earth 259 System Model version 1.2 (iCESM1.2) (Zhu et al 2020, Zhu et al 2019) to compare 260 with our proxy reconstructions and to aide climatic interpretation of $\delta^2 H_w$ (Lee et al 261 2007, Schmidt et al 2007). The iCESM1.2 simulations were performed following 262 protocols of the Deep-time Model Intercomparison Project (Lunt et al 2021, Lunt et al 263 264 2017) with the Eocene paleogeography and vegetation (56.0 - 47.8 Ma) (Herold et al 2014) and atmospheric CO₂ levels of ×1, ×3, ×6 and ×9 the preindustrial value (284.7) 265 ppmv). The different atmospheric CO₂ levels span the range of proxy-derived CO₂ 266 267 estimates for the early Eocene (Anagnostou et al, 2020). We also carried out a single pre-industrial simulation to isolate the non-CO₂ component on $\delta^2 H_w$ (i.e., changes due 268 to paleogeography, vegetation, aerosols, and lack of continental ice sheets). All 269 simulations were run at a horizontal resolution of $1.9 \times 2.5^{\circ}$ (latitude × longitude) for 270 the atmosphere and land, and a nominal 1° for the ocean and sea ice. Of particular 271 relevance to this study is the capability of iCESM1.2 to simulate the transport and 272 transformation of oxygen and hydrogen isotope ratios (δ^{18} O and δ^{2} H) in the climate 273 system (Brady et al 2019). Seawater δ^{18} O and δ^{2} H in the simulations were initialized 274 275 from constant values of -1.0‰ and -8.0‰, respectively, to account for the absence of ice sheets in a hothouse climate (Hollis et al 2019). The simulations were run for 276 more than 2000 years with the surface climate and water isotopes close to 277 278 equilibration. The simulations capture the magnitude of Eocene global warmth, the reduction in the meridional gradient of sea-surface temperature, and the overall values 279 and distribution of marine planktic foraminifera δ^{18} O. Readers are referred to Zhu et 280

al. (2019) and Zhu et al. (2020) for details of the experimental setup, equilibration
state, and assessment of the simulation results.

283

284 **3. Results**

3.1. Bulk geochemistry

Total organic carbon (TOC) content ranges between 0.1 and 1.5% (Figure 2). There 286 is a gradual increase in TOC values between 54.4 and 53.5 Ma (Core 106R to 105R) 287 followed by a gradual decrease thereafter (53.5-52.7 Ma, Core 104R to 101R). Bulk 288 $\delta^{13}C_{org}$ values range between -25.7 and -28.1 ‰ (Figure 2). The early Eocene record 289 from Site U1356 exhibits several $\delta^{13}C_{org}$ variations. These $\delta^{13}C_{org}$ cycles and 290 excursions have maximum values of up to -26‰ (in one case -25‰). The average 291 δ^{13} Corg values of -26 to -28 ‰ are typical for terrestrial organic matter (Hayes 1993), 292 although this value may be different in the Eocene (Sluijs & Dickens 2012). The 293 cyclicity in the $\delta^{13}C_{org}$ record is relatively pronounced in the lower part of the studied 294 section (Cores U1356-105R and -106R; Figure 2), where TOC values are high enough 295 (0.5 - 1.2 wt. %) to provide robust data. In the upper part of the early Eocene section 296 (e.g., Cores 103R and -104R), TOC contents are often lower than 0.5 wt. % and yield 297 a lower fidelity $\delta^{13}C_{\text{org}}$ signal. 298

299

300 3.2. Biomarker distributions and mass accumulation rates

The N1 fraction contains a range of *n*-alkanes (C₁₇ to C₃₃) and is dominated by longchain homologues (C₂₇ to C₃₃). The abundance of long-chain *n*-alkanes ranges between ~1 and 250 ng/g (average: 92 ng/g; Fig. 2d). Long-chain *n*-alkane (plantderived OC; Figure 3d) mass accumulation rates (MARs; in ng/cm²/kyr⁻¹) increase by two orders-of-magnitude between the earliest Eocene (~54 Ma) and the onset of the EECO (~53 Ma; Figure 3). CPI values (average: 2.8; Figure 4a) indicate that longchain n-alkanes have retained a biological odd-over-even predominance. In combination with high ACL values (~27 to 30; Supplementary Information), this confirms they are derived from terrestrial higher plants (Diefendorf & Freimuth 2017).

The apolar fraction also contains a range of bacterial-derived hopanes (C₂₇ to 310 C_{32}) and hopenes (C_{27} to C_{30}). The abundance of hopanes ranges from ~1 to 191 ng/g 311 312 (average: 54 ng/g) and exhibits a significant linear correlation with long-chain *n*-alkane abundance ($r^2 = 0.81$, p < 0.001; Figure S2). Hopane (soil- and peat-derived OC; 313 Figure 3d) mass accumulation rates (MARs; in ng/cm²/kyr⁻¹) increase by two orders-314 of-magnitude between the earliest Eocene (~54 Ma) and the onset of the EECO (~53 315 Ma; Figure 3). The dominant hopanes are (22R)-17 β ,21 β (H)-hopane (C₃₀), (22R)-316 317 17α , 21β (H)-homohopane (C₃₁) and (22R)- 17β , 21β (H)-homohopane (C₃₁). The C₃₁ hopane $\beta\beta/(\alpha\beta+\beta\beta)$ isomerisation ratio ranges between 0.31 and 0.82 (average: 0.65; 318 Figure 4b). The earliest Eocene (54.3 to 53.7 Ma) samples (Core 106R) are 319 320 characterised by the lowest $C_{31}\beta\beta/(\alpha\beta+\beta\beta)$ indices (0.4 to 0.6). $C_{31}\beta\beta/(\alpha\beta+\beta\beta)$ indices increase during the early Eocene (~53.7 Ma) and remain higher (~0.5 to 0.8) thereafter 321 (Cores 105R to 101R) with the exception of two relatively low values between 949 and 322 950 mbsf (Core 101R; Figure 4b). $C_{30}\beta\beta/(\alpha\beta+\beta\beta)$ indices were stable and high (~0.7-323 0.8). C_{31} hopane 22S/(22S + 22R) ratios were stable and low (<0.1). 324

Our analyses are combined with previously published Branched-versus-Isoprenoid Tetraether (BIT) values (Bijl et al 2013). BIT values range between 0.16 and 0.62 (average: 0.35) and exhibit higher values (> 0.4 to 0.5) during the EECO (Core 105R to 102R; Supplementary Information) compared to the earliest Eocene (Core 106R). 330

331 3.3. Long-chain *n*-alkane δ^2 H values

332 Long-chain *n*-alkane $\delta^2 H (\delta^2 H_{wax})$ values were determined for a subset of samples (*n* = 15) deposited during the earliest Eocene (54.3 to 53.9 Ma) and across the EECO 333 (53.3 to 49.1 Ma). C₂₇ *n*-alkane δ^2 H values average -190‰ (n = 15, standard error of 334 the mean [SEM]: $\pm 4.0\%$) with a range from -140 to -222‰ (Figure 5a). C₂₉ *n*-alkane 335 δ^2 H values average -194‰ (n = 15, SEM: ± 2.9‰) with a range from -158 to -224‰ 336 (Figure 5a). Both the C₂₇ and C₂₉ *n*-alkanes co-vary and exhibit a positive linear 337 relationship ($r^2 = 0.78$, p < 0.001), indicating that they are derived from a similar source 338 (i.e. higher plants) (Figure S3). 339

340

341 **4. Discussion**

342 4.1. Enhanced TerrOC burial on the East Antarctic margin during the EECO

The export of terrestrial OC along the terrestrial-aquatic continuum can be evaluated 343 by analysing the distribution of lipid biomarkers within the Wilkes Land sediment 344 samples. The hydrocarbon distribution is dominated by long-chain *n*-alkanes with an 345 odd-over-even predominance. High CPI values (~3; Figure 4a) together with the 346 dominance of long-chain *n*-alkanes (relative to shorter-chain homologues) confirms 347 that they are derived from the epicuticular wax of terrestrial higher plants (Eglinton & 348 Hamilton 1967). The hydrocarbon assemblage also contains abundant bacterial-349 derived hopane biomarkers. Hopanes can be produced in terrestrial and marine 350 environments by a range of bacteria (Talbot & Farrimond 2007). However, the positive 351 linear relationship between long-chain *n*-alkanes (terrestrial higher plants) and 352

hopanes ($r^2 = 0.81$; p < 0.001; Figure S2) indicates that here, both are sourced from the terrestrial biosphere.

Long-chain *n*-alkane (plant-derived OC; Figure 4d) and hopane (soil-derived 355 OC; Figure 4c) mass accumulation rates (MARs; in ng/cm²/kyr⁻¹) increase by two 356 orders-of-magnitude between the earliest Eocene (~54 Ma) and the onset of the EECO 357 (~53 Ma). This significant increase indicates enhanced burial of plant- and soil OC 358 during the early Eocene, with highest accumulation rates during the EECO. Note that 359 we performed the same calculations assuming a constant LSR (1.82 cm/year, i.e., the 360 361 average LSR rate) and find similar MARs during the EECO (~53 Ma; Figure S4-5). Delivery of TerrOC into the marine realm is consistent with the high abundance of 362 terrestrial palynomorphs (i.e., pollen and spores; (Contreras et al 2013, Pross et al 363 2012) and other terrestrial biomarkers (including high BIT indices; Pross et al., 2012; 364 Bijl et al., 2013; Figure 3a) in the same sediments. These findings are analogous to 365 those observed in modern (high-latitude) environments, where large river systems in 366 northern Eurasian and North American (Hilton et al., 2015; Sparkes et al., 2015; 367 Semiletov et al., 2011; Guo et al., 2004) are capable of transporting large quantities of 368 TerrOC from soils into the marine realm. 369

The earliest Eocene sediments also contain an unusually high abundance of 370 the 'thermally-mature' C₃₁ 17α , 21β (H) hopane stereoisomer and exhibit relatively low 371 372 C₃₁ hopane $\beta\beta/(\alpha\beta+\beta\beta)$ ratios (0.4-0.7; Figure 4b). This implies delivery of biospheric (i.e., thermally immature) and petrogenic OC (i.e., thermally mature) into the marine 373 realm. Input of petrogenic OC should be assosciated with the delivery of other 374 thermally-mature hopanes (e.g., $C_{30} \alpha\beta$ hopanes). However, C_{30} hopane $\beta\beta/(\alpha\beta+\beta\beta)$ 375 values remain relatively high (>0.7), implying minimal petrogenic OC input. Modern 376 acidic bogs can be dominated by the 'thermally mature' C_{31} 17 α ,21 β (H) isomer (Inglis 377

et al 2018), but typically lack other thermally-mature hopanes (e.g., $C_{30} \alpha \beta$ hopanes; 378 Inglis et al., 2018). We therefore argue that the occurrence of the 'thermally mature' 379 C_{31} 17 α ,21 β (H) stereoisomer within an otherwise immature hopane assemblage 380 represents input of acidic peat into the marine realm. The occurrence of the 'thermally 381 mature' C₃₁ 17 α ,21 β (H) stereoisomer within recent coastal marine sediments has also 382 been interpreted to reflect input of peat from the surrounding catchment (Smittenberg 383 et al 2004). This hypothesis helps explain why C₃₀ and C₂₉ hopane $\beta\beta/(\alpha\beta+\beta\beta)$ values 384 remain relatively high throughout (>0.7). It is also consistent with the lack of other 385 386 thermally-mature biomarkers (e.g. $\alpha\beta$ 22S-hopanoid isomers, bisnorhopanes, benzohopanes, triaromatic steroids) and relatively high CPI values (>3; Figure 4a). 387

Input of acidic peat into the marine realm is consistent with the occurrence of 388 389 Stereisporites spores in the Site U1356 sediments (Pross et al., 2012; Figure S6) that can be attributed to the Sphagnaceae family, which today only comprises the genus 390 Sphagnum (commonly known as peat moss). Despite the low abundances registered, 391 the occurrence of Stereisporites spores in the Site U1356 sediments appears 392 noteworthy for various reasons. Firstly, Stereisporites spores are relatively rare or 393 absent in early Cenozoic sediments (see Inglis et al., 2015 and ref. therein). Secondly, 394 spores are generally strongly underrepresented in sporomorph assemblages from 395 marine sediments due to the selective nature of sporomorph transport as a function of 396 397 transport distance (Contreras et al 2014, Moss et al 2005). As such, even their occurrence in low numbers (e.g., ~1% of total sporomorph assemblage) can have 398 substantial ecological significance and points towards the existence of peatlands 399 and/or forested mires within the Site U1356 catchment area. The input of acidic peat 400 into the marine realm is also consistent with the results of biome-based modelling 401

suggesting that ~15–20% of Antarctica was capable of supporting wetland and peat
formation during the Eocene (DeConto et al 2012).

404

405 4.2. Quantifying TerrOC burial on the East Antarctic margin during the EECO

Lipid biomarkers indicate that a considerable fraction of the OC pool on the early 406 Eocene Wilkes Land continental margin is derived from the terrestrial biosphere. 407 However, the relative proportion of terrestrial vs marine OC must be known in order to 408 quantify TerrOC burial (Weijers et al 2009). In modern settings, bulk OC δ^{13} C values 409 $(\delta^{13}C_{org})$ can discriminate between marine OC (¹³C-enriched) and vascular plant 410 and/or soil OC (¹³C-depleted). However, marine OC can be relatively ¹³C-depleted 411 during the Eocene (up to 7‰ relative to modern) (Sluijs & Dickens 2012) due to 412 enhanced fractionation under higher CO₂ (Freeman & Hayes 1992). 413

414 Here we use BIT indices (Hopmans et al 2004) to characterise the fraction of 415 terrestrial vs marine OC and employ a two end-member mixing-model:

416

418

where *f*_{Terrestrial} is the terrestrial OC fraction and X_{Sample} is the BIT index for the sediment 419 sample (following Weijers et al., 2009). The marine- (Xmarine) and terrestrial end-420 member (X_{terr}) for BIT is 0 and 0.91, respectively (Hopmans et al., 2004). The BIT 421 index can reach a theoretical value of 1. However, BIT values in globally-distributed 422 soil samples average 0.91 (Weijers et al 2006). Using our mixing-model approach, we 423 estimate that the proportion of terrestrial OC in the Wilkes Land sediments ranges 424 between 20% (minimum) and 65% (maximum). As the BIT index captures the 425 proportion of soil OC (rather than soil and plant OC), this approach may underestimate 426

the proportion of terrestrial OC in the Wilkes Land sediments. The BIT index has been 427 shown to be controlled strongly by crenarchaeol-rather than brGDGT-428 concentrations, and may lead to a decoupling between BIT values and other terrestrial 429 OC tracers (Smith et al 2012). However, the fractional abundance of crenarchaeol is 430 stable throughout the early Eocene (Bijl et al., 2013), arguing that BIT is largely 431 controlled by changes in brGDGT abundance. The BIT index can also be influenced 432 by in-situ marine or fluvial brGDGT production. However, brGDGTs reflect typical soil-433 distributions, with no abnormal Isomerization Ratio or #Ringstetra values (Sinninghe 434 435 Damsté 2016). This suggests negligible marine in situ or river production) and is consistent with other early Eocene sites in the southwest Pacific Ocean (e.g., Bijl et 436 al., 2021). 437

The proportion of TerrOC can then be multiplied alongside TOC MARs to 438 provide a first-order approximation of TerrOC sequestration along the Wilkes Land 439 margin. This first requires an estimate of the Wilkes Land continental shelf area 440 (118,675 km²). Here we assume that the early Eocene shelf was similar to that of the 441 latest Eocene (Paxman et al 2019) and was significantly smaller than the present day 442 continental shelf area (170,731 km²). We also assume that the sediment package 443 thickness (and thus, %TerrOC) is uniform. Assuming that 20 to 65% of the OC pool in 444 the Wilkes Land sediments is terrestrial-derived (see above), this implies the burial of 445 446 20 to 72 PgC of TerrOC the depositional interval (54.3 and 51.5 Ma). If we assume similar climate, vegetation distributions and transport mechanisms across the entire 447 Antarctic shelf area (3,947,850 km²), the potential mass of TerrOC sequestered is 448 much larger (~410 to 1300 PgC) and equates to a burial flux of 0.14-0.46 TgC/yr. 449 These estimates are relatively modest compared to highly-erosive mountainous river 450 catchments (e.g., Taiwan; > 8 TgC/yr; Kao et al., 2014) and large river systems (e.g., 451

the Mackenzie River; 2.2 (+1.3/-0.9) TgC/yr; Hilton et al., 2015). To refine these estimates, additional studies at different localities are required. Additional seismic data may help to improve estimates of offshore sediment thickness, whilst the application of binary (or ternary) mixing models based on other geochemical proxies (e.g., C/N ratios, *n*-alkane/alkenones ratios) will help to refine our estimates of TerrOC burial (see Weijers et al., 2009). Until then, our estimates should be treated with caution.

Although these estimates incorporate various uncertainties, our work highlights 458 the potential importance of continental margins as depocentres for TerrOC burial 459 during the early Eocene. This is consistent with High Arctic continental shelf sediments 460 deposited between the Palaeocene-Eocene Thermal Maximum (PETM; ~56 Ma) and 461 Eocene Thermal Maximum 2 (ETM2; ~53 Ma), which are dominated by long-chain n-462 alkyl lipids and low hydrogen indices (Boucsein & Stein 2009, Weller & Stein 2008). 463 Terrigenous input–which is strongly correlated with TerrOC export in modern settings 464 (e.g., Galy et al., 2015)-also increases during the EECO, including in New Zealand 465 (e.g. Mead Stream) (Nicolo et al 2007, Slotnick et al 2012) and the North Iberian 466 margin (Payros et al 2015). Enhanced TerrOC burial may be further promoted by 467 larger, flatter drowned shelf areas during the Eocene (Bowen 2013, Sømme et al 468 2009). Taken together, this suggests an important role for continental shelves in 469 470 storing terr(OC) during the Eocene. This is especially important given the evidence for 471 low (terr)OC burial in open ocean Eocene environments (Olivarez Lyle & Lyle 2006).

472

473 **4.3. Hydroclimate regulates TerrOC export during early Eocene**

474 Enhanced TerrOC burial in coastal marine sediments could be driven by expansion of 475 the terrestrial biosphere during the EECO. However, TerrOC export is largely

controlled by precipitation (Hilton 2017) and the capacity of rivers to erode and 476 transport TerrOC (Galy et al 2015). Here we explore whether hydroclimate regulates 477 OC export from the terrestrial biosphere. To assess this, we use the hydrogen isotopic 478 479 composition (δ^2 H) of leaf wax (C₂₇ and C₂₉ *n*-alkane) biomarkers in a subset of samples deposited during the earliest Eocene (54.3 to 53.9 Ma) and EECO. C₂₇ and 480 C_{29} *n*-alkane δ^2 H values average -190 and -195‰, respectively, and are comparable 481 to those reported from other early Eocene-aged sites from similar latitudes (Speelman 482 et al 2010). The isotopic composition of precipitation ($\delta^2 H_w$) is estimated by assuming 483 484 an apparent fractionation factor (${}^{2}H\epsilon_{wax/w}$) which integrates a range of variables (e.g. soil- and/or leaf water evapotranspiration, biosynthetic effects, vegetation type). 485 Theoretical models have incorporated evaporative ²H-enrichment of soil water into 486 predictions of ${}^{2}\varepsilon_{wax/w}$ (Konecky et al 2019, Smith & Freeman 2006). However, in 487 settings with extensive evaporation, woody plants take up rainwater opportunistically 488 via different rooting strategies (Fan et al 2017), resulting in minimal xylem water ²H-489 490 enrichment. Although leaf water ²H-enrichment is more variable (Daniels et al 2017, Feakins et al 2016, Kahmen et al 2013), it is significantly reduced in warm and wet 491 climates (Feakins et al 2016). As the East Antarctic margin was characterised by 492 elevated temperatures (> 16 ±5 °C) and high precipitation (>1300-1600 mm/year) 493 (Pross et al 2012), the impact of leaf water ²H- enrichment is likely minimal. 494

⁴⁹⁵ Changes in the plant community can also influence the apparent fractionation ⁴⁹⁶ between $\delta^2 H_{wax}$ and $\delta^2 H_w$ values. To account for the impact of vegetation isotope ⁴⁹⁷ effects upon leaf wax $\delta^2 H$ values, we developed a pollen-corrected fractionation factor ⁴⁹⁸ ($^2H\epsilon_{wax/w-corr}$) using a three endmember mixing model (following Feakins 2013). This ⁴⁹⁹ includes C₃ gymnosperms, C₃ dicots and pteridophytes (i.e. ferns) and is defined as:

500

501 ${}^{2}\text{H}\epsilon_{wax/w-corr} = f_{gymnosperm} * \epsilon_{gymnosperm}] + [f_{dicot} * \epsilon_{dicot}] + [f_{pteridophytes} * \epsilon_{pteridophytes}] (eq. 5)$

502

503 Where ε is based on the mean fractionation factor in modern plant types (Sachse et al 2012) and f is based upon the percentage of pollen in adjacent samples (Contreras 504 et al 2013, Pross et al 2012). Our pollen-corrected fractionation factor ranges between 505 506 -107 and -113‰ and is higher than assumed in some Eocene studies (-130‰) (Handley et al 2012, Pagani et al 2006) but similar to an updated global dataset of 507 ²H $\varepsilon_{wax/w}$ in modern systems (e.g., -121‰ for C₂₉ *n*-alkane; McFarlin et al., 2019). When 508 509 our pollen-corrected fractionation factor is applied to our leaf wax dataset, we obtain $\delta^2 H_{w-corr}$ values which average -82‰ (C₂₇ *n*-alkane; Figure 5b) and -83‰ (C₂₉ *n*-510 alkane; Figure 5b). These values are ²H-enriched relative to modern values (-99‰; 511 based on iCESM1.2 pre-industrial x1 CO₂ simulation; see also below). There are 512 several reasons for this. Firstly, local air temperatures will yield more ²H-enriched 513 514 water vapour (a temperature effect) (Poulsen et al 2007). Secondly, under warmer climates, decreased rainout efficiency at the low-latitudes (due to a reduction in vertical 515 moisture transport) will result in more ²H-enriched precipitation at the mid-to-high 516 latitudes (e.g., Pagani et al 2006). Our pollen-corrected $\delta^2 H_w$ values exhibit 517 considerable variability in the earliest Eocene interval (ca. 30 to 40%; Figure 5). This 518 may represent changes in the hydroclimate regime. However, it could also record 519 changes in OC source region. Indeed, sporomorph distributions indicate that TerrOC 520 is derived from both the lowlands and higher-altitude hinterlands (Pross et al., 2012). 521 522 Although leaf waxes typically provide a spatially-integrated perspective, the spatial and temporal integration may vary by compound type and/or change through time. Future 523 work using other compound classes (e.g., long-chain *n*-alkanoic acids) may help to 524

525 differentiate between lowland (proximal) and highland (distal) OC sources (see 526 Feakins et al 2018, Hemingway et al 2016).

Our pollen-corrected $\delta^2 H_w$ values indicate higher average $\delta^2 H_w$ values (e.g., -527 66‰ for the C₂₉ *n*-alkane) during the EECO compared to the earliest Eocene (e.g., 528 e.g., -90‰ for the C₂₉ *n*-alkane; Figure 5b). This is consistent with an increase in 529 poleward moisture transport in response to higher CO₂ and higher temperatures. To 530 confirm that the higher average $\delta^2 H_w$ values are due to higher CO₂ and/or higher 531 temperatures, we calculate the precipitation-amount weighted $\delta^2 H_w$ in isotope-enabled 532 CESM simulations with a range of atmospheric CO₂ concentrations (×1, ×3, ×6 and 533 ×9 the preindustrial level; see section 2.7). The modelled $\delta^2 H_w$ exhibits a monotonic 534 increase with the CO₂ concentrations in the simulations with values of -106‰ in ×1 535 CO₂, -96‰ in ×3 CO₂, -91‰ in ×6 CO₂ and -81‰ in ×9 CO₂ (Figure 6b). This $\delta^2 H_w$ 536 sensitivity to CO₂ levels in isotope-enabled climate models has been attributed to 537 warmer temperatures and/or the associated reduction in isotopic rainout at low-538 latitudes (Poulsen et al., 2007; Speelman et al., 2010). The gualitatively consistent 539 results between model simulations and proxy data supports our interpretation that the 540 observed increase in proxy-inferred $\delta^2 H_w$ values between the earliest Eocene and 541 EECO (~20 to 40‰) is attributable to a CO₂-induced warming. There is also close 542 data-model agreement in the absolute $\delta^2 H_w$ values (Figure 6), supporting our data-543 based reconstructions. The impact from non-CO₂ boundary conditions on $\delta^2 H_w$ can 544 also be evaluated by comparing iCESM1.2 Eocene ×1 simulations against the pre-545 industrial simulation. This shows that the combined non-CO₂ boundary conditions (i.e., 546 paleogeography, vegetation, aerosols, removal of continental ice sheets) decrease 547 $\delta^2 H_w$ by ~ 7‰. This implies that non-CO₂ boundary conditions exert a small secondary 548 control on $\delta^2 H_w$ values at our site. The iCESM1.2 simulations (x3, x6 and x9 PI CO₂ 549

simulations) also exhibit high MAP estimates (~1310, 1520, and 1720 mm/year, 550 respectively; Figure 7c-d) during the early Eocene. These are higher than previous 551 simulations (Carmichael et al 2016) but more consistent with existing sporomorph-552 based estimates (>1300 mm/year [paratropical rainforest biome] and >1600 mm/year 553 [temperate rainforest biome]; Figure 7a-b) (Pross et al 2012). Slightly lower values 554 (800–1350 mm/year) have been reconstructed for Site U1356 based on climofunctions 555 applied to detrital geochemistry (Passchier et al 2013) and likely reflects the 556 differences in the catchment sourcing. 557

Taken together, our results reveal that EECO was characterised by enhanced 558 poleward moisture transport relative to the earliest Eocene (~54 Ma; Figure 5-6). The 559 EECO also coincides with an interval of enhanced delivery of terrestrial OC into the 560 marine realm (Figure 3), implying a causal link between the hydrological cycle and 561 TerrOC burial at our site. Crucially, TerrOC burial can help to remove the atmospheric 562 CO₂ and could serve as a negative feedback to decrease the surface temperature 563 during intervals of global warmth. Compared to the silicate weathering feedback 564 (which operates on the timescales of a million years), the organic carbon cycle 565 operates over shorter timescales. As such, it could also be an important negative 566 feedback during shorter-term warming events (e.g., hyperthermals). 567

568

569 5. Conclusions

The transport and burial of biospheric organic carbon in coastal marine sediments is an important carbon sink in modern settings. However, the relative importance of this feedback in past warm climates remains a major gap in our understanding. Using a multi-proxy approach, we find a significant increase in the accumulation rate of terrestrial biomarkers in early Eocene coastal marine sediments from offshore East

Antarctica. As the early Eocene Antarctic continent was covered by a vast terrestrial 575 OC reservoir (> 10¹⁵ PgC), the transport and subsequent burial of biospheric organic 576 carbon in coastal marine sediments could have acted as a key CO₂ sink. This study 577 highlights the importance of the terrestrial biosphere during past warm climates and 578 its potential role as a negative feedback to stabilize the surface temperature. 579

580 **Open Research**

- The geochemical and numerical data used in the study are available at Pangaea 581
- (https://www.pangaea.de/) and associated with a CC-BY 4.0 license. 582

583

Authorship tiers and contributions 584

G.N.I and J.B. designed the study. GNI drafted the manuscript and designed the 585 figures. G.N.I., J.B. and J.L.T conducted biomarker analysis. U.R. conducted total 586 organic carbon (TOC) and bulk organic carbon isotope analysis. J.P provided pollen 587 data. C.P and J.Z. provided CESM1.2 model results. S.S.R.J provided continental 588 shelf estimates. All the authors discussed the results and contributed to the final text. 589

590

Declaration of competing interest 591

The authors declare that they have no known competing financial interests or personal 592 relationships that could have appeared to influence the work reported in this paper.

594

593

Acknowledgements 595

This research used samples and/or data provided by the International Ocean 596 Discovery Program (IODP). GNI was supported by a Royal Society Dorothy Hodgkin 597

Fellowship (DHF\R1\191178). JB and JLT were supported by NERC (NE/I00646X/2). 598 UR and JP were supported by the Deutsche Forschungsgemeinschaft (DFG, German 599 Research Foundation) (project no. 203022934, and no. 111964030, respectively). JP 600 JP also acknowledges support by the German Research Foundation (DFG; grant PR 601 651/10). CJP was supported by the Heising-Simons Foundation (grant nos. 2016-05 602 and 2016-12) and the National Science Foundation (NSF; grant no. 2002397). The 603 CESM project is supported primarily by the National Science Foundation (NSF). This 604 material is based upon work supported by the National Center for Atmospheric 605 606 Research, which is a major facility sponsored by the NSF under Cooperative Agreement No. 1852977. Computing and data storage resources, including the 607 Cheyenne supercomputer (doi:10.5065/D6RX99HX), were provided by the 608 Computational and Information Systems Laboratory (CISL) at NCAR. We thank Sarah 609 Feakins, Emily Tibbett, Bob Hilton and one anonymous reviewer whose comments 610 improved this manuscript significantly. 611

612

613 **References**

- Anagnostou, E., John, E.H., Babila, T.L., Sexton, P.F., Ridgwell, A., Lunt, D.J.,
 Pearson, P.N., Chalk, T.B., Pancost, R.D. and Foster, G.L., 2020. Proxy
 evidence for state-dependence of climate sensitivity in the Eocene
- 617 greenhouse. *Nature communications*, *11*(1), pp.1-9.
- 618 Berner RA. 1990. Atmospheric carbon dioxide levels over Phanerozoic time. *Science* 619 249: 1382-6
- Bijl PK, Bendle JAP, Bohaty SM, Pross J, Schouten S, et al. 2013. Eocene cooling
 linked to early flow across the Tasmanian Gateway. *Proceedings of the National Academy of Sciences* 110: 9645-50
- Bijl, P.K., Frieling, J., Cramwinckel, M.J., Boschman, C., Sluijs, A. and Peterse, F.,
 2021. Maastrichtian-Rupelian paleoclimates in the southwest Pacific–a critical
 evaluation of biomarker paleothermometry and dinoflagellate cyst
 paleoecology at Ocean Drilling Program Site 1172. *Climate of the Past*
- 627 *Discussions*, pp.1-82.

Boucsein B, Stein R. 2009. Black shale formation in the late Paleocene/early Eocene 628 Arctic Ocean and paleoenvironmental conditions: new results from a detailed 629 organic petrological study. Marine and Petroleum Geology 26: 416-26 630 Bowen GJ. 2013. Up in smoke: A role for organic carbon feedbacks in Paleogene 631 hyperthermals. Global and Planetary Change 109: 18-29 632 Bowen GJ, Revenaugh J. 2003. Interpolating the isotopic composition of modern 633 meteoric precipitation. Water Resources Research 39 634 Brady E, Stevenson S, Bailey D, Liu Z, Noone D, et al. 2019. The connected isotopic 635 water cycle in the Community Earth System Model version 1. Journal of 636 Advances in Modeling Earth Systems 11: 2547-66 637 Bray EE, Evans ED. 1961. Distribution of n-paraffins as a clue to recognition of 638 source beds. Geochimica et Cosmochimica Acta 22: 2-15 639 640 Carmichael MJ, Lunt DJ, Huber M, Heinemann M, Kiehl J, et al. 2016. A modelmodel and data-model comparison for the early Eocene hydrological cycle. 641 Climate of the Past 12: 455-81 642 Contreras L, Pross J, Bijl PK, Koutsodendris A, Raine JI, et al. 2013. Early to Middle 643 644 Eocene vegetation dynamics at the Wilkes Land Margin (Antarctica). Review of Palaeobotany and Palynology 197: 119-42 645 Contreras L, Pross J, Bijl PK, O'Hara RB, Raine JI, et al. 2014. Southern high-646 latitude terrestrial climate change during the Palaeocene-Eocene derived 647 from a marine pollen record (ODP Site 1172, East Tasman Plateau). Clim. 648 Past 10: 1401-20 649 Dadey KA, Janecek T, Klaus A. 1992. 37. Dry-bulk density: its use and 650 determination. Proceedings of the Ocean Driling Program, Scientific Results 651 126 652 653 Daniels WC, Russell JM, Giblin AE, Welker JM, Klein ES, Huang Y. 2017. Hydrogen isotope fractionation in leaf waxes in the Alaskan Arctic tundra. Geochimica et 654 Cosmochimica Acta 213: 216-36 655 DeConto RM, Galeotti S, Pagani M, Tracy D, Schaefer K, et al. 2012. Past extreme 656 warming events linked to massive carbon release from thawing permafrost. 657 Nature 484: 87-91 658 Diefendorf AF, Freimuth EJ. 2017. Extracting the most from terrestrial plant-derived 659 n-alkyl lipids and their carbon isotopes from the sedimentary record: A review. 660 Organic Geochemistry 103: 1-21 661 Eglinton G, Hamilton RJ. 1967. Leaf Epicuticular Waxes. Science 156: 1322-35 662 Eglinton TI, Galy VV, Hemingway JD, Feng X, Bao H, et al. 2021. Climate control on 663 terrestrial biospheric carbon turnover. Proceedings of the National Academy 664 of Sciences 118 665 Escutia C, Brinkhuis H, Klaus A, (2011) ES. 2011a. Proceedings of the Integrated 666 Ocean Drilling Program, Initial Reports, Volume 318. (Integrated Ocean 667 Drilling Program Management International, Inc., Tokyo). 668 Escutia C, Brinkhuis H, Klaus A, Bendle JAP, Bijl PK, et al. 2011b. IODP Expedition 669 318; from greenhouse to icehouse at the Wilkes Land Antarctic margin. 670 Scientific Drilling 12: 15 671 Fan Y, Miguez-Macho G, Jobbágy EG, Jackson RB, Otero-Casal C. 2017. 672 Hydrologic regulation of plant rooting depth. Proceedings of the National 673 Academy of Sciences 114: 10572-7 674 675 Feakins SJ. 2013. Pollen-corrected leaf wax D/H reconstructions of northeast African hydrological changes during the late Miocene. Palaeogeography, 676 Palaeoclimatology, Palaeoecology 374: 62-71 677

Feakins SJ, Bentley LP, Salinas N, Shenkin A, Blonder B, et al. 2016. Plant leaf wax 678 biomarkers capture gradients in hydrogen isotopes of precipitation from the 679 Andes and Amazon. Geochimica et Cosmochimica Acta 182: 155-72 680 Feakins, S.J., Wu, M.S., Ponton, C., Galy, V. and West, A.J., 2018. Dual isotope 681 evidence for sedimentary integration of plant wax biomarkers across an 682 Andes-Amazon elevation transect. Geochimica et Cosmochimica Acta, 242, 683 pp.64-81. 684 Freeman KH, Hayes J. 1992. Fractionation of carbon isotopes by phytoplankton and 685 estimates of ancient CO2 levels. Global Biogeochemical Cycles 6: 185-98 686 Fretwell P, Pritchard HD, Vaughan DG, Bamber JL, Barrand NE, et al. 2013. 687 Bedmap2: improved ice bed, surface and thickness datasets for Antarctica. 688 The Cryosphere 7: 375-93 689 Galy V, Peucker-Ehrenbrink B, Eglinton T. 2015. Global carbon export from the 690 terrestrial biosphere controlled by erosion. Nature 521: 204-7 691 Gaillardet, J., Dupré, B., Louvat, P. and Allegre, C.J., 1999. Global silicate 692 weathering and CO2 consumption rates deduced from the chemistry of large 693 694 rivers. Chemical geology, 159(1-4), pp.3-30. Guo, L., Semiletov, I., Gustafsson, Ö., Ingri, J., Andersson, P., Dudarev, O. and 695 White, D., 2004. Characterization of Siberian Arctic coastal sediments: 696 697 Implications for terrestrial organic carbon export. *Global Biogeochemical* Cycles, 18(1). 698 Francis, J.E. and Poole, I., 2002. Cretaceous and early Tertiary climates of 699 700 Antarctica: evidence from fossil wood. Palaeogeography, Palaeoclimatology, Palaeoecology, 182(1-2), pp.47-64. 701 Handley L, O'Halloran A, Pearson PN, Hawkins E, Nicholas CJ, et al. 2012. Changes 702 703 in the hydrological cycle in tropical East Africa during the Paleocene-Eocene Thermal Maximum. Palaeogeography, Palaeoclimatology, Palaeoecology 704 329: 10-21 705 Haves J. 1993. Factors controlling 13C contents of sedimentary organic compounds: 706 principles and evidence. Marine Geology 113: 111-25 707 Hein CJ, Usman M, Eglinton TI, Haghipour N, Galy VV. 2020. Millennial-scale 708 hydroclimate control of tropical soil carbon storage. Nature 581: 63-6 709 Hemingway, J.D., Schefuß, E., Dinga, B.J., Pryer, H. and Galy, V.V., 2016. Multiple 710 plant-wax compounds record differential sources and ecosystem structure in 711 large river catchments. Geochimica et Cosmochimica Acta, 184, pp.20-40. 712 Herold N, Buzan J, Seton M, Goldner A, Green J, et al. 2014. A suite of early 713 Eocene (~ 55 Ma) climate model boundary conditions. Geoscientific Model 714 Development 715 716 Hilton RG. 2017. Climate regulates the erosional carbon export from the terrestrial biosphere. Geomorphology 277: 118-32 717 Hilton RG, Galy A, Hovius N, Chen M-C, Horng M-J, Chen H. 2008. Tropical-718 cyclone-driven erosion of the terrestrial biosphere from mountains. Nature 719 Geoscience 1: 759-62 720 Hilton RG, Galy V, Gaillardet J, Dellinger M, Bryant C, et al. 2015. Erosion of organic 721 carbon in the Arctic as a geological carbon dioxide sink. Nature 524: 84-7 722 Hilton RG, West AJ. 2020. Mountains, erosion and the carbon cycle. Nature Reviews 723 Earth & Environment 1: 284-99 724 725 Hochmuth K, Gohl K, Leitchenkov G, Sauermilch I, Whittaker JM, et al. 2020a. The evolving paleobathymetry of the circum-Antarctic Southern Ocean since 34 726

Ma: A key to understanding past cryosphere-ocean developments. 727 Geochemistry, Geophysics, Geosystems 21: e2020GC009122 728 Hochmuth K, Paxman G, Jamieson SS, Gohl K, Leitchenkov G, et al. 2020b. 729 Combined palaeobathymetry and palaeotopography of the Southern Ocean 730 and the Antarctic continent 731 Hollis CJ, Dunkley Jones T, Anagnostou E, Bijl PK, Cramwinckel MJ, et al. 2019. 732 The DeepMIP contribution to PMIP4: methodologies for selection, compilation 733 and analysis of latest Paleocene and early Eocene climate proxy data, 734 incorporating version 0.1 of the DeepMIP database. Geoscientific Model 735 736 Development 12: 3149-206 Hopmans EC, Weijers JW, Schefuß E, Herfort L, Sinninghe Damsté JS, Schouten S. 737 2004. A novel proxy for terrestrial organic matter in sediments based on 738 739 branched and isoprenoid tetraether lipids. Earth and Planetary Science 740 Letters 224: 107-16 Inglis GN, Bragg F, Burls NJ, Cramwinckel MJ, Evans D, et al. 2020. Global mean 741 surface temperature and climate sensitivity of the early Eocene Climatic 742 743 Optimum (EECO), Paleocene–Eocene Thermal Maximum (PETM), and latest Paleocene. Climate of the Past 16: 1953-68 744 Inglis GN, Naafs BDA, Zheng Y, McClymont EL, Evershed RP, Pancost RD. 2018. 745 Distributions of geohopanoids in peat: Implications for the use of hopanoid-746 based proxies in natural archives. Geochimica et Cosmochimica Acta 224: 747 249-61 748 749 Inglis GN, Naafs BDA, Zheng Y, Schellekens J, Pancost RD. 2019. δ13C values of bacterial hopanoids and leaf waxes as tracers for methanotrophy in 750 peatlands. Geochimica et Cosmochimica Acta 260: 244-56 751 752 Kahmen A, Hoffmann B, Schefuß E, Arndt SK, Cernusak LA, et al. 2013. Leaf water deuterium enrichment shapes leaf wax n-alkane δD values of angiosperm 753 plants II: Observational evidence and global implications. Geochimica et 754 755 Cosmochimica Acta 111: 50-63 Kao S-J, Hilton R, Selvaraj K, Dai M, Zehetner F, et al. 2014. Preservation of 756 terrestrial organic carbon in marine sediments offshore Taiwan: mountain 757 building and atmospheric carbon dioxide sequestration. Earth Surface 758 Dynamics 2: 127-39 759 Konecky B, Noone D, Cobb K. 2019. The influence of competing hydroclimate 760 processes on stable isotope ratios in tropical rainfall. Geophysical Research 761 762 Letters 46: 1622-33 Lee, J.E., Fung, I., DePaolo, D.J. and Henning, C.C., 2007. Analysis of the global 763 distribution of water isotopes using the NCAR atmospheric general circulation 764 765 model. Journal of Geophysical Research: Atmospheres, 112(D16). Lunt DJ, Bragg F, Chan W-L, Hutchinson DK, Ladant J-B, et al. 2021. DeepMIP: 766 Model intercomparison of early Eocene climatic optimum (EECO) large-scale 767 climate features and comparison with proxy data. Climate of the Past 17: 203-768 27 769 Lunt DJ, Huber M, Anagnostou E, Baatsen ML, Caballero R, et al. 2017. The 770 771 DeepMIP contribution to PMIP4: Experimental design for model simulations of the EECO, PETM, and pre-PETM (version 1.0). Geoscientific Model 772 Development 10: 889-901 773 774 Mackenzie A, Patience R, Maxwell J, Vandenbroucke M, Durand B. 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France-I. 775

Changes in the configurations of acyclic isoprenoid alkanes, steranes and 776 triterpanes. Geochimica et Cosmochimica Acta 44: 1709-21 777 McFarlin JM, Axford Y, Masterson AL, Osburn MR. 2019. Calibration of modern 778 sedimentary δ2H plant wax-water relationships in Greenland lakes. 779 Quaternary Science Reviews 225: 105978 780 Moss PT, Kershaw AP, Grindrod J. 2005. Pollen transport and deposition in riverine 781 and marine environments within the humid tropics of northeastern Australia. 782 Review of Palaeobotany and Palynology 134: 55-69 783 Nicolo MJ, Dickens GR, Hollis CJ, Zachos JC. 2007. Multiple early Eocene 784 785 hyperthermals: Their sedimentary expression on the New Zealand continental margin and in the deep sea. Geology 35: 699-702 786 Olivarez Lyle A, Lyle MW. 2006. Missing organic carbon in Eocene marine 787 788 sediments: Is metabolism the biological feedback that maintains end-member 789 climates? Paleoceanography 21 Pagani M, Pedentchouk N, Huber M, Sluijs A, Schouten S, et al. 2006. Arctic 790 hydrology during global warming at the Palaeocene/Eocene thermal 791 792 maximum. Nature 442: 671-5 Pancost RD, Boot CS. 2004. The palaeoclimatic utility of terrestrial biomarkers in 793 marine sediments. Marine Chemistry 92: 239-61 794 Passchier S, Bohaty SM, Jiménez-Espejo F, Pross J, Röhl U, et al. 2013. Early 795 Eocene to middle Miocene cooling and aridification of East Antarctica. 796 797 Geochemistry, Geophysics, Geosystems 14: 1399-410 798 Paxman GJ, Jamieson SS, Hochmuth K, Gohl K, Bentley MJ, et al. 2019. Reconstructions of Antarctic topography since the Eocene–Oligocene 799 boundary. Palaeogeography, palaeoclimatology, palaeoecology 535: 109346 800 Payros A, Ortiz S, Millán I, Arostegi J, Orue-Etxebarria X, Apellaniz E. 2015. Early 801 Eocene climatic optimum: Environmental impact on the North Iberian 802 continental margin. Bulletin 127: 1632-44 803 Plank, T. and Manning, C.E., 2019. Subducting carbon. Nature, 574(7778), pp.343-804 352. 805 Polissar, P.J. and D'Andrea, W.J., 2014. Uncertainty in paleohydrologic 806 807 reconstructions from molecular δD values. Geochimica et Cosmochimica Acta, 129, pp.146-156. 808 Poulsen CJ, Pollard D, White TS. 2007. General circulation model simulation of the 809 δ18O content of continental precipitation in the middle Cretaceous: A model-810 811 proxy comparison. *Geology* 35: 199-202 Pross J, Contreras L, Bijl PK, Greenwood DR, Bohaty SM, et al. 2012. Persistent 812 near-tropical warmth on the Antarctic continent during the early Eocene 813 epoch. Nature 488: 73-7 814 Sachse D, Billault I, Bowen GJ, Chikaraishi Y, Dawson TE, et al. 2012. Molecular 815 paleohydrology: interpreting the hydrogen-isotopic composition of lipid 816 biomarkers from photosynthesizing organisms. Annual Review of Earth and 817 Planetary Sciences 40: 221-49 818 Schefuß E, Eglinton TI, Spencer-Jones CL, Rullkötter J, De Pol-Holz R, et al. 2016. 819 Hydrologic control of carbon cycling and aged carbon discharge in the Congo 820 River basin. Nature Geoscience 9: 687-90 821 Schmidt, G.A., LeGrande, A.N. and Hoffmann, G., 2007. Water isotope expressions 822 of intrinsic and forced variability in a coupled ocean-atmosphere 823 model. Journal of Geophysical Research: Atmospheres, 112(D10). 824

Sessions AL, Burgoyne TW, Schimmelmann A, Hayes JM. 1999. Fractionation of 825 hydrogen isotopes in lipid biosynthesis. Organic Geochemistry 30: 1193-200 826 Semiletov, I.P., Pipko, I.I., Shakhova, N.E., Dudarev, O.V., Pugach, S.P., Charkin, 827 A.N., McRoy, C.P., Kosmach, D. and Gustafsson, Ö., 2011. Carbon transport 828 by the Lena River from its headwaters to the Arctic Ocean, with emphasis on 829 fluvial input of terrestrial particulate organic carbon vs. carbon transport by 830 coastal erosion. *Biogeosciences*, 8(9), pp.2407-2426. 831 Sinninghe Damsté JS. 2016. Spatial heterogeneity of sources of branched 832 tetraethers in shelf systems: The geochemistry of tetraethers in the Berau 833 River delta (Kalimantan, Indonesia). Geochimica et Cosmochimica Acta 186: 834 835 13-31 Slotnick BS, Dickens GR, Nicolo MJ, Hollis CJ, Crampton JS, et al. 2012. Large-836 837 amplitude variations in carbon cycling and terrestrial weathering during the latest Paleocene and earliest Eocene: The record at Mead Stream, New 838 Zealand. The journal of geology 120: 487-505 839 Sluijs A, Dickens GR. 2012. Assessing offsets between the δ 13C of sedimentary 840 841 components and the global exogenic carbon pool across early Paleogene carbon cycle perturbations. Global Biogeochemical Cycles 26 842 Smith FA, Freeman KH. 2006. Influence of physiology and climate on δD of leaf wax 843 n-alkanes from C3 and C4 grasses. Geochimica et Cosmochimica Acta 70: 844 1172-87 845 Smith RW, Bianchi TS, Li X. 2012. A re-evaluation of the use of branched GDGTs as 846 847 terrestrial biomarkers: Implications for the BIT Index. Geochimica et Cosmochimica Acta 80: 14-29 848 Smittenberg R, Pancost R, Hopmans E, Paetzel M, Damsté JS. 2004. A 400-year 849 850 record of environmental change in an euxinic fjord as revealed by the sedimentary biomarker record. Palaeogeography, Palaeoclimatology, 851 Palaeoecology 202: 331-51 852 Sømme TO, Helland-Hansen W, Granjeon D. 2009. Impact of eustatic amplitude 853 variations on shelf morphology, sediment dispersal, and sequence 854 stratigraphic interpretation: Icehouse versus greenhouse systems. Geology 855 37: 587-90 856 Sparkes RB, Doğrul Selver A, Bischoff J, Talbot HM, Gustafsson Ö, et al. 2015. 857 GDGT distributions on the East Siberian Arctic Shelf: implications for organic 858 carbon export, burial and degradation. Biogeosciences 12: 3753-68 859 860 Speelman EN, Sewall JO, Noone D, Huber M, der Heydt Av, et al. 2010. Modeling the influence of a reduced equator-to-pole sea surface temperature gradient 861 on the distribution of water isotopes in the Early/Middle Eocene. Earth and 862 863 Planetary Science Letters 298: 57-65 Talbot HM, Farrimond P. 2007. Bacterial populations recorded in diverse 864 sedimentary biohopanoid distributions. Organic Geochemistry 38: 1212-25 865 Torres, M.A., West, A.J. and Li, G., 2014. Sulphide oxidation and carbonate 866 dissolution as a source of CO 2 over geological 867 timescales. Nature, 507(7492), pp.346-349. 868 Tauxe L, Stickley CE, Sugisaki S, Bijl PK, Bohaty SM, et al. 2012. 869 Chronostratigraphic framework for the IODP Expedition 318 cores from the 870 Wilkes Land margin; constraints for paleoceanographic reconstruction. 871 872 Paleoceanography 27 Weijers JW, Schouten S, Schefuß E, Schneider RR, Damste JSS. 2009. 873 Disentangling marine, soil and plant organic carbon contributions to 874

875 876	continental margin sediments: a multi-proxy approach in a 20,000 year sediment record from the Congo deep-sea fan. <i>Geochimica et Cosmochimica</i>
877 878 870	Acta 73: 119-32 Weijers JW, Schouten S, Spaargaren OC, Damsté JSS. 2006. Occurrence and distribution of totracthor membrane lipids in soils: Implications for the use of
879 880 881	the TEX86 proxy and the BIT index. <i>Organic Geochemistry</i> 37: 1680-93 Weller P. Stein R. 2008. Paleogene biomarker records from the central Arctic Ocean
882 883	(Integrated Ocean Drilling Program Expedition 302): Organic carbon sources, anoxia, and sea surface temperature. <i>Paleoceanography</i> 23
884 885	Zhu J, Poulsen CJ, Otto-Bliesner BL, Liu Z, Brady EC, Noone DC. 2020. Simulation of early Eccene water isotopes using an Earth system model and its
886 887	implication for past climate reconstruction. <i>Earth and Planetary Science</i> Letters 537: 116164
888 889	Zhu J, Poulsen CJ, Tierney JE. 2019. Simulation of Eocene extreme warmth and high climate sensitivity through cloud feedbacks. <i>Science Advances</i> 5:
890 891	eaax1874
001	
892	
893	
894	
895	
897	
898	
899	
900	
901	
902	
903	
904	
905	
906	
907	

908

- 909
- 910
- 911
- 912
- 913

914 Captions

915

Figure 1: Continental configurations of the Australian sector of the Southern Ocean during the early Eocene (subchron C24n; 53.8 Ma). Map shows the position of the study site (U1356). Dark grey areas reflect present day shorelines, and light grey areas are submerged continental blocks above 3,000 m water depth. Modified from Bijl et al., 2013.

921

Figure 2: Organic carbon burial along the East Antarctic margin during the early Eocene. a) $\delta^{13}C_{org}$ (‰), b) total organic carbon (TOC; wt. %), c) bacterial-derived hopanoids (ng/g), d) plant-derived long-chain *n*-alkanes (ng/g). Black segments indicate intervals of no core recovery.

926

Figure 3: Enhanced terrestrial organic carbon burial along the East Antarctic margin
during the Eocene. a) branched-versus-isoprenoidal tetraether (BIT) index (Bijl et al.,
2013), b) total organic carbon (TOC; g/cm²/kyr¹) mass accumulation rate (MAR), c)
hopanioid MAR (ng/cm²/kyr¹), d) long-chain *n*-alkane MAR (ng/cm²/kyr¹). Note that

931 (a), (b) and (c) are on a logarithmic scale. Black segments indicate intervals of no core932 recovery.

933

Figure 4: Lipid biomarker thermal maturity ratios in early Eocene-aged Wilkes Land sediments. a) long-chain *n*-alkane carbon preference index (CPI), b) C₃₁ hopane $\beta\beta/(\alpha\beta+\beta\beta)$ indices. Black segments indicate intervals of no core recovery.

937

Figure 5: Enhanced poleward moisture transport to the East Antarctic margin during 938 the early Eocene). a) $\delta^2 H_{wax}$ estimates inferred from the C₂₇ *n*-alkane (orange) and C₂₉ 939 *n*-alkane (blue). Error bars represent $\pm 1\sigma_{\overline{x}}$ (following Polissar and D'Andrea, 2014). 940 b) pollen-corrected proxy-derived $\delta^2 H_w$ estimates inferred from the C₂₇ *n*-alkane 941 942 (orange) and C_{29} *n*-alkane (blue). Error bars indicate $\pm 1\sigma$ propagated errors of the analytical error and the fractionation uncertainty (following Feakins, 2013). Here we 943 944 use the standard deviation from modern plant type groups (i.e., C₃ angiosperms, C₃ gymnosperms, ferns; Sachse et al., 2012) to calculate the fractionation uncertainty 945 (see Appendix). 946

947

Figure 6: Reconstructed and simulated $\delta^2 H_w$ on the East Antarctic margin during the early Eocene: a) $\delta^2 H_{w-corr}$ estimates inferred from the C₂₇ *n*-alkane (light grey) and C₂₉ *n*-alkane (dark grey). Dashed line represents median value. Box represents 1st and 3rd interquartile range. Whiskers represent 95% confidence interval. b) model-derived $\delta^2 H_w$ estimates inferred from iCESM1.2. Open triangle represents pre-industrial x1 CO₂ simulation. Closed circles represent Eocene simulations at four different CO₂ levels (x1, x3, x6 and x9 pre-industrial CO₂). 955

Figure 7: Long-term hydroclimate variability along the East Antarctic margin during 956 the early Eocene. a) mean annual precipitation (MAP) estimates for the temperate 957 rainforest biome based on bioclimatic analysis (Pross et al., 2012), b) MAP estimates 958 for the paratropical rainforest biome based on bioclimatic analysis (Pross et al., 2012), 959 c) and d) MAP estimates obtained via iCESM1.2 for four different CO₂ levels (x1, x3, 960 x6 and x9 pre-industrial CO₂). Whiskers represent precipitation estimates during 961 962 summer (JJA) and winter (DJF) months. Black segments indicate intervals of no core recovery. 963

964













