

1 Fire and ecosystem change in the Arctic across the Paleocene-
2 Eocene Thermal Maximum

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17

18 **Abstract**¹

19 Fire has been an important component of ecosystems on a range of spatial and temporal
20 scales. Fire can affect vegetation distribution, the carbon cycle, and climate. The relationship
21 between climate and fire is complex, in large part because of a key role of vegetation type. Here,
22 we evaluate regional scale fire-climate relationships during a past global warming event, the
23 Paleocene-Eocene Thermal Maximum (PETM), in order to understand how vegetation
24 influenced the links between climate and fire occurrence in the Arctic region. To document
25 concurrent changes in climate, vegetation, and fire occurrence, we evaluated biomarkers,

¹Abbreviations: carbon isotope excursion (CIE); cyclisation of branched tetraether (CBT); dichloromethane (DCM); glycerol dialkyl glycerol tetraether (GDGT); mass spectrometer (MS); mean annual temperature (MAT); methylation of branched tetraether (MBT); Paleocene-Eocene Thermal Maximum (PETM); polycyclic aromatic hydrocarbon (PAH); pristane (Pr); phytane (Ph); total lipid extract (TLE); total organic carbon (TOC)

26 including polycyclic aromatic hydrocarbons (PAHs), terpenoids, and alkanes, from the PETM
27 interval at a marine depositional site (IODP site 302, the Lomonosov Ridge) in the Arctic Ocean.

28 Biomarker, fossil, and isotope evidence from site 302 indicates that terrestrial vegetation
29 changed during the PETM. The abundance of the C₂₉ *n*-alkanes, pollen, and the ratio of leaf-wax
30 *n*-alkanes relative to diterpenoids all indicate that proportional contributions from angiosperm
31 vegetation increased relative to that from gymnosperms. These changes accompanied increased
32 moisture transport to the Arctic and higher temperatures, as recorded by previously published
33 proxy records. We find that PAH abundances were elevated relative to total plant biomarkers
34 throughout the PETM, and suggest that fire occurrence increased relative to plant productivity.
35 The fact that fire frequency or prevalence may have increased during wetter Arctic conditions
36 suggests that changes in fire occurrence were not a simple function of aridity, as is commonly
37 conceived. Instead, we suggest that the climate-driven ecological shift to angiosperm-dominated
38 vegetation was what led to increased fire occurrence. Potential increases in terrestrial plant
39 biomass that arose from warm, wet, and high CO₂ conditions were possibly attenuated by
40 biomass burning associated with compositional changes in the plant community.

41

42 **Keywords**

43 Paleocene-Eocene Thermal Maximum (PETM); polycyclic aromatic hydrocarbon (PAH); fire;
44 angiosperms; organic carbon; Arctic

45

46 **1. Introduction**

47 Many climate modeling studies predict increases in wildfire activity in future decades
48 associated with globally warming climates and shifting hydrologic patterns. Even so,

49 mechanisms controlling fire patterns are complex and the primary controls are not always clear
50 (Hessl, 2011). Today, increased atmospheric CO₂ concentrations, higher temperatures, and
51 longer dry seasons are associated with increases in fire activity in the western USA (Westerling,
52 2006). However, shifts in vegetation (e.g., type, abundance, structure, and continuity) can
53 override the influence of warmer and drier conditions (Higuera et al., 2014). In addition, most
54 empirical evidence, which is also the basis of many models, covers centennial scales (or less),
55 and may not readily translate to climate-vegetation-atmospheric CO₂ relationships recorded in
56 the paleorecord on 1,000 to 10,000 year scales (Hessl, 2011). Records of fire occurrence during
57 past major warming events, such as the Paleocene-Eocene Thermal Maximum (PETM), can
58 potentially elucidate fire dynamics during abrupt and extreme warming, and provide insights
59 relevant to anticipating climate, vegetation, and fire associations under future climate scenarios.

60 The PETM was a geologically abrupt period of global warming that occurred
61 approximately 55.5 million years ago (Westerhold et al., 2012). This climatic event is widely
62 invoked as a geologic analog for modern climate change, even though modern carbon release
63 (~10 Pg C/yr) may be 10 times faster (Cui et al., 2011). The hyperthermal event is marked by a
64 negative carbon isotope excursion (CIE), signifying a major perturbation to the carbon cycle
65 (McInerney and Wing, 2011, and references therein). At least 3,000 Pg of ¹³C-depleted carbon
66 was released into the atmosphere over ~10,000 years and global temperatures rose ~5-8°C over
67 ~170,000 years (Cui et al., 2011; McInerney and Wing, 2011; Peterse et al., 2012; Sluijs et al.,
68 2006; Weijers et al., 2007; Wing et al., 2005). Concurrently, there were dramatic shifts in
69 vegetation and precipitation patterns around the world (Kraus and Riggins, 2007; Pagani et al.,
70 2006; Wing et al., 2005; Wing and Currano, 2013).

71 For example, in the Bighorn Basin, Wyoming, USA, where there has been extensive
72 plant fossil research, flora shifted considerably during the PETM (McInerney and Wing, 2011;
73 Wing and Currano, 2013). Plants that are typically adapted to intermediate moisture levels
74 (particularly conifers) decreased, and thermophilic and dry-tolerant species (particularly
75 Fabaceae (legumes)) surged in abundance (Wing and Currano, 2013). Hence, the western USA
76 flora during the PETM was most similar to dry tropical forests.

77 Despite some regional variations, generally flora expanded toward higher latitudes, such
78 as was observed in the Bighorn Basin (Wing and Currano, 2013). In the Arctic, pollen counts
79 and biomarkers indicate that angiosperm abundance increased at the expense of gymnosperms
80 (Schouten et al., 2007; Sluijs et al., 2006), while moisture transport increased, as suggested by
81 changes in the δD of *n*-alkanes (Pagani et al., 2006).

82 Boucsein and Stein (2009) analyzed characteristics of organic particles, or macerals, in
83 Arctic Ocean sediments (Integrated Ocean Drilling Program (IODP) site 302) from the late
84 Cretaceous to the Eocene. Based on changes in the proportion of inertinite (regarded as an
85 indicator of fire occurrence) relative to other terrigenous and aquatic macerals, the authors
86 suggested that greater inputs of burned vegetation were deposited in the marine sediments during
87 the Paleocene relative to the PETM and early Eocene.

88 Moore and Kurtz (2008) examined graphitic black carbon, a combustion byproduct, from
89 two IODP sites: site 1210 (Shatsky Rise) and the Bass River section (New Jersey Margin). At
90 Shatsky Rise, black carbon concentrations were below detection (<0.5 ppm), while at the New
91 Jersey Margin, there was no clear pattern in black carbon flux at the onset or during the CIE.
92 Carbon isotope analyses of black carbon revealed a $\sim 3.5\%$ negative CIE, which linked burned

93 material to PETM biomass, rather than burning of older Paleocene peat or coal (Moore and
94 Kurtz, 2008).

95 Collinson et al. (2009) linked a shift in fire regime to changes in vegetation composition
96 across the PETM in England. Late Paleocene samples, from the Cobham Lignite Bed in southern
97 England, were dominated by charcoal associated with episodic fires and by fern spores, which
98 suggested a low diversity, fire-prone community mainly composed of ferns and woody
99 angiosperms. The PETM vegetation was characterized by a loss of ferns, an increase in wetland
100 plants, and decreased fire occurrence. This study highlights the importance of vegetation (e.g.,
101 composition and fire-prone species) in determining fire propensity. Given the global geographic
102 and compositional changes in PETM vegetation, which are often linked to precipitation and
103 temperature patterns, predictions of fire occurrence are not easily extrapolated from changes in
104 the quantity of biomass and aridity.

105 The concept of biomass and aridity as key fire drivers has its roots in fire history
106 reconstructions of the past decades to 21,000 years, mainly derived from sedimentary charcoal
107 and tree ring fire scar analyses. These reconstructions provide information regarding fire
108 frequency, fire extent, and the timing of past fires in relation to climate (Daniau et al., 2012;
109 Margolis and Balmat, 2009). The records reveal complexity and that multiple factors influence
110 the relationship between fire occurrence and climate. But overall and in simplified terms, wet
111 periods allow for the buildup of biomass (fuel) and dry periods facilitate the burning of
112 vegetation (fuel availability). Increased precipitation can result in opposite effects on the
113 susceptibility to fire depending on the initial wetness of the environment. In relatively wet
114 environments that are likely not limited by fuel abundance, precipitation increases fuel moisture

115 and dampens fire occurrence; in dry environments that are fuel-limited, precipitation increases
116 the amount of fuel and increases the ecosystems tendency toward fire (Daniau et al., 2012).

117 The length of wet and dry periods can also have different effects on fire occurrence
118 depending on fuel type. Holocene fire frequency records in the western USA indicate that
119 enhanced seasonality and anomalously wet years followed by anomalously dry years promoted
120 fire conditions for vegetation with annual fuel production, such as grass (Margolis and Balmat,
121 2009). Other studies have suggested that extended dry periods led to widespread fires, such as
122 the 1997 Indonesian fires that spread wildly during the long El Niño dry season, likely because
123 heavier fuels (e.g., branches and logs) respond to humidity changes more slowly than finer fuels
124 (e.g., grass and small twigs) (Page et al., 2002). Alternatively, during long-term droughts, fire
125 occurrence can decrease if there is insufficient biomass to burn (Flannigan et al., 2009).

126 Changes in vegetation type can modify the link between climate and fire by affecting, for
127 example, the abundance, structure, and moisture content of fuels (Higuera et al., 2014). In
128 ecosystems with dense, continuous vegetation, fire occurrence is limited by climatic conditions
129 that facilitate the drying of fuels. In contrast, in systems with low biomass abundance or
130 discontinuous fuels, fire occurrence can be limited by the scarcity of burnable materials, even if
131 climate conditions may have been conducive for fire (Higuera et al., 2014).

132 From the analysis of a global compilation of charcoal records covering the last 21,000
133 years, Daniau et al. (2012) found an overall increase in fire occurrence with increased
134 temperature. Such findings tend to influence studies of ancient climate, and authors often
135 postulate that hotter and drier conditions likely increased fire occurrence (Secord et al., 2010;
136 Wing et al., 2005).

137 Pyrogenic carbon is a continuum of combustion products generated as solid residue or
138 volatiles, ranging from slightly charred material to soot (Knicker, 2011; von Lützow et al.,
139 2006). Polycyclic aromatic hydrocarbons (PAHs), which are part of this continuum, are
140 byproducts of combustion released as volatiles and in association with particles. In the
141 sedimentary record, changes in PAH concentrations are usually interpreted to indicate changes in
142 fire occurrence, with more PAHs linked to increased fire occurrence (e.g., Marynowski and
143 Simoneit, 2009; Denis et al., 2012). Aromatic structures tend to make pyrogenic carbon,
144 including larger PAHs (≥ 5 rings), relatively resistant to degradation in soil environments and
145 marine sediments (Knicker, 2011; von Lützow et al., 2006). For example, charcoal, another
146 byproduct of fire, has a relatively long residence time in modern soils, estimated on the order of
147 500 – 10,000 years, and in marine sediments with oxygen exposure, 10,000 – 20,000 years
148 (Knicker, 2011; von Lützow et al., 2006). Thus, in soils, larger fire-derived PAHs represent an
149 intermediate-phase of refractory carbon that is relatively stable and less reactive than fresh
150 biomass or litter, although they are not as refractory as fossil kerogens that may end up in
151 paleosols from weathered parent lithologies (Denis, 2016). In marine sediments, however, PAHs
152 likely reflect production (via combustion) to a greater extent than weathered inputs given the
153 significantly better preservation of all carbon phases relative to soils (Freeman and Colarusso,
154 2001).

155 In this study, we analyzed PAHs and plant biomarkers in a sediment core from the central
156 Arctic Ocean (IODP Hole 302-4A) in relation to biomass proxies for vegetation and precipitation
157 in the Arctic before, during, and after the PETM. PAH and plant biomarker abundances provide
158 a unique set of tools to evaluate to what extent the combination of hotter and wetter conditions
159 (Pagani et al., 2006) and major changes in vegetation composition (Schouten et al., 2007; Sluijs

160 et al., 2006) impacted fire occurrence. If the ecosystem was not biomass-limited, then inferred
161 wetter conditions would have dampened fire occurrence during the PETM in the Arctic. By
162 evaluating changes in combustion (using PAHs) relative to terrestrial productivity (based on
163 terpenoid biomarkers and pollen records), we seek insights into potential changes in biomass
164 carbon in the Arctic region during a warm, wet, and high-CO₂ climate.

165

166 **2. Study Section**

167 Core samples were collected from IODP Hole 302-4A on the Lomonosov Ridge in the
168 central Arctic Ocean (Figure 1). Several previous studies have analyzed these samples, or
169 samples from similar stratigraphic intervals, for a variety of geochemical, biomarker, and
170 palynomorph data (Backman et al., 2006; Boucsein and Stein, 2009; Knies et al., 2008; Pagani et
171 al., 2006; Schouten et al., 2007; Sluijs et al., 2008b, 2006; Stein, 2008; Stein et al., 2014, 2006;
172 Weller and Stein, 2008). The organic-rich siliciclastic claystone sediments contain well-
173 preserved biomarkers and palynomorphs (Pagani et al., 2006; Schouten et al., 2007; Sluijs et al.,
174 2006; Stein et al., 2006; Weller and Stein, 2008) before, during, and after the PETM interval.
175 Anoxic bottom-water conditions (interpreted based on the presence of laminated sediments, the
176 absence of benthic foraminiferal linings, C/S ratios, and biomarkers) and euxinic conditions in
177 the photic zone (interpreted based on the presence of isorenieratene and other isorenieratene
178 derivatives) facilitated organic carbon preservation during the PETM interval (Schouten et al.,
179 2007; Sluijs et al., 2006; Stein et al., 2006; Weller and Stein, 2008). Average sedimentation rates
180 from the late Paleocene to the early Eocene were 1 to 3 cm/kyr (Sluijs et al., 2008b; Stein et al.,
181 2006) and were estimated to have increased during the PETM to 5.0 ± 1.2 cm/kyr (Sluijs et al.,
182 2008b). Sea level rose during the event by approximately 20 to 30 m (Sluijs et al., 2008a).

183 The Arctic region was hotter and wetter during the PETM than before and after the event
184 (Pagani et al., 2006; Sluijs et al., 2008b, 2006). Air temperatures increased 6°C during the PETM
185 from ~15°C to ~21°C (Peterse et al., 2012; Weijers et al., 2007). Pagani et al. (2006) suggested a
186 greater export of moisture from the tropics towards higher latitudes. The isotopic composition of
187 Arctic PETM precipitation was considerably ²H-enriched compared to today, indicating reduced
188 rainout along the source airmass' trajectory from lower latitudes to the poles. In addition, low-
189 salinity-tolerant dinocyst assemblages (Sluijs et al., 2006) suggest increased precipitation and
190 runoff during the PETM (Pagani et al., 2006). Sluijs et al. (2006) suggested that higher
191 temperatures and enhanced fluvial runoff increased nutrient inputs, which increased marine
192 productivity, and caused water column stratification. Furthermore, because the Arctic Basin may
193 have been a restricted basin, high terrestrial runoff during the PETM could have helped create a
194 freshwater upper layer that resulted in water column stratification (Sluijs et al., 2006).

195

196 **3. Methods**

197 *3.1. Samples*

198 Sediments were obtained from IODP Expedition 302 Hole 4A on the Lomonosov Ridge
199 (Backman et al., 2006; Pagani et al., 2006) (Figure 1). An age model for the core was previously
200 determined from palynological data and index events, which put the base of the Eocene at the top
201 of Core 32x (Backman et al., 2006) (Figure 2 and Figure 3). The PETM interval was marked
202 based on the negative carbon isotope excursion from $\delta^{13}\text{C}$ of total organic carbon and of leaf-wax
203 *n*-alkanes (Pagani et al., 2006; Schouten et al., 2007).

204

205 *3.2. Extraction and analysis*

206 Lipid extracts analyzed in this paper were a subset of those processed and analyzed in
207 Pagani et al. (2006). Sediments were prepared for analysis as described in Pagani et al. (2006).
208 Briefly, sediments were freeze-dried and extracted with dichloromethane (DCM) using
209 accelerated solvent extraction. Total lipid extracts (TLEs) were separated by column
210 chromatography into three fractions using hexane (S1), hexane/DCM (9:1 v:v) (S2), and
211 DCM/methanol (2:1 v:v) (S3). The first fraction (S1) was further separated into two fractions
212 (adducts and non-adducts) via urea adduction.

213 PAHs and terpenoids were analyzed using an Agilent 6890 GC with an Agilent 5973
214 quadrupole mass spectrometer (MS) and a fused silica capillary column (Agilent J&W DB-5; 30
215 m, 250 μ m, 0.25 μ m). The column flow rate was 2.0 ml/min and the oven program started at
216 60°C for 1 min, ramped to 320°C at 6°C/min, and had a final hold time of 15 min. The MS had
217 an ionization energy of 70 eV with a scanning mass range of m/z 40-700 in Full Scan mode.
218 PAHs were identified and quantified in Full Scan mode based on authentic standards, NIST 98
219 spectral library, fragmentation patterns, and retention times. For quantification, extracted ions
220 were (m/z): 202 (pyrene), 237 (simonellite), 252 (simonellite, benzo[a]pyrene,
221 benzofluoranthene, perylene, 1,2,3,4-tetrahydro-2,2,9-trimethylpicene (i.e., “ β -amyrin
222 derivative”, referred to as “tetra-aromatic triterpane” in Schouten et al. (2007)), 255
223 (dehydroabietane), 268 (β -amyrin derivative), 300 (coronene), 324 (β -amyrin derivative), 367
224 (hope-(17,21)-ene). *n*-Alkanes were from S1 Adducts (m/z): 43 and 57; pristane and phytane
225 were from S1 Non-adducts (m/z): 57. Relative abundances were determined based on relative
226 peak areas of compounds within a given fraction.

227

228 *3.3. Normalized plant biomarker abundance to terrestrial organic carbon inputs*

229 To account for production and preservation changes in TOC and eliminate the influence
230 of changing marine organic carbon ($\text{TOC}_{\text{marine}}$) inputs, we normalized plant biomarker
231 abundances (Schouten et al., 2007) to terrestrial organic carbon (TOC_{terr}) (Figure 3) rather than
232 TOC ($\text{TOC}_{\text{marine}} + \text{TOC}_{\text{terr}}$). We used two proxies for terrestrial and marine biomass contributions
233 (Sluijs and Dickens, 2012) to estimate the relative proportions of TOC_{terr} and $\text{TOC}_{\text{marine}}$, the BIT
234 index and the relative portions of terrestrial (pollen and spores) and marine (primarily
235 dinoflagellate cysts) palynomorphs. The BIT index is based on the proportion of specific ether
236 lipids (glycerol dialkyl glycerol tetraethers (GDGTs)) as defined by Hopmans et al. (2004).
237 Distinctive terrestrial GDGTs are produced by bacteria in soils and rivers, while the marine
238 GDGT is primarily produced by pelagic archaea in the ocean. To calculate TOC_{terr} , for each
239 sample we multiplied the TOC value by the percentage of terrestrial inputs based on
240 palynomorphs or the BIT index based on values reported by Sluijs et al. (2006). Because both
241 proxies have limitations (Sluijs and Dickens, 2012), we used the average of the TOC_{terr}
242 calculated by the two proxies. Uncertainty was the difference between TOC_{terr} calculated from
243 the proxies individually for a given sample (Figure 2 and Figure S1).

244

245 **4. Results**

246 PAH abundance increased relative to both diterpenoid and triterpenoid abundances in
247 PETM sediments compared to late Paleocene sediments (Figure 2). Coronene/coronene+pyrene
248 ratios across the section were an average of 0.3 and ranged from 0.1 to 0.7 (Figure S1).

249 The ratio of the sum of odd $n\text{-C}_{25}$ to $n\text{-C}_{33}$ alkanes relative to diterpenoids (simonellite
250 and dehydroabietane derived from gymnosperms) was similar to pollen composition trends and
251 significantly greater than the ratio of β -amyryn derivative relative to diterpenoids (based on n -

252 alkanes, pollen, and terpenoid data from Schouten et al. (2007)) (Figure 2). The percent of the
253 sum of the *n*-alkanes ratio ranged from 46% to 58% in the late Paleocene, 55% to 88% in the
254 PETM, and 52% to 77% in the early Eocene. Air temperature and percent of angiosperms
255 (pollen) in the PETM and post-PETM section are linearly correlated ($R^2 = 0.68$), but not as well
256 correlated across the section ($R^2 = 0.33$) (Figure S2) (based on temperature data from Peterse et
257 al. (2012)).

258 Pristane/phytane ratios (Pr/Ph) (Figure 2) were generally lower in PETM sediments than
259 before or after the event and ranged from 0.1 to 3.1 throughout the whole sampled section. Pr/Ph
260 ratios in Paleocene pre-PETM sediments ranged from 0.1 to 1.6. Ratios for PETM interval
261 sediments were less than 1 for most of the PETM, except for elevated values at ~382.5 mcd.
262 Ratios for Eocene post-PETM sediments ranged from 0.3 to 3.1, with Eocene Pr/Ph ratios less
263 than 1 immediately after the PETM interval, and then greater than 1 at 379 to 378 mcd.

264 Concentrations (ng/g TOC_{terr}) of dehydroabietane, simonellite, β -amyrin derivative, and
265 C₂₅₋₃₃ *n*-alkanes had little variation across the PETM event (though they were more variable
266 before and after the event) except for a peak in biomarker and angiosperm pollen abundance at
267 the end of the CIE (Figure 3).

268

269 **5. Discussion**

270 *5.1. Relationship between PAHs and plant biomarkers*

271 PAH concentrations increased relative to plant aromatic biomarkers in PETM sediments
272 compared to pre-PETM sediments (Figure 2). Differential preservation, transportation, or
273 production could explain the observed increase in PAH abundance, but changes in PAH
274 production was more likely for several reasons.

275 Transportation differences cannot fully explain the observed increase in the abundance of
276 PAHs relative to plant biomarkers because the transport mechanisms of both compounds by air
277 and water are similar (Baek et al., 1991). Both PAHs and aromatic plant biomarkers have similar
278 chemical structures with multiple aromatic rings and would likely have similar preservation
279 potential (Sluijs et al., 2006). Each class has compounds that cover a range of sizes; for example,
280 PAHs analyzed here range from 202 g/mol to 300 g/mol, while simonellite has a mass of 252
281 g/mol and 1,2,3,4-tetrahydro-2,2,9-trimethylpicene (i.e., “ β -amyrin derivative”, referred to as
282 “tetra-aromatic triterpane” in Schouten et al. (2007)) has a mass of 324 g/mol.

283 Favorable conditions for organic carbon preservation before, during, and after the PETM
284 (Pagani et al., 2006; Schouten et al., 2007; Sluijs et al., 2006; Stein et al., 2006; Weller and Stein,
285 2008) are further supported by the dominance of pyrene (4-ring PAH) over coronene (7-ring
286 PAH) throughout the section (Figure S1). Lower molecular weight PAHs are more susceptible to
287 degradation than higher molecular weight PAHs because of their greater solubility and
288 bioavailability (May et al., 1978). The coronene/coronene+pyrene ratio averaged 30% and had
289 no trend across the section. The dominance of pyrene in the Arctic marine sediments contrasts
290 starkly with the dominance of larger PAHs like coronene in highly degraded PETM terrestrial
291 paleosols (Denis, 2016). Therefore, the ratio of PAHs to plant biomarkers should not have been
292 altered due to lack of preservation. We conclude that PAH abundances primarily reflect changes
293 in PAH production and, thus, general trends in fire occurrence.

294

295 *5.2. Percent of angiosperms relative to gymnosperms based on plant biomarkers and pollen*

296 Schouten et al. (2007) observed that plant biomarker (triterpenoid/diterpenoid) ratios
297 underestimated plant type composition (angiosperms versus gymnosperms) compared to

298 estimates using pollen, and the authors suggested that taphonomic differences accounted for the
299 observed discrepancies in the percentage of angiosperms relative to gymnosperms. Based on
300 more recent literature, triterpenoids (derived from angiosperms), such as β -amyryn derivative, are
301 not preserved as well as diterpenoids (derived from gymnosperms) in terrestrial sediments
302 (Diefendorf et al., 2014). Triterpenoid-to-diterpenoid ratios, therefore, underestimate the
303 abundance of angiosperms in the source paleovegetation, which accounts for the discrepancy
304 between biomarker and pollen indicators of angiosperms reported by Schouten et al. (2007).
305 Following the suggested practice of Diefendorf et al. (2014), we used the ratio of plant wax *n*-
306 alkanes to diterpenoids as a proxy for the relative abundance of angiosperms to gymnosperms in
307 paleovegetation.

308 Across the PETM section, the concentration profile of the C₂₉ *n*-alkane is similar to the
309 angiosperm pollen abundance profile and is dissimilar to that of the terrestrial plant aromatic
310 biomarkers (Figure 3). Although many angiosperms and gymnosperms produce *n*-alkanes, the
311 conifer families that do are primarily common today in Asia and the Southern Hemisphere (e.g.,
312 Podocarpaceae (Diefendorf et al., 2015)). It is unlikely that these conifers lived in the Arctic
313 during the PETM (Basinger et al., 1994). Aside from Podocarpaceae, the major conifer groups
314 produce hardly any C₂₉ *n*-alkane; therefore, the C₂₉ *n*-alkane provides a strong phylogenetic
315 signal for angiosperm inputs (Diefendorf et al., 2015). The paleovegetation proxy introduced by
316 Diefendorf et al. (2014), which quantifies the ratio of *n*-alkanes to diterpenoids, yields estimates
317 of angiosperm inputs that match the pollen record (Figure 2). These findings are consistent with
318 the work by Diefendorf et al. (2014) on terpenoid preservational biases. Both the *n*-alkanes-to-
319 diterpenoids ratios and pollen data indicate that the relative contribution of angiosperms

320 increased during the PETM from ~55% to ~80%, reflecting a significant ecological shift to
321 angiosperm-dominated vegetation.

322

323 5.3. Terrestrial plant inputs

324 Organic geochemical studies typically normalize biomarker abundances to total organic
325 carbon (TOC) in order to account for changes in organic carbon production and preservation.
326 However, in these sediments there are two sources of carbon, marine-derived (TOC_{marine}) and
327 terrestrially derived (TOC_{terr}). Because TOC_{marine} can vary independently from terrestrial organic
328 contributions (Sluijs et al., 2006; Stein et al., 2006), normalizing the abundance of plant-derived
329 compounds to TOC_{terr}, will better represent landscape signals. A variety of evidence indicates
330 that the relative proportions of TOC_{terr} and TOC_{marine} changed before, during, and after the
331 PETM.

332 Evidence from palynomorphs (dinoflagellate cysts, pollen, and spores), the Branched and
333 Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004), biomarkers (e.g., high amounts of
334 long-chain *n*-alkanes and long-chain *n*-fatty acids), and the Rock Eval hydrogen index suggested
335 that the uppermost Paleocene sediments were proximal to the coast and were more terrestrially
336 influenced by riverine inputs (Sluijs et al., 2006; Stein et al., 2006; Weller and Stein, 2008).
337 During the PETM interval, evidence indicates that aquatic carbon dominated inputs (Sluijs et al.,
338 2006; Stein et al., 2006; Weller and Stein, 2008). Pr/Ph ratios are consistent with these
339 interpretations (Figure 2). Pr/Ph ratios <1 indicate marine inputs and ratios >1 indicate increasing
340 dominance of terrestrial inputs (typically >3) (Peters et al., 2005). At the end of the PETM, Pr/Ph
341 ratios >1 coincide with low and non-detectable amounts of isorenieratene and monoaromatic
342 isorenieratene derivatives, which signify a return to an oxic photic zone and oxic depositional

343 conditions. Overall, multiple lines of evidence indicate that elevated marine sourced organic
344 inputs were preserved during the CIE interval (Knies et al., 2008; Sluijs et al., 2006; Stein, 2008;
345 Stein et al., 2006; Weller and Stein, 2008; Figure 2). Although there is evidence for increased
346 terrestrial runoff during the CIE elsewhere (e.g., Crouch et al., 2003), a rise in sea level during
347 the PETM likely reduced the amount of terrestrial material that reached the Lomonosov Ridge
348 (Sluijs et al., 2008a). In addition, increased marine productivity (Knies et al., 2008; Sluijs et al.,
349 2008b; Stein, 2008; Stein et al., 2014) likely further diluted the relative proportion of TOC_{terr}
350 preserved in the PETM sediments.

351 Normalized concentrations (ng/g TOC_{terr}) of dehydroabietane, simonellite, β -amyrin
352 derivative, and C₂₅₋₃₃ *n*-alkanes, provide a means of investigating a general pattern of biomarker
353 input (without getting quantitative accumulation numbers) across the PETM. Biomarker data
354 show that plant input did not change drastically across the PETM event (Figure 3). As previously
355 noted, biomarkers and pollen data indicate greater inputs from angiosperms during the PETM,
356 and both biomarker (*n*-alkanes/diterpenoids) and pollen indicators show similar trends for most
357 of the record, although they diverged at the end of the PETM. The discrepancy occurs from
358 382.4 to 381.4 ‰ as $\delta^{13}\text{C}_{\text{org}}$ values and temperatures recovered to pre-PETM values and when
359 isorenieratene and monoaromatic isorenieratene derivatives were below detection limit in the
360 samples, which signified a return to an oxic photic zone (Figure 2 and Figure 3).

361

362 *5.4. Fire and ecosystem change implications*

363 Changes in angiosperm inputs correlate with proxy evidence for warming air
364 temperatures based on the Methylation of Branched Tetraether (MBT) and the Cyclisation of
365 Branched Tetratether (CBT) indices (Weijers et al., 2007; Peterse et al., 2012; Figure S2) and

366 followed an inferred increase in moisture to the Arctic (Pagani et al., 2006). As temperature
367 increased, angiosperm pollen increased at the expense of both gymnosperm pollen and fern
368 spores, and then angiosperm pollen decreased at the end of the PETM, as the climate cooled. The
369 trend of increased angiosperms and decreased gymnosperms was observed elsewhere during the
370 PETM, including Spitsbergen, the North Sea, Spain, and New Zealand (Wing and Currano,
371 2013, and references therein). Sluijs et al. (2006) suggested that the increased abundance of
372 angiosperm vegetation (Figure S3) in the Arctic reflected an expanded growing season. Based on
373 the taxonomy of the pollen from the Arctic sediments, during the body of the CIE the vegetative
374 landscape may have been an angiosperm-dominated temperate forest, which included some
375 tropical plants (such as palms) (D. Willard, pers. comm. 2016). During the CIE recovery, as
376 environmental conditions started to recover to pre-PETM conditions, angiosperms decreased and
377 gymnosperms and ferns increased giving way to an ecosystem with more swampy or wetland
378 plants (D. Willard, pers. comm. 2016).

379 We interpret PAH abundances relative to aromatic plant biomarkers to reflect changes in
380 PAH production. The rise in normalized PAH values suggests that increased fire occurrence was
381 associated with the angiosperm vegetation shift, perhaps indicating greater prevalence of more
382 fire-prone or fire-adapted species, as was observed in England (Collinson et al., 2009), greater
383 biomass abundance, or increased continuity of fuels that enhanced the ability for fire to spread.
384 Based on empirical fire models of the modern in the United States, doubling of atmospheric CO₂
385 increased the frequency of lightning strikes and increased fire occurrence by nearly 50%, which
386 suggests that the CO₂-rich atmosphere during the PETM may have increased lightning strike
387 frequency and enhanced fire occurrence in the Arctic (Price and Rind, 1994).

388 The increased moisture transport to the Arctic (Pagani et al., 2006) preceded the
389 coincident increases in temperature, angiosperms, and PAHs (Figure 2). The time lag emphasizes
390 that a combination of factors influenced changes in fire occurrence, including a balance of fuel
391 composition (e.g., vegetation amount and type), fuel availability (e.g., amount of vegetation that
392 can burn based on humidity, precipitation, and temperature), and ignition sources (e.g.,
393 lightning).

394 The high-latitude position of the Arctic means that the Paleocene-Eocene ecosystems
395 functioned under strong light seasonality (continuous winter darkness, continuous summer light)
396 and short transitional seasons (e.g., lasting less than 60 days). Despite these extreme natural light
397 conditions, a diverse forest ecosystem can survive, such has been observed from fossil evidence
398 in terrestrial sediments deposited in the early to mid-Eocene, a different time period but still a
399 warm and humid climate (Jahren and Sternberg, 2003). The terrestrial mean annual temperature
400 (MAT) for the Arctic in the early Eocene was $13.2 \pm 2.0^{\circ}\text{C}$, as estimated from oxygen-isotope
401 equilibration between environmental water and pedogenic carbonate from Axel Heiberg Island
402 (Jahren and Sternberg, 2003; Figure 1). In addition, cold-month temperatures were above 0°C ,
403 which implies a lack of freeze events (Basinger et al., 1994; Jahren and Sternberg, 2003). The
404 estimated terrestrial MAT for the late Paleocene was $\sim 15^{\circ}\text{C}$ and increased to $\sim 21^{\circ}\text{C}$ during the
405 PETM based on the distribution of branched glycerol dialkyl glycerol tetraether (GDGT)
406 membrane lipids (the MBT-CBT proxy) (Peterse et al., 2012; Weijers et al., 2007). Similar to
407 Axel Heiberg Island in the early Eocene, the continental Arctic during the PETM likely had cold-
408 month temperatures above freezing.

409 The warmer temperatures and wetter conditions during the PETM may have stymied
410 gymnosperm growth and, by reducing competition, opened up the ecosystem to angiosperms.

411 Alternatively, angiosperms may have migrated, with rising temperatures, from lower latitudes.
412 The angiosperm community may have recovered more rapidly after fire disturbances than
413 gymnosperms, potentially due to higher productivity or higher reproductive rates (Bond and
414 Midgley, 2012). As temperatures cooled at the end of the PETM, gymnosperm populations were
415 revived, and the ecosystem shifted back to a less fire-prone community. A potential scenario is
416 that fire increased in an angiosperm-dominated temperate forest, which included some tropical
417 plants (e.g., palms), and then as pre-PETM conditions began to return, gymnosperms and ferns
418 recovered, angiosperms decreased, and there was a greater abundance of swampy or wetland
419 plants (D. Willard, pers. comm. 2016), which were not as conducive to fire.

420 Based on our study and the few other studies of fire occurrence during the PETM,
421 changes in fire occurrence varied by location. At IODP site 1210 (Shatsky Rise) in the west-
422 central Pacific, there was no evidence of fire occurrence; at the New Jersey margin (Bass River
423 section) there was evidence of fire, but no clear change in occurrence during the PETM (Moore
424 and Kurtz, 2008). In England, fire occurrence decreased and was associated with a change in
425 vegetation; in this case, a shift from an herbaceous fern and woody angiosperm fire-prone system
426 to less ferns and woody plants, and increased wetland plants (Collinson et al., 2009). Although
427 during the PETM fire occurrence decreased in England but increased in the Arctic, in both
428 records, increased fire occurrence corresponded to an angiosperm-dominated community and
429 decreased fire occurrence was associated with increased wetland plants. Overall, the variability
430 in the effect of global warming on fire occurrence likely reflects local or regional variations in
431 ecosystems (e.g., vegetation type, structure, and amount) and environmental conditions (e.g.,
432 precipitation).
433

434 5.5. Carbon cycle implications

435 Plant CO₂-enrichment studies (Bowes, 1993) suggest that plant biomass may have
436 increased during the high CO₂ conditions of the PETM. In these studies, plants accumulated 30%
437 more biomass when atmospheric CO₂ was doubled (*p*CO₂ was increased from ~350 ppm to ~650
438 ppm) (Bowes, 1993). Angiosperms tend to have higher maximum growth rates than
439 gymnosperms (Bond, 1989), thus increased angiosperm production during the PETM is
440 consistent with higher terrestrial productivity. Increased terrestrial plant productivity had
441 potential to help sequester CO₂ from the atmosphere through greater accumulation of biomass in
442 soils or coastal marine sediments, both of which can serve as a sink for carbon. Yet, despite the
443 potential for greater terrestrial organic matter burial, the site 302 record shows a relatively
444 constant pattern of %TOC_{terr} before and during the PETM event. In contrast, %TOC_{marine}
445 increased significantly during the PETM, which is consistent with increased marine productivity
446 and greater marine organic matter burial (Knies et al., 2008; Sluijs et al., 2006; Stein, 2008; Stein
447 et al., 2014). While there likely was increased terrestrial productivity in the warmer and wetter
448 Arctic region, our PAH record indicates that it is possible that fire occurrence was a major factor
449 that reduced the transfer of terrestrial plant carbon to soil and sedimentary carbon. Because plant
450 biomass burning adds CO₂ to the atmosphere, greater fire occurrence may have prevented a
451 significant sequestration of carbon by terrestrial plant photosynthesis.

452

453 6. Conclusions

454 In the Arctic during the PETM, the landscape shifted to an angiosperm-dominated
455 ecosystem, but terrestrial plant input into the marine realm remained nearly constant. Similar to
456 observations by Diefendorf et al. (2014), the triterpenoid to diterpenoid ratio for the composition

457 of angiosperms relative to gymnosperms underestimated the percentage of angiosperms. Instead,
458 a ratio of *n*-alkanes to diterpenoids was similar to the angiosperm composition observed in
459 pollen.

460 During the PETM, PAH abundance increased relative to plant biomarkers compared to
461 before or after the event. Wetter conditions followed by higher temperatures favored
462 angiosperms, and this compositional shift in vegetation was associated with enhanced fire
463 occurrence. Hence, in paleoenvironments, increased fire occurrence was not always directly
464 linked to drier conditions. In the Arctic during the PETM, a climate-driven shift to an
465 angiosperm-dominated plant community spurred greater fire occurrence. Greater biomass
466 burning may have attenuated the effects of increases in plant productivity on the carbon cycle,
467 and thus potentially hindered any significant changes in terrestrial organic carbon sequestration.

468

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480

481 **References**

482

483 Backman, J., Moran, K., MicInroy, D.B., Mayer, L.A., the Expedition 302 Scientists, 2006. Sites
484 M0001–M0004, in: Proceedings of the Integrated Ocean Drilling Program, 302. Integrated
485 Ocean Drilling Program Management International, Inc., Edinburgh.

486 doi:10.2204/iodp.proc.302.104.2006

487 Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of
488 atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. *Water. Air. Soil*
489 *Pollut.* 60, 279–300. doi:10.1007/BF00282628

490 Basinger, J.F., Greenwood, D.R., Sweda, T., 1994. Early Tertiary vegetation of Arctic Canada
491 and its relevance to paleoclimatic interpretation, in: Boulter, M.C. (Ed.), *Arctic Plants and*
492 *Climates: 65 Million Years of Change*. Springer-Verlag, Berlin.

493 Bond, W.J., 1989. The tortoise and the hare: ecology of angiosperm dominance and gymnosperm
494 persistence. *Biol. J. Linn. Soc.* 36, 227–249. doi:10.1111/j.1095-8312.1989.tb00492.x

495 Bond, W.J., Midgley, J.J., 2012. Fire and the angiosperm revolutions. *Int. J. Plant Sci.* 173, 569–
496 583. doi:10.1086/665819

497 Boucsein, B., Stein, R., 2009. Black shale formation in the late Paleocene/early Eocene Arctic
498 Ocean and paleoenvironmental conditions: New results from a detailed organic petrological
499 study. *Mar. Pet. Geol.* 26, 416–426. doi:10.1016/j.marpetgeo.2008.04.001

500 Bowes, G., 1993. Facing the inevitable: Plants and increasing atmospheric CO₂. *Annu. Rev.*
501 *Plant Physiol. Plant Mol. Biol.* 44, 309–332.

502 Collinson, M.E., Steart, D.C., Harrington, G.J., Hooker, J.J., Scott, A.C., Allen, L.O., Glasspool,
503 I.J., Gibbons, S.J., 2009. Palynological evidence of vegetation dynamics in response to
504 palaeoenvironmental change across the onset of the Paleocene-Eocene Thermal Maximum
505 at Cobham, Southern England. *Grana* 48, 38–66. doi:10.1080/00173130802707980

506 Crouch, E.M., Dickens, G.R., Brinkhuis, H., Aubry, M.P., Hollis, C.J., Rogers, K.M., Visscher,
507 H., 2003. The Apectodinium acme and terrestrial discharge during the Paleocene-Eocene
508 thermal maximum: New palynological, geochemical and calcareous nannoplankton
509 observations at Tawanui, New Zealand. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 194, 387–
510 403. doi:10.1016/S0031-0182(03)00334-1

511 Cui, Y., Kump, L.R., Ridgwell, A.J., Charles, A.J., Junium, C.K., Diefendorf, A.F., Freeman,
512 K.H., Urban, N.M., Harding, I.C., 2011. Slow release of fossil carbon during the
513 Palaeocene–Eocene Thermal Maximum. *Nat. Geosci.* 4, 481–485. doi:10.1038/ngeo1179

514 Daniau, A.L., Bartlein, P.J., Harrison, S.P., Prentice, I.C., Brewer, S., Friedlingstein, P.,
515 Harrison-Prentice, T.I., Inoue, J., Izumi, K., Marlon, J.R., Mooney, S., Power, M.J.,
516 Stevenson, J., Tinner, W., Andrič, M., Atanassova, J., Behling, H., Black, M., Blarquez, O.,
517 Brown, K.J., Carcaillet, C., Colhoun, E.A., Colombaroli, D., Davis, B.A.S., D’Costa, D.,
518 Dodson, J., Dupont, L., Eshetu, Z., Gavin, D.G., Genries, A., Haberle, S., Hallett, D.J.,
519 Hope, G., Horn, S.P., Kassa, T.G., Katamura, F., Kennedy, L.M., Kershaw, P., Krivonogov,
520 S., Long, C., Magri, D., Marinova, E., McKenzie, G.M., Moreno, P.I., Moss, P., Neumann,
521 F.H., Norström, E., Paitre, C., Rius, D., Roberts, N., Robinson, G.S., Sasaki, N., Scott, L.,
522 Takahara, H., Terwilliger, V., Thevenon, F., Turner, R., Valsecchi, V.G., Vannièrè, B.,

523 Walsh, M., Williams, N., Zhang, Y., 2012. Predictability of biomass burning in response to
524 climate changes. *Global Biogeochem. Cycles* 26, 1–12. doi:10.1029/2011GB004249

525 Denis, E.H., 2016. Production and preservation of organic and fire-derived carbon across the
526 Paleocene-Eocene Thermal Maximum. The Pennsylvania State University.

527 Denis, E.H., Toney, J.L., Tarozo, R., Anderson, R.S., Roach, L.D., Huang, Y., 2012. Polycyclic
528 aromatic hydrocarbons (PAHs) in lake sediments record historic fire events: Validation
529 using HPLC-fluorescence detection. *Org. Geochem.* 45, 7–17.
530 doi:10.1016/j.orggeochem.2012.01.005

531 Diefendorf, A.F., Freeman, K.H., Wing, S.L., 2014. A comparison of terpenoid and leaf fossil
532 vegetation proxies in Paleocene and Eocene Bighorn Basin sediments. *Org. Geochem.* 71,
533 30–42. doi:10.1016/j.orggeochem.2014.04.004

534 Diefendorf, A.F., Leslie, A.B., Wing, S.L., 2015. Leaf wax composition and carbon isotopes
535 vary among major conifer groups. *Geochim. Cosmochim. Acta* 170, 145–156.
536 doi:10.1016/j.gca.2015.08.018

537 Flannigan, M.D., Krawchuk, M.A., De Groot, W.J., Wotton, B.M., Gowman, L.M., 2009.
538 Implications of changing climate for global wildland fire. *Int. J. Wildl. Fire* 18, 483–507.
539 doi:10.1071/WF08187

540 Freeman, K.H., Colarusso, L.A., 2001. Molecular and isotopic records of C4 grassland
541 expansion in the late Miocene. *Geochim. Cosmochim. Acta* 65, 1439–1454.
542 doi:10.1016/S0016-7037(00)00573-1

543 Hessel, A.E., 2011. Pathways for climate change effects on fire: Models, data, and uncertainties.
544 *Prog. Phys. Geogr.* 35, 393–407. doi:10.1177/0309133311407654

545 Higuera, P.E., Brubaker, L.B., Anderson, P.M., Hu, F.S., Brown, T.A., 2014. Vegetation
546 mediated the impacts of postglacial climate change on fire regimes in the south-central
547 Brooks Range, Alaska 79, 201–219. doi:10.1890/07-2019.1

548 Hopmans, E.C., Weijers, J.W.H., Schefuß, E., Herfort, L., Sinnighe Damsté, J.S., Schouten, S.,
549 2004. A novel proxy for terrestrial organic matter in sediments based on branched and
550 isoprenoid tetraether lipids. *Earth Planet. Sci. Lett.* 224, 107–116.
551 doi:10.1016/j.epsl.2004.05.012

552 Jahren, A.H., Sternberg, L.S.L., 2003. Humidity estimate for the middle Eocene Arctic rain
553 forest. *Geology* 31, 463–466. doi:10.1130/0091-7613(2003)031<0463:HEFTME>2.0.CO;2

554 Knicker, H., 2011. Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and
555 survival in soil environments. *Quat. Int.* 243, 251–263. doi:10.1016/j.quaint.2011.02.037

556 Knies, J., Mann, U., Popp, B.N., Stein, R., Brumsack, H.J., 2008. Surface water productivity and
557 paleoceanographic implications in the Cenozoic Arctic Ocean. *Paleoceanography* 23, 1–12.
558 doi:10.1029/2007PA001455

559 Kraus, M.J., Riggins, S., 2007. Transient drying during the Paleocene-Eocene Thermal
560 Maximum (PETM): Analysis of paleosols in the Bighorn Basin, Wyoming. *Palaeogeogr.*
561 *Palaeoclimatol. Palaeoecol.* 245, 444–461. doi:10.1016/j.palaeo.2006.09.011

562 Margolis, E.Q., Balmat, J., 2009. Fire history and fire-climate relationships along a fire regime
563 gradient in the Santa Fe Municipal Watershed, NM, USA. *For. Ecol. Manage.* 258, 2416–
564 2430. doi:10.1016/j.foreco.2009.08.019

565 Marynowski, L., Simoneit, B.R.T., 2009. Widespread Upper Triassic to Lower Jurassic Wildfire
566 records From Poland: Evidence From charcoal and pyrolytic polycyclic aromatic
567 hydrocarbons. *Palaios* 24, 785–798. doi:10.2110/palo.2009.p09-044r

568 May, W.E., Wasik, S.P., Freeman, D.H., 1978. Determination of the solubility behavior of some

569 polycyclic aromatic hydrocarbons in water. *Anal. Chem.* 50, 997–1000.
570 doi:10.1021/ac50029a042

571 McInerney, F.A., Wing, S.L., 2011. The Paleocene-Eocene Thermal Maximum: A perturbation
572 of carbon cycle, climate, and biosphere with implications for the future. *Annu. Rev. Earth
573 Planet. Sci.* 39, 489–516. doi:10.1146/annurev-earth-040610-133431

574 Moore, E.A., Kurtz, A.C., 2008. Black carbon in Paleocene-Eocene boundary sediments: A test
575 of biomass combustion as the PETM trigger. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 267,
576 147–152. doi:10.1016/j.palaeo.2008.06.010

577 Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., Sinninghe
578 Damsté, J.S., Dickens, G.R., 2006. Arctic hydrology during global warming at the
579 Palaeocene/Eocene thermal maximum. *Nature* 442, 671–675. doi:10.1038/nature05043

580 Page, S.E., Siegert, F., Rieley, J.O., Boehm, H.-D. V., Jaya, A., Limin, S., 2002. The amount of
581 carbon released from peat and forest fires in Indonesia during 1997. *Nature* 420, 61–66.
582 doi:10.1038/nature01141.1.

583 Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide. Volume 2:
584 Biomarkers and Isotopes in Petroleum Exploration and Earth History*, 2nd ed. Cambridge
585 University Press, Cambridge.

586 Peterse, F., van der Meer, J., Schouten, S., Weijers, J.W.H., Fierer, N., Jackson, R.B., Kim, J.H.,
587 Sinninghe Damsté, J.S., 2012. Revised calibration of the MBT-CBT paleotemperature
588 proxy based on branched tetraether membrane lipids in surface soils. *Geochim. Cosmochim.
589 Acta* 96, 215–229. doi:10.1016/j.gca.2012.08.011

590 Price, C., Rind, D., 1994. The impact of a 2-X-Co2 climate on lightning-caused fires. *J. Clim.*
591 doi:10.1175/1520-0442(1994)007<1484:TIOACC>2.0.CO;2

592 Schouten, S., Woltering, M., Rijpstra, W.I.C., Sluijs, A., Brinkhuis, H., Sinninghe Damsté, J.S.,
593 2007. The Paleocene-Eocene carbon isotope excursion in higher plant organic matter:
594 Differential fractionation of angiosperms and conifers in the Arctic. *Earth Planet. Sci. Lett.*
595 258, 581–592. doi:10.1016/j.epsl.2007.04.024

596 Secord, R., Gingerich, P.D., Lohmann, K.C., Macleod, K.G., 2010. Continental warming
597 preceding the Palaeocene-Eocene thermal maximum. *Nature* 467, 955–958.
598 doi:10.1038/nature09441

599 Sluijs, A., Brinkhuis, H., Crouch, E.M., John, C.M., Handley, L., Munsterman, D., Bohaty, S.M.,
600 Zachos, J.C., Reichart, G.J., Schouten, S., Pancost, R.D., Sinninghe Damsté, J.S., Welters,
601 N.L.D., Lotter, A.F., Dickens, G.R., 2008a. Eustatic variations during the Paleocene-Eocene
602 greenhouse world. *Paleoceanography* 23, 1–18. doi:10.1029/2008PA001615

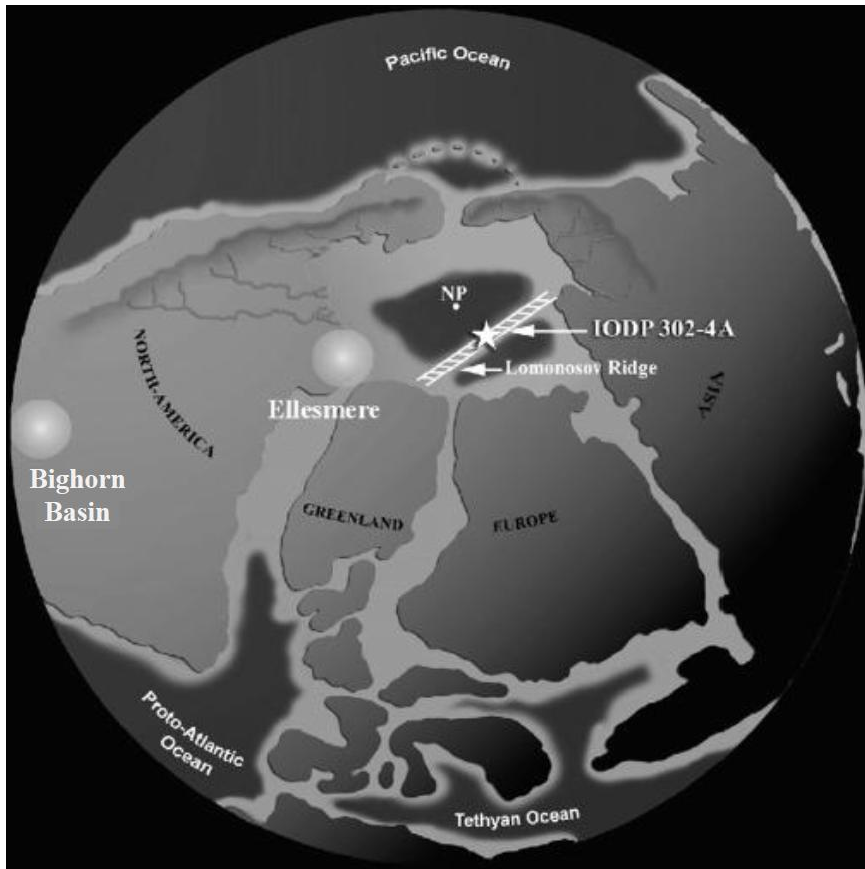
603 Sluijs, A., Dickens, G.R., 2012. Assessing offsets between the $\delta^{13}\text{C}$ of sedimentary components
604 and the global exogenic carbon pool across early Paleogene carbon cycle perturbations.
605 *Global Biogeochem. Cycles* 26, 1–14. doi:10.1029/2011GB004224

606 Sluijs, A., Röhl, U., Schouten, S., Brumsack, H.J., Sangiorgi, F., Sinninghe Damsté, J.S.,
607 Brinkhuis, H., 2008b. Arctic late Paleocene-Early Eocene paleoenvironments with special
608 emphasis on the Paleocene-Eocene thermal maximum (Lomonosov Ridge, Integrated Ocean
609 Drilling Program Expedition 302). *Paleoceanography* 23, 1–17.
610 doi:10.1029/2007PA001495

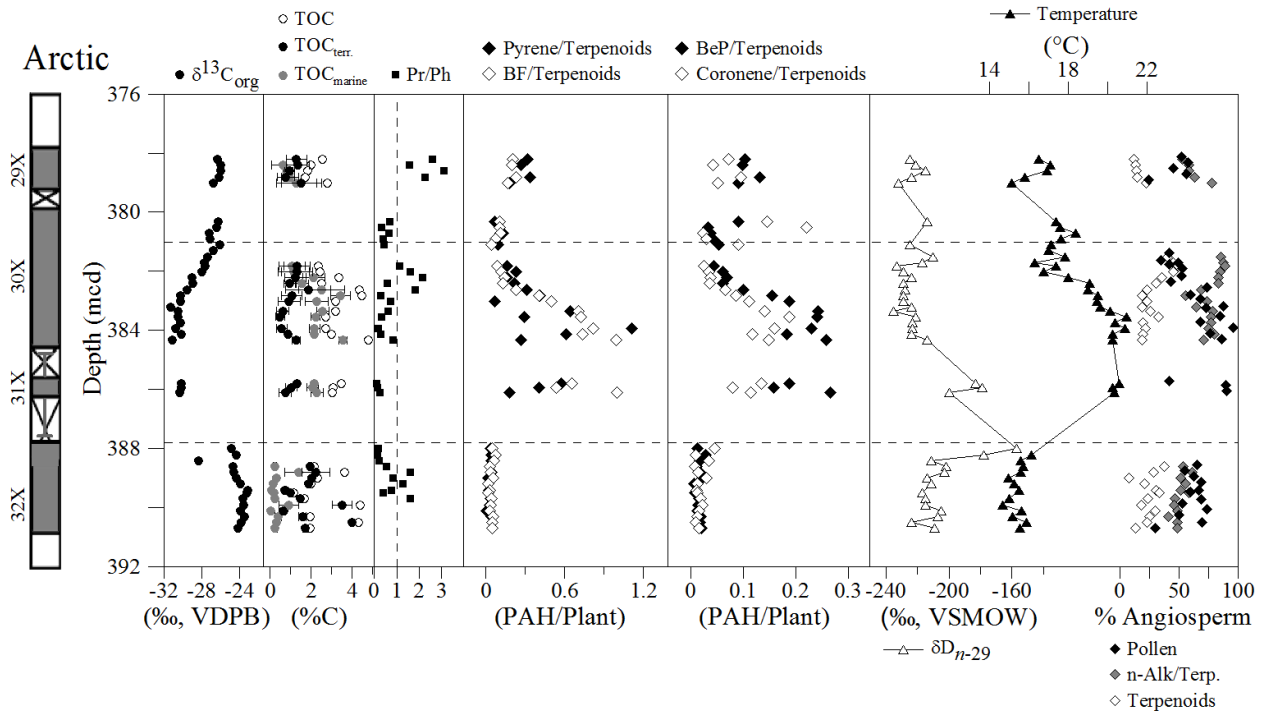
611 Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H., Sinninghe Damsté, J.S.,
612 Dickens, G.R., Huber, M., Reichart, G.-J., Stein, R., Matthiessen, J., Lourens, L.J.,
613 Pedentchouk, N., Backman, J., Moran, K., the Expedition, S., 2006. Subtropical Arctic
614 Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature* 441, 610–

- 615 613. doi:10.1038/nature04668
616 Stein, R., 2008. Mesozoic to cenozoic palaeoenvironmental records of high northern latitudes, in:
617 Developments in Marine Geology. Elsevier, Amsterdam, pp. 439–496. doi:10.1016/S1572-
618 5480(08)00007-9
619 Stein, R., Boucsein, B., Meyer, H., 2006. Anoxia and high primary production in the Paleogene
620 central Arctic Ocean: First detailed records from Lomonosov Ridge. *Geophys. Res. Lett.*
621 33, 2–7. doi:10.1029/2006GL026776
622 Stein, R., Weller, P., Backman, J., Brinkhuis, H., Moran, K., Pälike, H., 2014. Cenozoic Arctic
623 Ocean Climate History: Some highlights from the IODP Arctic Coring Expedition (ACEX),
624 in: Stein, R., Blackman, D., Inagaki, F., Larsen, H.-C. (Eds.), *Earth and Life Processes*
625 *Discovered from Subseafloor Environment - A Decade of Science Achieved by the*
626 *Integrated Ocean Drilling Program (IODP)*, Series *Developments in Marine Geology*, Vol.
627 7. Elsevier, Amsterdam, pp. 259–293.
628 von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner,
629 B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: Mechanisms and
630 their relevance under different soil conditions - A review. *Eur. J. Soil Sci.* 57, 426–445.
631 doi:10.1111/j.1365-2389.2006.00809.x
632 Weijers, J.W.H., Schouten, S., Sluijs, A., Brinkhuis, H., Sinninghe Damsté, J.S., 2007. Warm
633 arctic continents during the Palaeocene-Eocene thermal maximum. *Earth Planet. Sci. Lett.*
634 261, 230–238. doi:10.1016/j.epsl.2007.06.033
635 Weller, P., Stein, R., 2008. Paleogene biomarker records from the central Arctic Ocean
636 (Integrated Ocean Drilling Program Expedition 302): Organic carbon sources, anoxia, and
637 sea surface temperature. *Paleoceanography* 23, 1–15. doi:10.1029/2007PA001472
638 Westerhold, T., Röhl, U., Laskar, J., 2012. Time scale controversy: Accurate orbital calibration
639 of the early Paleogene. *Geochemistry, Geophys. Geosystems* 13, 1–19.
640 doi:10.1029/2012GC004096
641 Westerling, A.L., 2006. Warming and Earlier Spring Increase Western U.S. Forest Wildfire
642 Activity 1161, 940–943. doi:10.1126/science.1128834
643 Wing, S.L., Currano, E.D., 2013. Plant response to a global greenhouse event 56 million years
644 ago. *Am. J. Bot.* 100, 1234–1254. doi:10.3732/ajb.1200554
645 Wing, S.L., Harrington, G.J., Smith, F.A., Bloch, J.I., Boyer, D.M., Freeman, K.H., 2005.
646 Transient floral change and rapid global warming at the Paleocene-Eocene Boundary.
647 *Science* (80-.). 310, 993–996. doi:10.1126/science.1116913
648

649 **Figures**
650



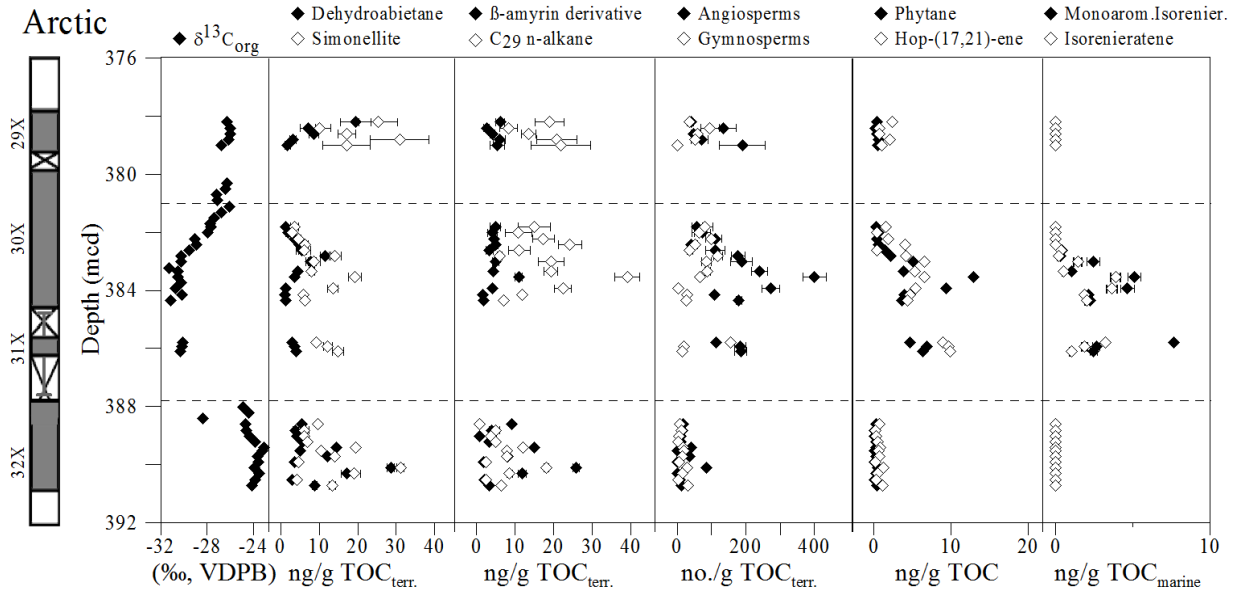
651
 652 Figure 1. Paleogeographic map of the late Paleocene-early Eocene with the location of IODP
 653 Hole 302-4A marked with a star (from Weijers et al., 2007).
 654 For reference, circles highlight the Bighorn Basin, Wyoming and Ellesmere Island (includes
 655 Axel Heiberg Island). NP is North Pole.



656

657 Figure 2. Depth profile of geochemical data.

658 Core recovery column, grey represents recovered core and “x” marks intervals without material;
 659 error bars connected to Core 31X mark the uncertainty of its stratigraphic position (Sluijs et al.,
 660 2006). Depth profile of carbon isotope ($\delta^{13}\text{C}_{\text{org}}$; black circle) and total organic carbon (TOC;
 661 white circle) (from Schouten et al., 2007), terrestrial organic carbon ($\text{TOC}_{\text{terr.}}$; black circle);
 662 marine organic carbon ($\text{TOC}_{\text{marine}}$; grey circle), Pristane/Phytane (black square) and dashed line
 663 at a ratio of 1, Pyrene/Terpenoids (terpenoids are simonellite and β -amyrin derivative; black
 664 diamond), benzo[fluoranthene] (BF)/Terpenoids (white diamond),
 665 Benzo[e]pyrene(BeP)/Terpenoids (black diamond), Coronene/Terpenoids (white diamond); δD
 666 values (white triangles with line) (Pagani et al., 2006) and air temperature based on MBT-CBT
 667 indices (black triangles with line) (Weijers et al., 2007; Peterse et al., 2012). %Angiosperm:
 668 Pollen (black diamond) and Triterpenoid/Diterpenoid (white triangle) ratios (Schouten et al.,
 669 2007); *n*-Alkanes/Diterpenoids ratio (grey diamond). Horizontal dashed lines mark the PETM
 670 interval. Horizontal bars connected to TOC represent the uncertainty in $\text{TOC}_{\text{terr.}}$ or $\text{TOC}_{\text{marine}}$
 671 since each was determined from an average of the BIT index and %Terrestrial Palynomorphs
 672 (from Sluijs et al. (2006)). If bar is not visible, uncertainty is less than the size of symbol.



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674 Figure 3. Depth profile of molecular compounds and pollen.

675 Core recovery column, where grey represents recovered core and “x” marks intervals without
 676 recovered material; error bars connected to Core 31X mark the uncertainty of its stratigraphic
 677 position (Sluijs et al., 2006). Carbon isotope values and biomarker concentrations were
 678 determined by Schouten et al. (2007). Depth profiles of organic carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$; black
 679 circle), dehydroabietane (black diamond), simonellite (white diamond), β -amyrin derivative
 680 (black diamond), C_{29} *n*-alkane (white diamond), angiosperms (black diamond) and gymnosperms
 681 (white diamond) pollen abundance (number/g TOC_{terr}), phytane (black diamond), hop-(17,21)-
 682 ene (white diamond), monoaromatic derivative of isorenieratene (black diamond), isorenieratene
 683 (white diamond). Horizontal dashed lines mark the PETM interval. TOC_{terr} is the estimated
 684 terrestrial organic carbon and $\text{TOC}_{\text{marine}}$ is the estimated marine organic carbon. Horizontal bars
 685 represent the uncertainty in TOC_{terr} or $\text{TOC}_{\text{marine}}$ since each was determined from an average of
 686 the BIT index and % Terrestrial Palynomorphs (from Sluijs et al. (2006)). If bar is not visible,
 687 uncertainty is less than the size of symbol.

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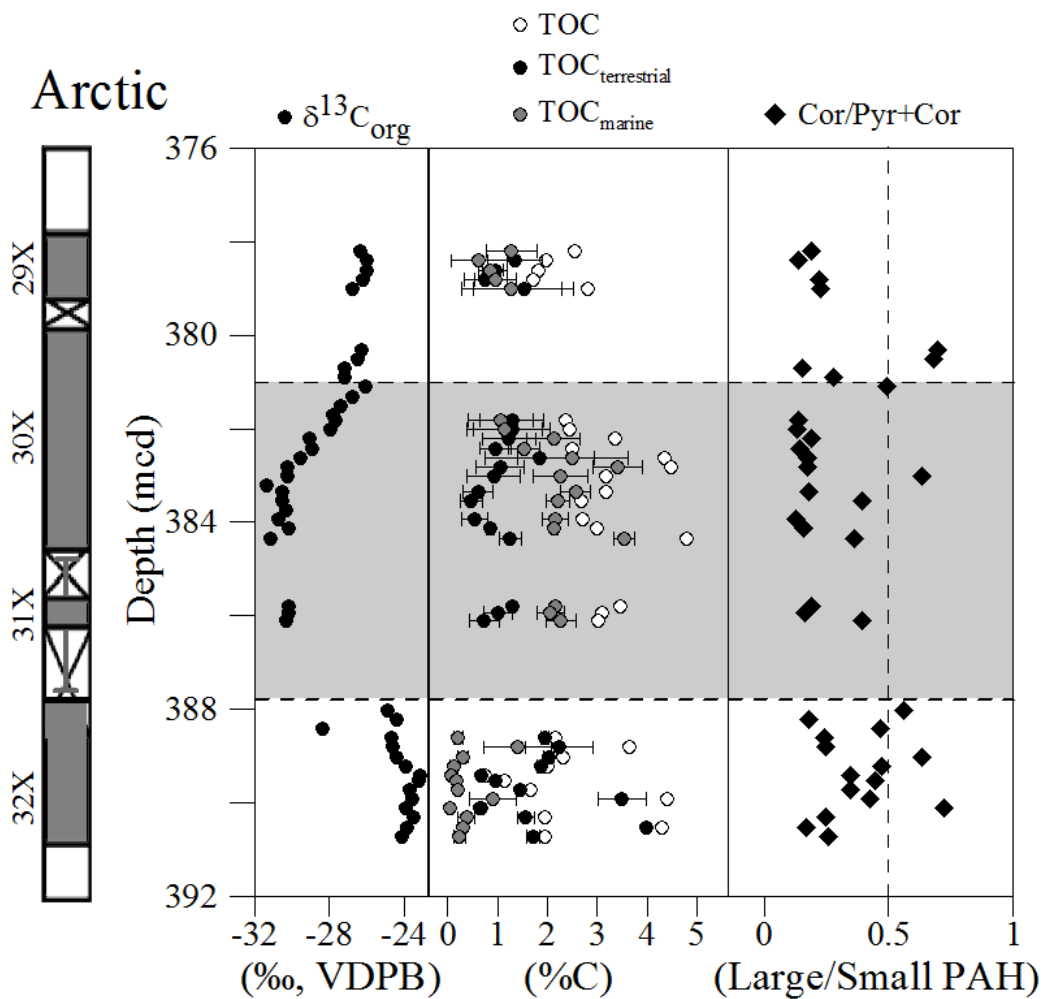
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Supplemental Figures

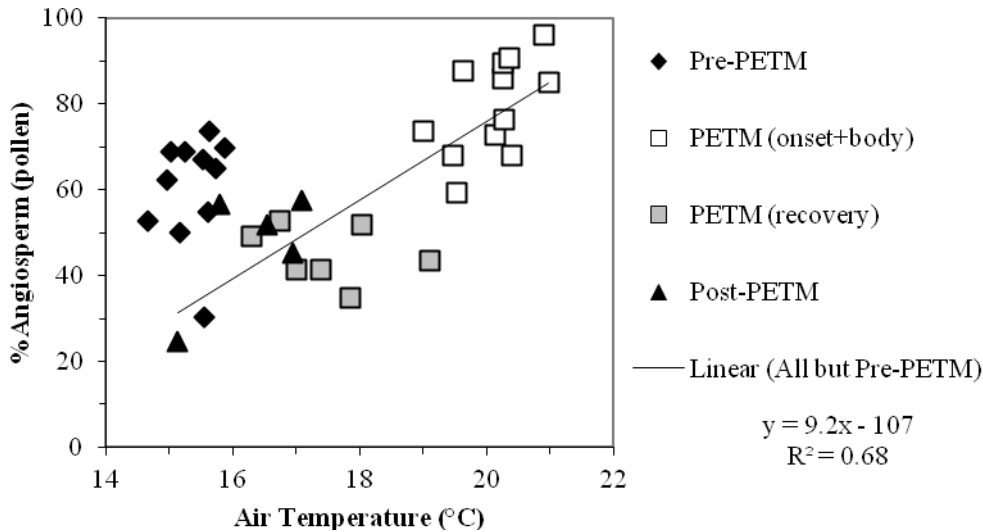


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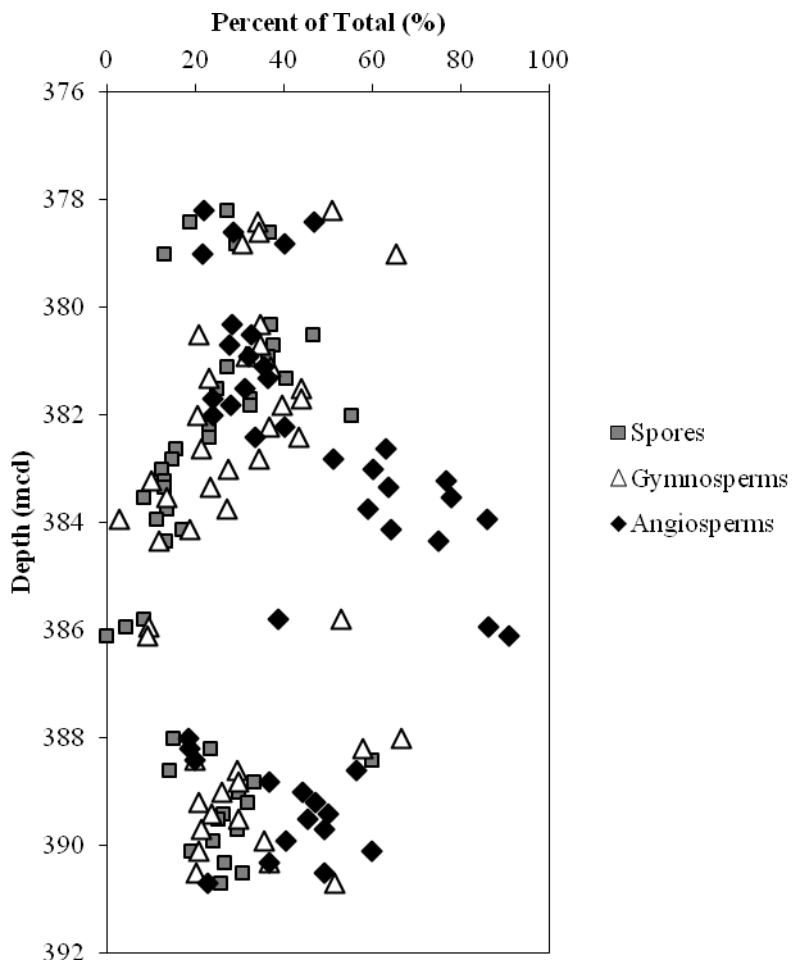
Figure S1. Depth profile from IODP Hole 302-4A of carbon isotope values, total organic carbon (TOC), and Coronene/Pyrene+Coronene ratio.

Core recovery column, where grey represents recovered core and “x” marks intervals without recovered material; error bars connected to Core 31X mark the uncertainty of its stratigraphic position (Sluijs et al., 2006). Depth profile of carbon isotope ($\delta^{13}\text{C}_{\text{org}}$; black circle), total organic

723 carbon (TOC; white circle) (from Schouten et al., 2007)), terrestrial organic carbon (TOC_{terr.};
 724 black circle); marine organic carbon (TOC_{marine}; grey circle) values, Coronene/Pyrene+Coronene
 725 ratio (black diamond) with dashed line at a ratio of 0.5. Horizontal dashed lines mark the PETM
 726 interval. Horizontal bars represent the uncertainty in TOC_{terr.} or TOC_{marine} since each was
 727 determined from an average of the BIT index and %Terrestrial Palynomorphs (from Sluijs et al.
 728 (2006)). If bar is not visible, uncertainty is less than the size of symbol.
 729



730
 731 Figure S2. Correlation of percent of angiosperms (%Angiosperm) with air temperature.
 732 Plot is based on pollen data from Sluijs et al. (2006) and air temperature (based on the MBT-
 733 CBT indices) from Weijers et al. (2007) and Peterse et al. (2012). Symbols represent: Paleocene
 734 Pre-PETM samples (solid diamond), PETM samples (square); carbon isotope excursion (CIE)
 735 onset and body (open) and CIE recovery (grey fill), Eocene Post-PETM samples (white triangle).
 736 Linear trendline for all but Pre-PETM samples (black line).
 737
 738



739
 740 Figure S3. Relative percentage of terrestrial palynomorphs by type: spores (square); angiosperms
 741 (black diamond), gymnosperms (white triangle) (data from Sluijs et al. (2006)).

Figure 1
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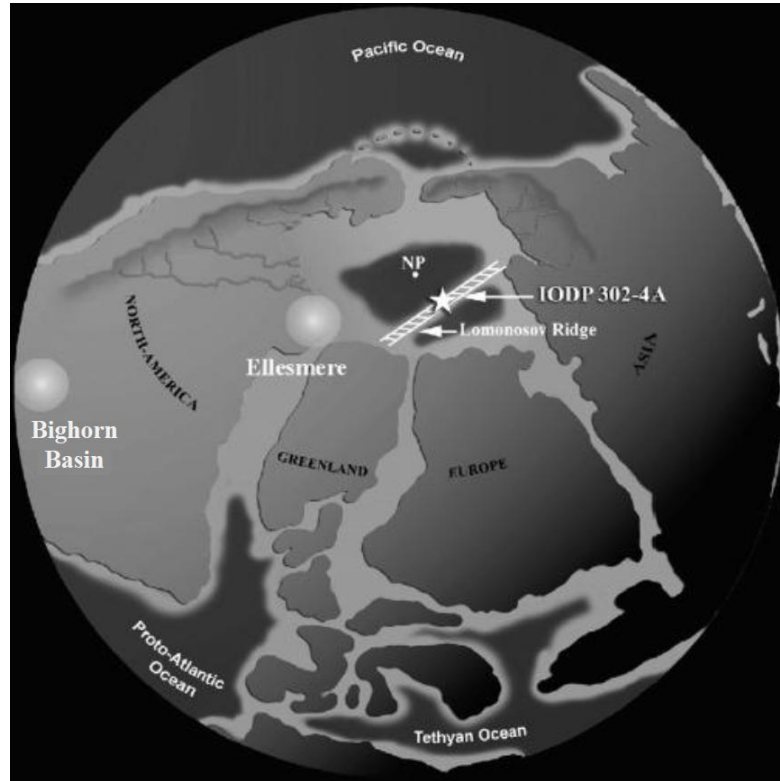


Figure 2

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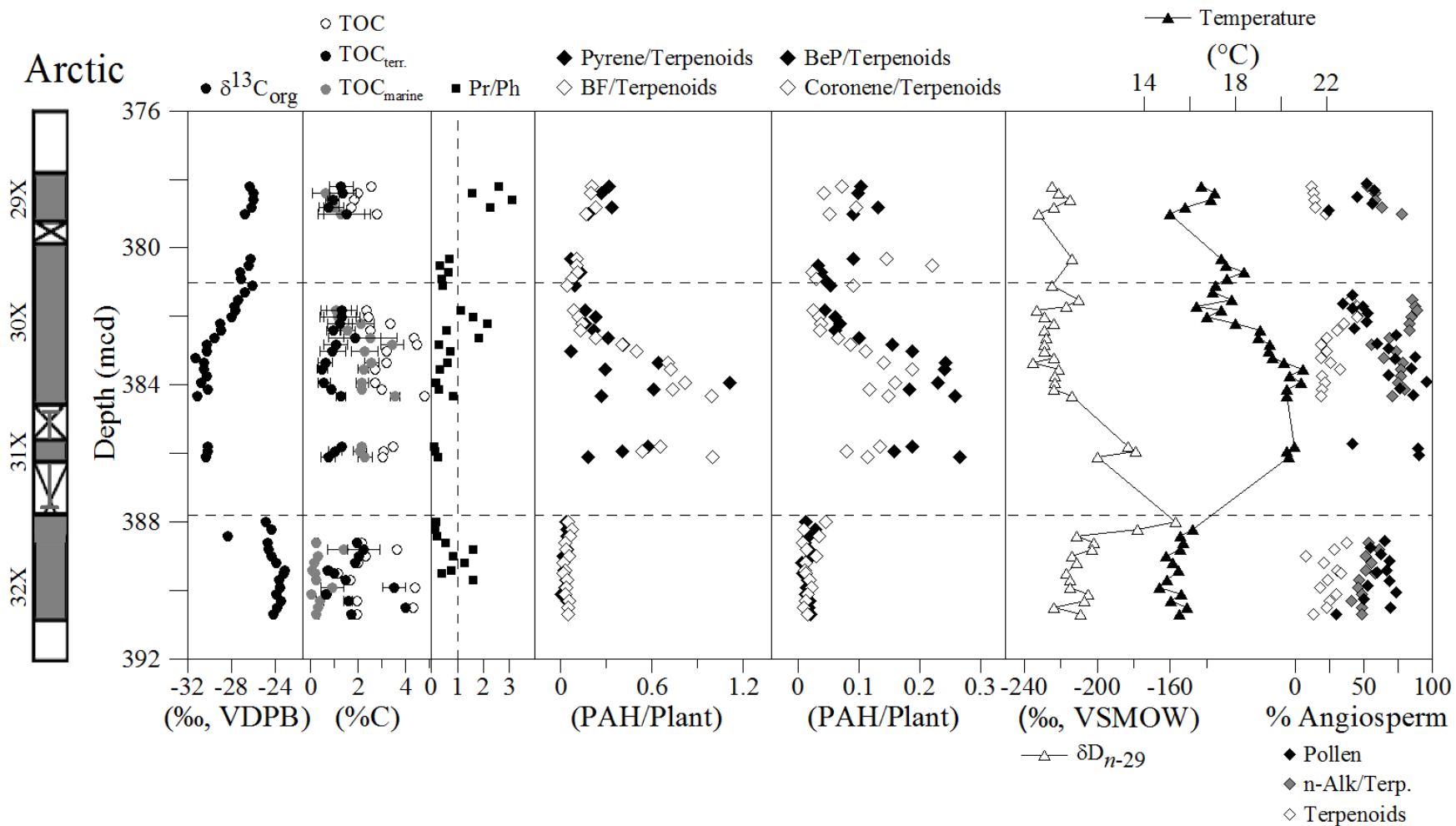
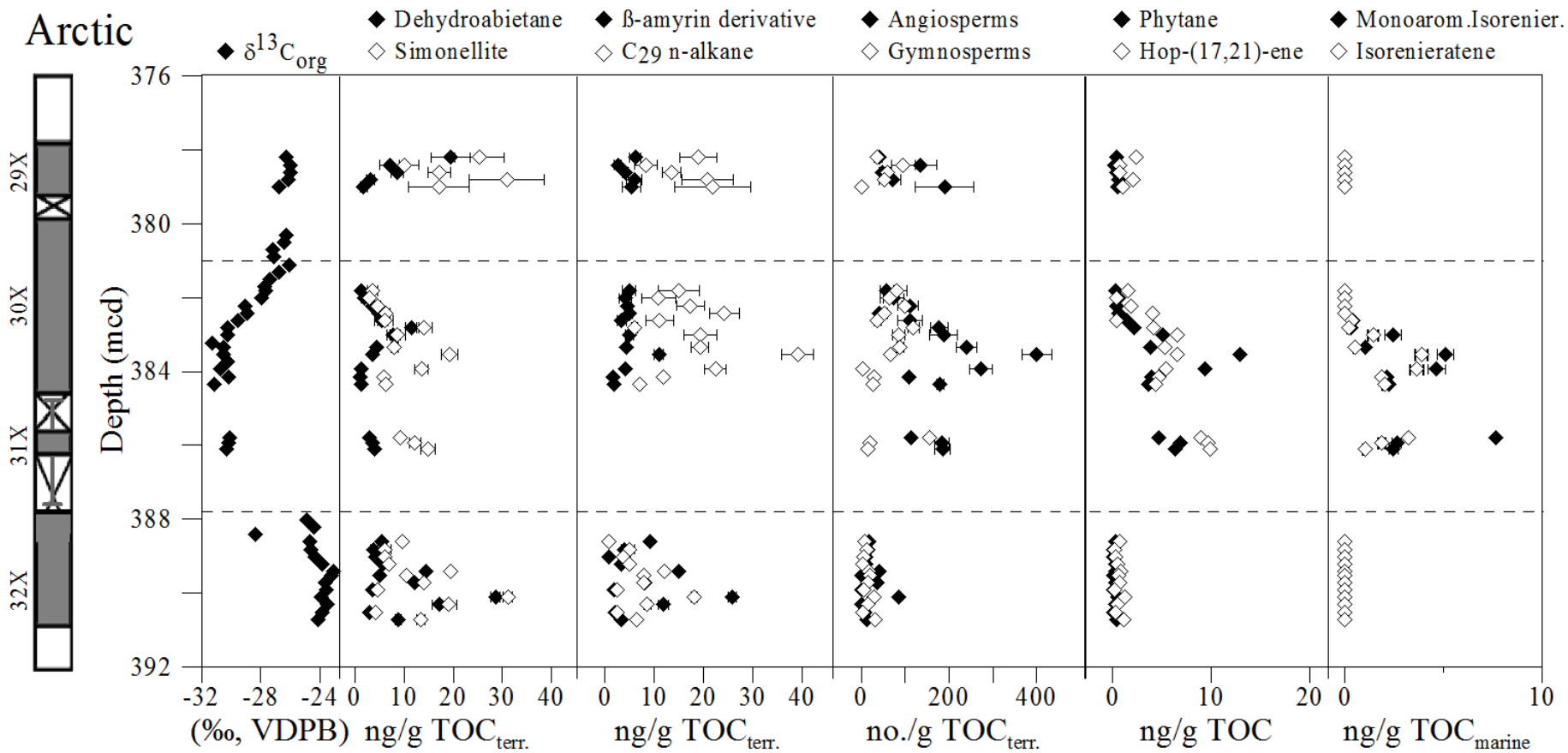


Figure 3

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