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Terrestrial environmental change across the onset of the PETM and the associated impact on biomarker proxies: a cautionary tale

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25 **Abstract:**

26 The Paleocene-Eocene Thermal Maximum (PETM; ~ 56 million years ago) is the most
27 severe carbon cycle perturbation event of the Cenozoic. Although the PETM is
28 associated with warming in both the surface (up to 8°C) and deep ocean (up to 5°C),
29 there are relatively few terrestrial temperature estimates from the onset of this interval.
30 The associated response of the hydrological cycle during the PETM is also poorly
31 constrained. Here, we use biomarker proxies (informed by models) to reconstruct
32 temperature and hydrological change within the Cobham Lignite (UK) during the latest
33 Paleocene and early PETM. Previous work at this site indicates warm terrestrial
34 temperatures during the very latest Paleocene (ca. 22-26°C). However, biomarker
35 temperature proxies imply cooling during the onset of the PETM (ca. 5-11°C cooling),
36 inconsistent with other local, regional and global evidence. This coincides with an
37 increase in pH (ca. 2 pH units with pH values > 7), enhanced waterlogging, a major
38 reduction in fires and the development of areas of open water within a peatland
39 environment. This profound change in hydrology and environment evidently biases
40 biomarker temperature proxies, including the branched GDGT paleothermometer.
41 This serves as a cautionary tale on the danger of attempting to interpret biomarker
42 proxy records without a wider understanding of their environmental context.

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47 **Keywords:** lignite, biomarkers, GDGTs, hydrology, Eocene, peat

48 **1. Introduction**

49 The Paleocene-Eocene Thermal Maximum (PETM; ca. 56 million years ago; Ma) is a
50 rapid global warming event associated with the release of ^{13}C -depleted carbon into
51 the ocean-atmosphere system. During the PETM, the deep ocean warmed by $\sim 5^\circ\text{C}$
52 (Tripathi and Elderfield, 2005; Zachos et al., 2008) while sea surface temperatures
53 increased by up to 8°C (Aze et al., 2014; Frieling et al., 2017; Frieling et al., 2014;
54 Schoon et al., 2015; Sluijs et al., 2011; Sluijs et al., 2006; Sluijs et al., 2014; Zachos
55 et al., 2006). During the same interval, continental temperatures increased significantly
56 (ca. 4 to 7°C) (Fricke and Wing, 2004; Gehler et al., 2016; Secord et al., 2010; Wing
57 et al., 2005). There is other evidence for increasing terrestrial temperatures during the
58 PETM, including floral turnover (Schouten et al., 2007; Wing et al., 2005), enhanced
59 insect herbivory (Currano et al., 2008) and mammalian (Secord et al., 2012) and soil
60 faunal dwarfing (Smith et al., 2009). However, our understanding of continental
61 temperature change during the PETM remains restricted to a few, well-sampled
62 regions (primarily western North America), and additional records are required to fully
63 evaluate climate model simulations.

64 Continental temperatures are also important because they exert a first-order
65 control upon the hydrological cycle. During the PETM, the hydrological cycle broadly
66 exhibits a globally 'wet-wetter, dry-drier' style response (Carmichael et al., 2017).
67 However, there can be significant regional and temporal variability in both proxy and
68 model data. For example, high-latitude and coastal settings are generally
69 characterised by stable and/or increasing rainfall (Carmichael et al., 2017), with proxy
70 evidence for both enhanced terrigenous sediment flux to marginal marine sediments
71 (John et al., 2008) and enhanced chemical weathering (Dickson et al., 2015; Ravizza
72 et al., 2001). In contrast, mid-to-low latitude and continental interior settings are

73 typically characterised by decreasing rainfall (Carmichael et al., 2017) but an increase
74 in extreme precipitation rates (Carmichael et al., 2018; Handley et al., 2012; Schmitz
75 and Pujalte, 2007). Perturbations to the hydrological cycle also impacted vegetation
76 patterns (Collinson et al., 2009; Jaramillo et al., 2010) and various biogeochemical
77 cycles (e.g. methane cycling; Pancost et al., 2007), potentially playing an important
78 role in maintaining the warmth of the PETM (Zachos et al., 2008) and in the
79 subsequent recovery phase (Gutjahr et al., 2017).

80 To reconstruct temperature and hydrological change during the PETM, we
81 investigate the biomarker distributions within an immature lignite seam from Cobham,
82 Kent, UK (~48°N palaeolatitude). The Cobham Lignite Bed is inferred to represent an
83 ancient continental mire system and is characterised by a negative carbon isotope
84 excursion characteristic at the PETM onset (Collinson et al., 2003; Pancost et al.,
85 2007; see Collinson et al., 2009 for details on age model). We consider our new results
86 in the context of previously published indicators of vegetation and hydrological change
87 (Collinson et al., 2003; Steart et al., 2007; Collinson et al., 2009; Collinson et al., 2013)
88 and new climate model simulations to develop a holistic and nuanced understanding
89 of paleoenvironmental change in northern Europe across the onset and during the
90 early PETM. Our results refine the understanding of environmental change at this site
91 and serve as a cautionary tale on interpreting biomarker proxies without a wider
92 understanding of their environmental context.

93

94 **2. Methods**

95 **2.1. Sample site**

96 The Cobham Lignite Bed was deposited in a low-lying freshwater setting very near
97 sea-level (~48 °N palaeolatitude). The Cobham Lignite Bed is underlain by a sand and
98 mud unit (shallow marine; S&M). It comprises a thin clay layer (<10 cm) at the base,
99 overlain, in succession, by a charcoal-rich lower laminated lignite (ca. 43 cm thick;
100 lower LL), a charcoal-poor upper laminated lignite (ca. 2 cm thick; upper LL), a middle
101 clay layer (MCL < 10 cm thick) and a charcoal-poor blocky lignite (ca. 130 cm thick;
102 BL). The Woolwich Shell Beds (marginal marine/lagoonal, containing the
103 *Apectodinium* acme; WSB) overly the Cobham Lignite (Collinson et. al. 2009).

104

105 2.1.1. Age control

106 The Cobham Lignite Bed is underlain by the Upnor Formation, which at a nearby site
107 is dated as latest Palaeocene by means of the occurrence of calcareous
108 nannoplankton zone NP9 and magnetochron C25n in its lower part (Collinson et al.,
109 2009). A negative carbon isotope excursion (CIE) of ~ 1.5 ‰ is present near the top
110 of the charcoal-poor upper laminated lignite (54.45 cm), slightly below the middle clay
111 layer. This is interpreted as being the negative CIE characteristic of the PETM
112 (Collinson et al., 2003; 2007; 2009). As such, we interpret the uppermost laminated
113 lignite (54.45 to 57.6cm), middle clay layer (57.6 to 65.3 cm) and blocky lignite (65.3
114 to 194.8 cm) to reflect PETM age. Based on peat to lignite compaction ratios, the
115 blocky lignite (65.3 to 194.8 cm) is likely to have accumulated as peat during 4–12 kyr
116 (range 1–42 kyr) (Collinson et al., 2009) and thus represents only the early part of the
117 PETM. The shallow-marine Woolwich Formation, which overlies the Cobham Lignite
118 Bed at Cobham, contains the *Apectodinium* acme indicating that it is also within the
119 PETM. For a full description of the stratigraphy, see Collinson et al. (2009).

120

121 2.2. Organic Geochemistry

122 The current study utilised aliquots of total lipid extract (TLE) originally prepared
123 by Pancost et al. (2007) and which had been stored dry and frozen (-20 °C). We focus
124 here exclusively on the lignite sediments (see Supplementary Information). Briefly,
125 the powdered samples were extracted by sonication with a sequence of increasingly
126 polar solvents (four times with dichloromethane (DCM), four times with
127 DCM/methanol (MeOH) (1:1, v/v), and three times with MeOH). The total lipid
128 extracts were separated into three fractions using a column packed with (activated)
129 alumina by elution with hexane (apolar fraction), hexane/DCM (9:1 v/v), and
130 DCM/MeOH (1:2 v/v; polar fraction). The polar fraction, containing the GDGTs, was
131 dissolved in hexane/*iso*-propanol (99:1, v/v) and passed through a 0.45 µm PTFE filter.

132 Apolar fractions were analysed using a Thermoquest Finnigan Trace GC
133 interfaced to a Thermoquest Finnigan Trace MS. This was achieved using a fused
134 silica capillary column (50 m × 0.32 mm) coated with CP-Sil-5 (film thickness
135 0.12 µm) and via the following temperature programme: 40 °C to 140 °C at
136 20 °C min⁻¹, then to 300 °C at 4 °C min⁻¹, maintained at 300 °C for 22 min. Polar
137 fractions were analysed by high performance liquid chromatography/atmospheric
138 pressure chemical ionisation – mass spectrometry (HPLC/APCI-MS). Samples were
139 analysed following Hopmans et al. (2016). Normal phase separation was achieved
140 using two Waters Acquity UPLC BEH HILIC columns (2.1 x 150 mm; 1.7 µm i.d.) with a
141 flow rate of 0.2 ml min⁻¹. Samples were eluted isocratically with 78% A and 18% B for
142 25 min followed by a linear gradient to 35% B over 25 minutes, then a linear gradient
143 to 100% B in 30 minutes, where A = hexane and B = hexane:IPA (9:1, v/v) (Hopmans
144 et al., 2016). Injection volume was 15 µL, typically from 100 µL. Analyses were

145 performed using selective ion monitoring mode (SIM) to increase sensitivity and
146 reproducibility (m/z 1302, 1300, 1298, 1296, 1294, 1292, 1050, 1048, 1046, 1036,
147 1034, 1032, 1022, 1020, 1018, 744, and 653).

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149 2.3. Biomarker proxies

150 2.3.1. Biomarker-based temperature proxies

151 Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are membrane lipids
152 produced by Bacteria (likely Acidobacteria; Sinninghe Damsté et al., 2018). The
153 distribution of brGDGTs in peats is influenced by mean annual near-surface air
154 temperature (MAAT), with the degree of methylation decreasing as temperature
155 increases (Weijers et al., 2007; Naafs et al., 2017). This is represented by the
156 methylation of branched tetraether (MBT'_{5ME}) index (De Jonge et al., 2014):

$$157 \quad (1) \text{MBT}'_{5ME} = (Ia + Ib + Ic)/(Ia + Ib + Ic + IIa + IIb + IIc + IIIa)$$

158 For application to peats and lignites, MBT'_{5ME} is translated to MAAT using the peat-
159 specific calibration (Naafs et al., 2017):

$$160 \quad (2) \text{MAAT}_{\text{peat}} = 52.18 * \text{MBT}'_{5ME} - 23.05 \quad (n = 96, r^2 = 0.76; \text{RMSE} = 4.7^\circ\text{C})$$

161 Roman numerals refer to individual GDGT structures shown in the Supplementary
162 Information (Figure S1). In brief, I, II and III represent the tetra-, penta- and
163 hexamethylated components, respectively, and a, b and c represent the brGDGTs
164 bearing 0, 1 or 2 cyclopentane moieties. Penta- and hexamethylated brGDGTs can be
165 methylated at the C-5 position or C-6 position on the alkyl chain. The latter are
166 indicated by an apostrophe (e.g. IIa' – see equation (8)). Note that samples from the

167 lower laminated lignite (i.e. pre-PETM; n = 7) were previously analysed for branched
168 GDGTs. For more details, see Naafs et al., (2018b).

169 We also calculate the degree of methylation of brGDGTs with no cyclopentane
170 moieties. This is represented in the MBT_{acyclic} index (Naafs et al., 2018a):

$$171 \quad (3) \text{ MBT}_{\text{acyclic}} = (Ia) / ([Ia] + [IIa] + [IIa'] + [IIIa] + [IIIa'])$$

172 Recent work has demonstrated that the distribution of bacterial-derived branched
173 glycerol monoalkyl glycerol tetraethers (brGMGTs) in peat can also be influenced by
174 MAAT, with the degree of methylation decreasing as temperature increases (Naafs et
175 al., 2018a). This is represented in the H-MBT_{acyclic} index:

$$176 \quad (4) \text{ H-MBT}_{\text{acyclic}} = (\text{H-Ia}) / ([\text{H-Ia}] + [\text{H-IIa}] + [\text{H-IIIa}])$$

177 In addition to brGDGTs and brGMGTs produced by Bacteria, peats also contain a
178 wide variety of isoprenoidal (iso)GDGTs, produced by Archaea (Weijers et al., 2004).
179 Of these compounds, isoGDGT-5 occurs exclusively within acidic (pH < 5.1) tropical
180 (> 19°C) peats (Naafs et al., 2018b). The relative abundance of isoGDGT-5 is
181 represented using the following index:

$$182 \quad (5) \% \text{GDGT-5} = (\text{isoGDGT-5}) / (\text{isoGDGT-1} + \text{isoGDGT-2} + \text{isoGDGT-3} + \\ 183 \quad \text{isoGDGT-5})$$

184 %GDGT-5 values > 1% are only found in peats with both a MAAT > 19.5°C and pH <
185 5.1. isoGDGT-4 is excluded from this ratio due to co-elution with crenarchaeol. Note
186 that samples from the lower laminated lignite (i.e. pre-PETM; n = 7) were previously
187 analysed for isoGDGT-5. For more details, see Naafs et al., (2018b).

188 *2.3.2. Biomarker-based pH proxies*

189 In addition to temperature, the distribution of brGDGTs can also be influenced by other
190 environmental parameters, such as pH. For instance, both 5- and 6-methyl brGDGTs
191 are more abundant at higher pH (De Jonge et al., 2014). This is represented by a
192 modified version of the cyclisation of branched tetraether (CBT) index (Naafs et al.,
193 2017):

$$194 \quad (6) \text{ CBT}_{\text{peat}} = \log(\text{Ib} + \text{IIa}' + \text{IIb} + \text{IIb}' + \text{IIIa}') / (\text{Ia} + \text{IIa} + \text{IIIa})$$

195 CBT_{peat} is translated to peat pH using the following equation (Naafs et al., 2017):

$$196 \quad (7) \text{ pH} = 2.49 * \text{CBT}_{\text{peat}} + 8.07 \quad (n = 51; r^2 = 0.58; \text{RMSE} = 0.8)$$

197 6-methyl brGDGTs are also more abundant at higher pH (De Jonge et al., 2014; Yang
198 et al., 2015), represented by the IR6_{ME} index (Yang et al., 2015):

$$199 \quad (8) \text{ IR6}_{\text{ME}} = (\text{IIa}' + \text{IIb}' + \text{IIc}' + \text{IIIa}' + \text{IIIb}' + \text{IIIc}') / (\text{IIa} + \text{IIa}' + \text{IIb} + \text{IIb}' + \text{IIc} + \text{IIc}' + \\ 200 \quad \text{IIIa} + \text{IIIa}' + \text{IIIb} + \text{IIIb}' + \text{IIIc} + \text{IIIc}')$$

201 Peat pH can also be reconstructed using the isomerisation of bacterial-derived
202 hopanoids (C_{31} hopane $\beta\beta/(\beta\beta+\alpha\beta)$; Pancost et al., 2003). This index is translated to
203 pH using the following equation (Inglis et al., 2018):

$$204 \quad (9) \text{ pH} = 5.22 * (\text{C}_{31} \text{ hopane } \beta\beta/(\beta\beta+\alpha\beta)) + 3.11 \quad (n = 94, r^2 = 0.64; \text{RMSE} = 1.4)$$

205 2.4. Modelling simulations

206 Temperature and precipitation estimates were obtained for the Early Eocene
207 (Ypresian) from an ensemble of coupled atmosphere–ocean GCMs. These
208 simulations include the EoMIP ensemble (Lunt et al., 2012), but also more recent
209 simulations (Inglis et al., 2017; Kiehl and Shields, 2013; Sagoo et al., 2013) (Table 1).

210 We also generate new temperature and precipitation estimates using a revised
211 version of HadCM3L, HadCM3L-I2 (Table 1). Using the nomenclature of Valdes et al.
212 (2017) these new model simulations are carried out using the HadCM3L-M2.1aD
213 version of the model. The boundary conditions (paleogeography, solar forcing, orbit)
214 representing the Ypresian are the same as in Lunt et al. (2016) but with modifications
215 made to the ozone distribution such that it more closely reproduces modern ozone
216 and consequently surface air temperature values when run under modern conditions.
217 A dynamic vegetation model, TRIFFID (Top-down Representation of Interactive
218 Foliage and Flora Including Dynamics; Cox, et al. 1998), was utilized alongside the
219 MOSES 2.1 land surface scheme (Cox, et al. 1999). This allows a stage specific,
220 realistic representation of vegetation patterns and feedbacks on the climate system.
221 These new simulations were initialised from a previous fully equilibrated (10,422
222 model years), 2x preindustrial CO₂ run of the Ypresian (Farnsworth et al., 2019). One
223 simulation was kept constant at 2x preindustrial CO₂ for 1,000 model years, while the
224 second experiment used 6x preindustrial CO₂ for 1,000 model years. A mean of the
225 last 50 years is used to produce the reported climatologies from both simulations. To
226 study changes in the occurrence of extreme events, we also include the simulations
227 by Carmichael et al. (2018) (HadCM3L-C; Table 1). Those simulations are performed
228 with atmospheric CO₂ at 2x and 4x preindustrial concentrations. However, unlike other
229 HadCM3L simulations, precipitation rates were recorded at every model hour for the
230 99-year run. Within the simulated palaeogeography, the nearest land point to the
231 Cobham locality was identified using the Getech Plc. plate model at the mid-point of
232 the appropriate geological stage (mid-Ypresian), which is consistent with the
233 paleogeographies used in HadCM3L-I and HadCM3L-V simulations.

Simulation	CO ₂ (relative to pre-industrial)	Reference
HadCM3L	x2, x4, x6	Lunt et al. (2012)
HadCM3L-I	x2, x4	Inglis et al. (2017)
HadCM3L-I2	x2, x6	<i>This paper</i>
HadCM3L-C	x2, x4	Carmichael et al., (2018)
HadCM3L-V	x6	Inglis et al. (2017)
ECHAM	x2	Heinemann et al. (2009)
CCSM3W	x4, x8, x16	Winguth et al. (2010; 2012)
CCSM3H	x2, x4, x8, x16	Huber and Caballero (2011)
CCSM3K	x5	Kiehl and Shields (2013)
GISS	x4, x8, x16	Roberts et al. (2009)
FAMOUS-1	x2	Sagoo et al. (2013)
FAMOUS-2	x2	Sagoo et al. (2013)

234 **Table 1:** Summary of model simulations. See the supplementary information and
235 original references for more details

236

237 **3. Results**

238 3.1. Biomarker distributions in Cobham lignite sediments

239 The branched GDGT (brGDGT) distribution within the lower laminated lignite (4.65 to
240 43.3 cm) is dominated by tetramethylated brGDGTs (average: 90% of the total
241 brGDGT assemblage; Fig. 1a). Within the upper laminated lignite (54.15 to 55.9 cm),
242 the relative abundance of tetramethylated brGDGTs decreases (average: 78 % of the
243 total brGDGT assemblage). The relative abundance of tetramethylated brGDGTs
244 decreases further within the blocky lignite (average: 65% of the total brGDGT
245 assemblage; 67.5 to 194.8 cm).

246 The isoprenoidal GDGT (isoGDGT) distribution within the lower laminated
247 lignite (4.65 to 43.3 cm) is dominated by GDGTs with 0 to 5 cyclopentane moieties,
248 and the abundance of isoGDGT-5 is high (average %GDGT-5: 3.0%). Within the upper
249 laminated lignite (54.15 to 55.9 cm), the abundance of isoGDGT-5 is slightly lower

250 (average %GDGT-5: 2.3%). Within the blocky lignite (67.5 to 194.8 cm), isoGDGT-5
251 is typically absent (although there are exceptions; e.g. 121.9cm) and the relative
252 abundance of isoGDGT-0 increases significantly (average: 80% of total isoGDGT
253 assemblage).

254 The Cobham lignite also contains recently identified branched and isoprenoidal
255 glycerol monoalkyl glycerol tetraethers (brGMGTs and isoGMGTs, respectively; Naafs
256 et al., 2018a). The isoGMGT distribution is dominated by isoGMGT-0 throughout (*m/z*
257 1300; average: 95 % of the total isoGMGT assemblage). The brGMGT distribution
258 within the lower laminated lignite (4.65 to 43.3 cm) is dominated by brGMGT-1a (*m/z*
259 1020; average: 85 % of the total brGMGT assemblage; Fig. 1a). Within the upper
260 laminated lignite (54.15 to 55.9 cm), the relative abundance of brGMGT-1a decreases
261 (average: 75 % of the total brGMGT assemblage). The relative abundance of
262 brGMGT-1a decreases further within the blocky lignite (average: 65% of the total
263 brGMGT assemblage; 67.5 to 194.8 cm).

264 The Cobham lignite also contains a range of bacterial-derived C₂₇–C₃₂ hopanes
265 and C₂₇–C₃₀ hopenes (see Pancost et al., 2007 for full details). The hopanoid
266 distribution within the lower laminated lignite (4.65 to 43.3 cm) is dominated by the
267 (22R)-17 α ,21 β (H)-homohopane (C₃₁) (average: 31% of total hopanoid assemblage).
268 This is one of the most abundant hopanoids in modern peats and typically dominates
269 the hopane distribution within acidic, ombrotrophic bogs (Inglis et al., 2018). The
270 relative abundance of the (22R)-17 α ,21 β (H)-homohopane (C₃₁) decreases within the
271 upper laminated lignite (average: 15% of total hopanoid assemblage) and the blocky
272 lignite (average: 5% of total hopanoid assemblage).

273

274 3.2. MAAT and pH trends in the Cobham Lignite inferred from biomarker proxies

275 Branched GDGT-derived MAAT estimates from the lower laminated lignite (4.65 to
276 43.3 cm) are relatively stable and range between ca. 22 and 26 °C (average: 24°C;
277 Naafs et al., 2018b; Fig. 2). Lower MAAT estimates are observed within the upper
278 laminated lignite and blocky lignite. However, see Section 4.1 and 4.2 for further
279 discussion on the validity of these results. CBT_{peat} and C_{31} hopane $\beta\beta/(\beta\beta+\alpha\beta)$ -derived
280 pH estimates from the lower laminated lignite (4.65 to 43.3 cm) are relatively low
281 (average: 5.3 and 4.4 pH units, respectively; Fig. 3a-b). Both pH estimates increase
282 slightly in the upper laminated lignite (average: 6.0 and 4.6 pH units, respectively; Fig.
283 3a-b), and then increase further within the blocky lignite (average: 6.8 and 6.3 pH units,
284 respectively; Fig. 3a-b).

285

286 **4. Discussion**

287 *4.1. Biomarker-derived temperature estimates across the onset of the PETM*

288 Branched GDGT-derived MAAT estimates from the lower laminated lignite pre-PETM
289 interval (i.e. 4.65 to 54.15 cm) indicate warm terrestrial temperatures (ca. 22 to 26°C;
290 average: 24°C; Naafs et al., 2018b; Fig. 2). Naafs et al., (2018b) also identified the
291 occurrence of isoGDGTs with > 5 cyclopentane moieties during the pre-PETM interval,
292 indicating minimum MAAT estimates of 19°C. High H-MBT_{acyclic} values within the lower
293 laminated lignite (4.65 to 54.15 cm) would also imply elevated terrestrial temperatures
294 (Naafs et al., 2018a). Our biomarker-based temperature estimates agree with MAAT
295 estimates for the Cobham region simulated by climate model simulations run at high
296 CO₂ concentrations (e.g. CCSM3-H 8x and 16x PI; CCSM3-W 16x PI; Figure 4a;
297 Table 1). They also agree with climate model simulations which have modified
298 specific model parameters (e.g. CCSM3-K 5x PI, HadCM3L-V 6x PI, FAMOUS-1 2x

299 PI; Figure 4a). The latter are in close agreement with existing proxy-based CO₂
300 estimates for the PETM (Hollis et al., 2019).

301 Branched GDGT-derived MAAT estimates decrease within the PETM-aged
302 upper laminated lignite (54.45 to 55.9 cm) and blocky lignite (67.5 to 194.8 cm),
303 indicating lower terrestrial temperatures at the onset and during the early PETM (ca.
304 11 to 20°C; average: 15°C; Fig. 2). The PETM-aged blocky lignite (67.5 to 194.8 cm)
305 also contains a lower abundance of isoGDGT-5 (Fig. 2d; but see pH discussion below;
306 section 4.2.3) and lower H-MBT_{acyclic} values (Fig. 2c), both suggesting lower
307 temperatures. Although the absolute temperature estimates agree with MAAT
308 estimates for this region derived from climate model simulations run at lower CO₂
309 concentrations (e.g. HadCM3L 2x and 4x PI; ECHAM 2x PI; CCSM3-H 2x and 4x
310 PI, GISS 4x PI; Figure 4a) or that have modified specific model parameters (e.g.
311 HadCM3L-I2 x2 and x6 PI; FAMOUS-2 x2 PI; Figure 4a), for all model simulations in
312 our ensemble with more than one CO₂ concentration (Table 1; Supplementary
313 Information), there is warming at the Cobham location as CO₂ increases.

314 Decreasing terrestrial temperatures in the upper laminated lignite and the
315 blocky lignite are inconsistent with the presence of the *Apectodinium* acme throughout
316 the overlying Woolwich Shell Beds and the short accumulation time estimated for the
317 BL, both of which suggest that the blocky lignite accumulated as peat during the early
318 part of the PETM (Collinson et al 2009). Lower temperatures are also inconsistent with
319 increasing palm pollen in some BL samples (Collinson et al., 2009). Decreasing
320 temperatures are also at odds with the regional response, with proxy evidence for
321 increasing terrestrial temperatures in northern Europe during the PETM (up to 6°C;
322 Schoon et al., 2015). The marine realm also indicates increasing temperatures in
323 northern Europe during the PETM, with evidence for 3 to 4°C of surface ocean

324 warming in both the Bay of Biscay (Bornemann et al., 2014) and the North Sea
325 (Schoon et al., 2015). Decreasing terrestrial temperatures also differ from the global
326 response during the PETM (Hollis et al., 2019; Jones et al., 2013; McInerney and
327 Wing, 2011). Collectively, this implies that the biomarker-based paleotemperature
328 proxies in the upper laminated lignite and blocky lignite are impacted by non-thermal
329 influences or ecological signals; below we explore what these controls could be.

330

331 *4.2. Exploring additional controls upon peat-specific biomarker temperature proxies*

332 4.2.1. Vegetation

333 The lower laminated lignite (pre-PETM) is dominated by fern spores and is rich in
334 charcoal, including fern leaf stalks, all of which were interpreted to indicate a fire-
335 prone, low-diversity vegetation (Collinson et al., 2009). In contrast, the upper
336 laminated lignite and blocky lignite (PETM) are characterised by the reduction then
337 loss of ferns and charcoal, an increase in wetland plants (including cupressaceous
338 conifers) and a more varied flowering plant community with palms and eudicots.
339 Although it has been previously argued that changes in vegetation could have
340 influenced the distribution of brGDGTs in peatlands (e.g. Weijers et al., 2011), this was
341 later attributed to the overly strong pH correction on the MBT/CBT proxy (Inglis et al.,
342 2017). Indeed, recent studies within modern peatlands (Naafs et al., 2017; Naafs et
343 al., 2019) and ancient lignites (Inglis et al., 2017) have indicated that vegetation
344 change is less of a concern than originally inferred by Weijers et al. (2011). As such,
345 we argue that, although there is vegetation change, it is unlikely to have exerted a
346 primary control upon biomarker paleotemperature proxies in the Cobham Lignite.

347

348 4.2.2. Lithofacies

349 The Cobham Lignite Bed is characterised by two different lithofacies (laminated vs
350 blocky lignite). The laminated lignite is characterised by repeated (episodic) deposition
351 of charcoal (mostly from local sources, via run-off related local transport; Steart et al.,
352 2007), whereas the overlying blocky lignite is dominated by continuous deposition of
353 non-woody material in a persistent peat-forming environment (Steart et al., 2007).
354 Whilst previous studies have noted subtle differences in brGDGT distributions (and
355 therefore, MAAT estimates; up to 4°C) between different lithofacies (e.g. lignite vs
356 shallow marine sediments; Inglis et al., 2017), a decline in biomarker-based
357 temperature estimates within the Cobham Lignite Bed occurs within the upper
358 laminated lignite (54 to 56 cm; Figure 2) and prior to changes in lithofacies. Therefore,
359 lithofacies are not a primary control upon biomarker paleotemperature proxies in the
360 Cobham Lignite.

361

362 4.2.3. pH, hydrology and presence of open water areas

363 Within the Cobham Lignite Bed, we reconstruct pH using two independent, peat-
364 specific pH proxies: 1) CBT_{peat} , based upon the cyclisation of brGDGTs (Naafs et al.,
365 2017), and 2) the C_{31} hopane $\beta\beta/(\alpha\beta+\beta\beta)$ index, based upon the isomerisation of C_{31}
366 hopanes (Inglis et al., 2018). Within the lower laminated lignite (pre-PETM), brGDGT-
367 and hopanoid-derived pH estimates (pH: ca. 4 to 5.5) are low and indicate acidic
368 conditions (Fig. 3). The occurrence of isoGDGT-5 (> 1%; Fig. 2d), the absence of 6-
369 methyl brGDGTs ($IR_{6ME} < 0.01$; Fig. 3c) and the dominance of the C_{31} $\alpha\beta$ hopane
370 provides additional evidence for acidic conditions within the lower laminated lignite.
371 We observe a remarkable increase in hopanoid- and brGDGT-derived pH estimates

372 within the upper laminated lignite (0.5 pH unit) and especially the blocky lignite (ca. 2
373 pH units to pH values > 7.5; Fig. 3). The upper laminated lignite and blocky lignite also
374 contain a higher abundance of pH-sensitive 6-methyl brGDGTs (average IR_{6ME}: 0.23
375 and 0.29, respectively; Fig. 3) and a lower abundance of the C₃₁ αβ hopane. This
376 indicates a profound change in the environment during the onset and early PETM and
377 provides an alternative explanation for the decrease in the abundance of isoGDGT-5
378 (see 4.1; Naafs et al., 2018b).

379 An increase in pH values within the onset and early PETM implies changes in
380 local hydrology, supported by other hydrological and botanical indicators at Cobham
381 (UK), including those discussed above. In addition, the blocky lignite is characterised
382 by an increased percentage of *Inaperturopollenites* pollen (representing swamp-
383 dwelling cupressaceous conifers) and *Sparganiaceapollenites* pollen (representing
384 marginal aquatic monocotyledonous angiosperm herbs), indicating the development
385 of waterlogged swamp environments (Collinson et al., 2009). The base of the blocky
386 lignite also includes the unusual co-occurrence of two genera of freshwater, free-
387 floating water plants, the heterosporous ferns *Salvinia* and *Azolla* (Collinson et al.,
388 2013). There is also the loss of wildfires, with both the upper laminated lignite and
389 blocky lignite having a significant reduction in, or loss of, both macroscopic and
390 microscopic charcoal (Collinson et al., 2009).

391 Taken together, the evidence indicates enhanced waterlogging during the
392 onset of the PETM and the development a persistent peatland with patches of open
393 water. The development of open water conditions is likely to be associated with the
394 input of brGDGTs from aquatic sources (as observed in lakes and ponds; e.g. Colcord
395 et al., 2015; Huguet et al., 2015; Tierney and Russell, 2009; Weber et al., 2018).
396 Aquatic brGDGTs can reflect near-bottom water temperatures (Weber et al., 2018)

397 and application of mineral soil or peat calibrations in modern lacustrine settings
398 consistently yields colder-than-predicted temperatures (up to 10°C in modern
399 systems; Tierney et al., 2010; Zink et al., 2010). The input of GGDs from aquatic
400 sources can therefore explain the apparent cooling in our brGDGT-derived
401 temperature estimates during the onset of the PETM. This also indicates that the
402 brGDGT paleothermometer in terrestrial archives should not be employed in settings
403 where major changes in pH and hydrology took place. Future work aiming to determine
404 palaeotemperatures would therefore benefit from accompanying proxy-based pH
405 reconstructions based on the distribution of hopanes (Inglis et al., 2018) or branched
406 glycerol dialkyl glycerol tetraethers (brGDGTs) (Naafs et al., 2017) or alternative
407 palaeohydrological indicators (e.g. *n*-alkane $\delta^2\text{H}$ values; Sachse et al., 2012).

408

409 4.3. A shift towards wetter conditions in northern Europe during the PETM

410 Our data – as well as previously published proxy evidence – suggest a shift towards
411 wetter conditions during the PETM at Cobham (see section 4.2). To test these
412 observations, we used the same ensemble of model simulations (see section 4.1;
413 Table 1) to investigate changes in mean annual precipitation (MAP) at Cobham (UK)
414 for two PETM-type scenarios (i.e. doubling or tripling of CO_2 ; Fig. 4b). For a tripling of
415 CO_2 , model simulations indicate stable (e.g. HadCM3L) or decreasing MAP (22%; e.g.
416 HadCM3L-I2). For a doubling of CO_2 , model simulations indicate increasing (6 to 7 %;
417 CCSM3-H, HadCM3L-C), stable (e.g. HadCM3L) or decreasing MAP (5 to 22%;
418 HadCM3L-I, CCSM3-W). Stable or decreasing MAP is inconsistent with proxy
419 evidence at Cobham. However, model simulations run at hourly resolution (i.e.
420 HadCM3L-C) also show a change in precipitation extremes at Cobham for a doubling
421 of CO_2 , with an increase in the 90th percentile storm extreme rate (+7%; HadCM3L-

422 C). This indicates an increase towards more intense rainfall events. Furthermore, an
423 increase in tail width (+28%) indicates more frequent heavy rainfall events of a given
424 size (Carmichael et al., 2018), which could induce waterlogging events. Decoupling
425 between MAP and extreme events has previously been noted for other mid-latitude
426 PETM settings (e.g. Tunisia; Carmichael et al. 2018) and should be considered in
427 future proxy-model comparisons.

428 Geochemical and botanical proxies at other sites provide evidence for
429 enhanced rainfall in northern Europe during the PETM, with evidence for an increase
430 in wetland-type environments in northern France (Garel et al., 2013) and other parts
431 of the region surrounding the North Sea (Eldrett et al., 2014; Kender et al., 2012).
432 There is also evidence for abundant low-salinity tolerant dinocysts (Sluijs et al., 2007),
433 enhanced clay mineral deposition (Bornemann et al., 2014) and isotopically-depleted
434 tooth apatite $\delta^{18}\text{O}$ values (Myhre et al., 1995) within North Sea marine sediments, all
435 of which indicate wetter conditions during the PETM. This indicates a shift towards
436 wetter conditions in northern Europe during the PETM and perhaps an increase in the
437 occurrence of extreme rainfall events (Carmichael et al., 2018). In these settings,
438 terrestrial biomarker proxies may be subject to additional controls (e.g. pH, hydrology
439 and/or the presence of open water areas) and should therefore be interpreted within
440 a multi-proxy framework.

441

442 **5. Conclusions**

443 Here we have reconstructed terrestrial paleoenvironmental change within the Cobham
444 Lignite Bed, which spans the very latest Paleocene, onset and early part of the PETM.
445 Proxies indicate high terrestrial temperatures prior to the PETM (22 to 26°C),
446 consistent with model simulations. However, inconsistent with local, regional and

447 global evidence, the biomarker proxies seem to indicate significant cooling during the
448 onset and early PETM (ca. 5 to 11°C). We attribute this to enhanced waterlogging and
449 the development of a persistent peatland with areas of open water, biasing the
450 brGDGT paleothermometer. This study implies the need for care when applying
451 biomarker-based temperature proxies in highly dynamic terrestrial environments (e.g.
452 lacustrine/mire settings). It also serves as a cautionary tale on the danger of attempting
453 to interpret wetland proxy records without a wider understanding of the environmental
454 context, especially pH and hydrology.

455 ***Acknowledgements***

456 This research was funded through the advanced ERC grant 'The Greenhouse Earth
457 System' (T-GRES. Project reference: 340923). RDP also acknowledges the Royal
458 Society Wolfson Research Merit Award and funding from the NERC. BDAN
459 acknowledges additional funding from a Royal Society Tata University Research
460 Fellowship. We thank the NERC Life Sciences Mass Spectrometry Facility (Bristol) for
461 analytical support. A.F., D.J.L. and R.D.P acknowledge funding from NERC through
462 NE/K014757/1, NE/I005722/1, NE/I005714/1, and (PJV also) NE/P013805/1. We
463 gratefully acknowledge funding to M.E.C. from NERC grant NE/J008656/1 and to
464 R.D.P. from NERC grant NE/J008591/1. M.E.C. thanks the Leverhulme Trust for
465 providing funding (Grant number F/07/537/0) and Alfred McAlpine, AMEC and
466 Channel Tunnel Rail Link for access to the Cobham site. Finally, we thank Alan
467 Haywood and two anonymous reviewers for their constructive comments.

468 **Data availability**

469 Data can be accessed via the online supporting information, via <http://www.pangaea.de/>, or from the author (email: gordon.inglis@bristol.ac.uk).

471

472 **Figure captions**

473 **Figure 1:** Fractional abundance of (a) branched GDGT and (b) isoprenoidal GDGT
474 lipids within the lower laminated lignite (pre-PETM), upper laminated lignite (PETM
475 onset) and blocky lignite (early PETM)

476 **Figure 2:** Terrestrial biomarker proxies before, across the onset and during the early
477 part of the PETM at Cobham. a) Branched GDGT-implied MAAT estimates obtained
478 via MAAT_{peat} proxy, b) MBT_{acyclic}, c) H-MBT_{acyclic} and d) %GDGT-5. Dashed line
479 corresponds to onset of CIE (54.45 cm). Note that MAAT_{peat} and %GDGT-5 estimates
480 from the charcoal-rich lower laminated lignite (i.e. pre-CIE; n = 7) were published in
481 Naafs et al. (2018).

482 **Figure 3:** Peat pH before, across the onset and during the early part of the PETM at
483 Cobham, a) C₃₁ hopane ($\beta\beta/\alpha\beta+\beta\beta$)-derived pH estimates, b) CBT_{peat}-derived pH
484 estimates, b c) IR_{6ME} (the ratio between 5- and 6-methyl brGDGTs. High values imply
485 higher pH). Dashed line corresponds to onset of CIE.

486 **Figure 4.** Model-derived mean annual surface temperature (a) and mean annual
487 precipitation (b) estimates as a function of CO₂ at Cobham (UK). Simulations represent
488 the mid-point of the most appropriate geological stage (Ypresian; 56 to 47.8 Ma). For
489 full details on each model simulation, see Supplementary Information. (For
490 interpretation of the references to color in this figure legend, the reader is referred to
491 the web version of this article.)

492

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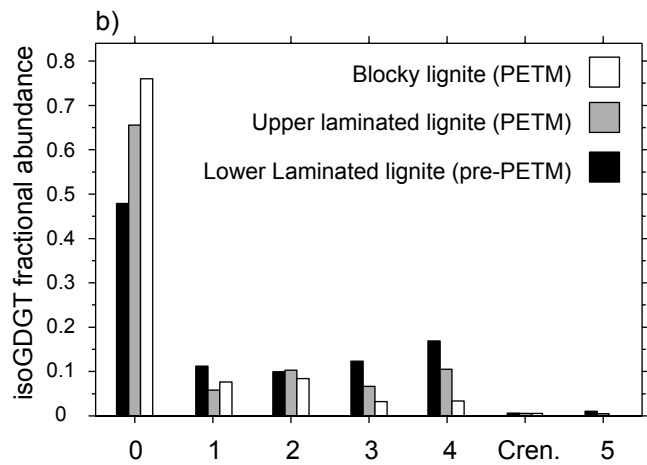
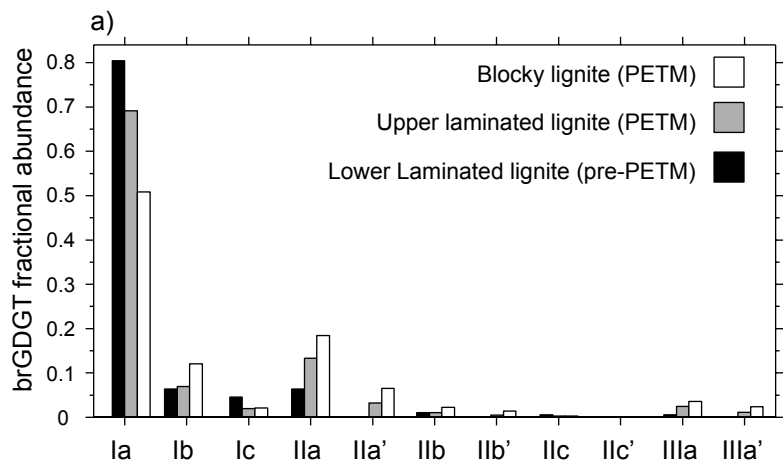
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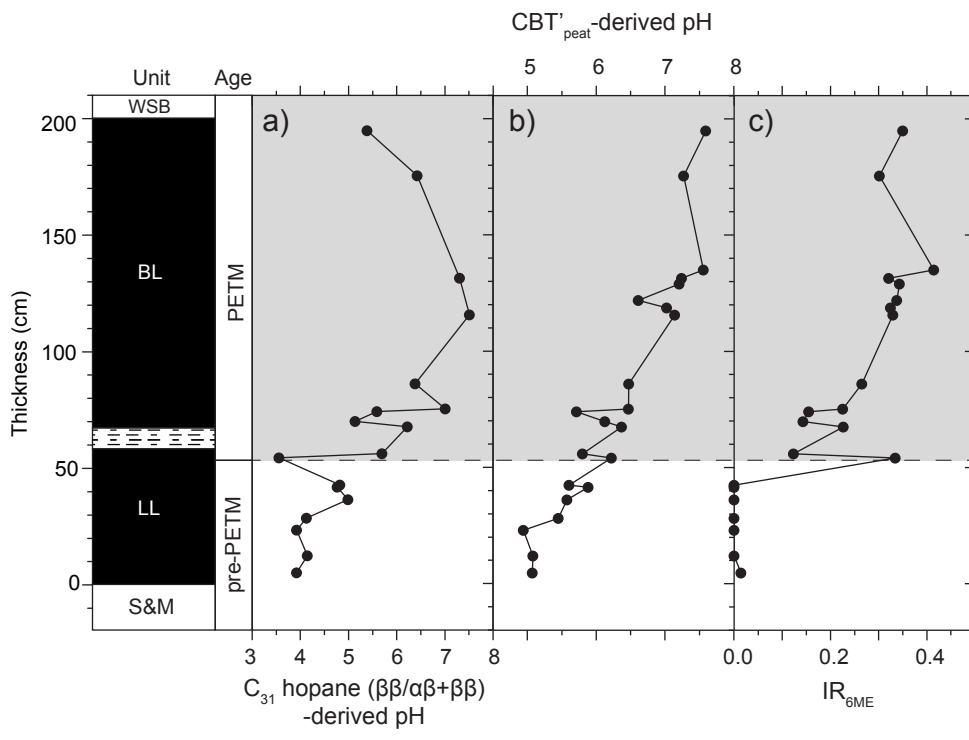
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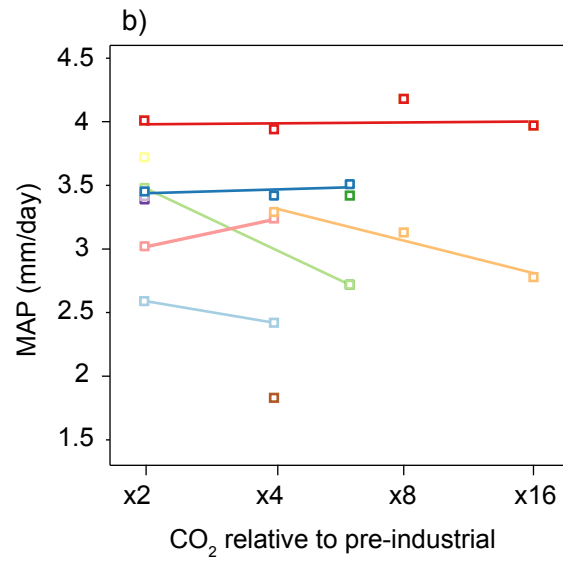
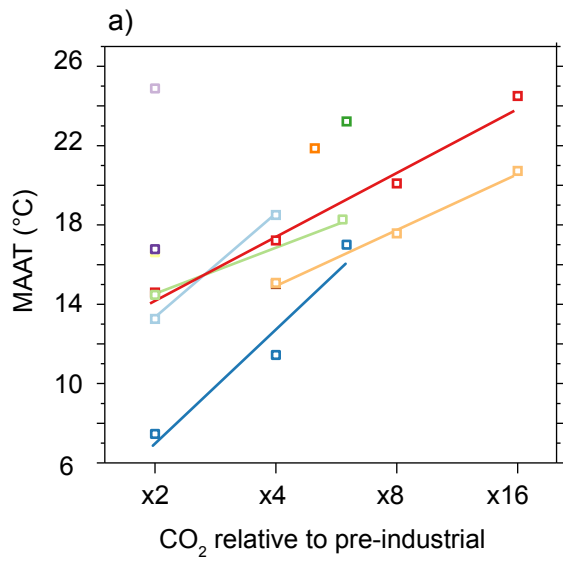
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Key:

