Late Paleocene – early Eocene Arctic Ocean Sea Surface Temperatures: reassessing biomarker paleothermometry at Lomonosov Ridge

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Abstract

A series of papers shortly following Integrated Ocean Drilling Program Arctic Coring Expedition (ACEX, 2004) on Lomonosov Ridge indicated remarkably high early Eocene sea surface temperatures (SST; ca. 23 to 27 °C) and land air temperatures (ca. 17 to 25 °C) based on the distribution of isoprenoid and branched glycerol dialkyl glycerol tetraether (isoGDGT and brGDGT) lipids, respectively. Here, we revisit these results using recent analytical developments – which have led to improved temperature calibrations and the discovery of new temperature-sensitive glycerol monoalkyl glycerol tetraethers (GMGTs) – and currently available proxy constraints.

The isoGDGT assemblages support temperature as the dominant variable controlling TEX_{86} values for most samples. However, contributions of isoGDGTs from land, which we characterize in detail, complicate TEX_{86} paleothermometry in the late Paleocene and part of the interval between the Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma) and Eocene Thermal Maximum 2 (ETM2; ~54 Ma). Background early Eocene SSTs generally exceeded 20 °C, with peak warmth during the PETM (~26 °C) and ETM2 (~27 °C). We find abundant branched GMGTs, likely dominantly marine in origin, and their distribution responds to environmental change. Further modern work is required to test to what extent temperature and other environmental factors determine their distribution.

Published Arctic vegetation reconstructions indicate coldest month mean continental air temperatures of 6-13 °C, which reinforces the question if TEX_{86}-derived SSTs in the Paleogene Arctic are skewed towards the summer season. The exact meaning of TEX_{86} in the Paleogene Arctic thus remains a fundamental issue, and one that limits our assessment of the performance of fully-coupled climate models under greenhouse conditions.

1. Introduction

The Eocene epoch (56 to 34 million years ago; Ma) has long been characterized by warm climates. The earliest signs of a balmy Eocene Arctic region – fossil leaves of numerous plant species – were documented 150 years ago (Heer, 1869). Subsequent findings identified palms, baobab and mangroves, indicating the growth of temperate rainforests and year-round frost-free conditions in the Eocene Arctic region (Schweitzer, 1980; Greenwood and Wing, 1995; Suan et al., 2017; Willard et al., 2019). Fossils of animals, including varanid lizards, tortoises and alligators also indicate warm Arctic climates (Dawson et al., 1976; Estes and Hutchinson, 1980). These earliest findings sparked interest into the climatological mechanisms allowing for such polar warmth about a century ago (Berry, 1922). Ever since, paleobotanists have focused on the Arctic plant fossils and have significantly refined their paleoclimatological interpretation towards estimates of precipitation as well as seasonal and mean annual temperature (e.g. Uhl et al., 2007; Greenwood et al., 2010; Eberle and Greenwood, 2012; Suan et al., 2017; Willard et al., 2019).

Novel insights in Paleogene Arctic paleoclimate research were made in the years following the Arctic Coring Expedition 302 (ACEX, Integrated Ocean Drilling Program (IODP) 2004, Figure 1). This expedition recovered upper Paleocene and lower Eocene siliciclastic sediments, deposited in a shallow marine environment, in Hole 4A (87° 52.00 ‘N; 136° 10.64 ’E; 1,288 m water depth), on the Lomonosov Ridge in the central Arctic Ocean (Backman et al., 2006). The succession was deposited at a paleolatitude of ~78 °N, based on a geological reconstruction (Seton et al., 2012) projected using a paleomagnetic reference frame (Torsvik et al., 2012) (see paleolatitude.org, Van Hinsbergen et al., 2015). The sediments are devoid of biogenic calcium carbonate, but rich in immature organic matter, including terrestrial and marine

70 microfossil assemblages and molecular fossils (e.g. Pagani et al., 2006; Sluijs et al.,
71 2006; Stein et al., 2006).
72 As the upper Paleocene and lower Eocene sediments of the ACEX core lack biogenic
73 calcium carbonate and alkenones, SST reconstructions are based on the biomarker-
74 based paleothermometer TEX_{86}. This proxy is based on membrane lipids (isoprenoid
75 glycerol dibiphytanyl glycerol tetraethers; isoGDGTs) of Thaumarchaeota, which adapt
76 the fluidity of their membrane according to the surrounding temperature by increasing
77 the number of cyclopentane rings at higher temperatures (De Rosa et al., 1980; Wuchter
78 et al., 2004; Schouten et al., 2013, and references therein). The proxy was introduced
79 in 2002 by Schouten et al. (2002) and was calibrated to mean annual SST using modern
80 marine surface sediments.
81 Initial papers suggested that Arctic SST increased significantly during two episodes of
82 transient global warming. Maximum values of ~23°C and ~27 °C occurred during the
83 Paleocene-Eocene Thermal Maximum (PETM-56 Ma ago, Sluijs et al., 2006) and
84 Eocene Thermal Maximum 2 (ETM2-54 Ma ago, Sluijs et al., 2009), respectively.
85 Lower SSTs, generally exceeding 20 °C, characterized the remainder of the early
86 Eocene (Sluijs et al., 2008b). Such temperatures were immediately recognized to be
87 remarkably high and could not be explained using fully-coupled climate model
88 simulations (Sluijs et al., 2006). Even the current-generation of IPCC-class models are
89 unable to match early Eocene Arctic mean annual SSTs, although reconstructions of
90 tropical and mid-latitude SSTs and deep ocean temperatures are consistent with some
91 newer simulations (Frieling et al., 2017; Cramwinckel et al., 2018; Evans et al., 2018;
92 Zhu et al., 2019).
93 Since the publication of the ACEX SST records, constraints on the applicability of the
94 TEX_{86} proxy have tremendously improved (see review by Schouten et al., 2013, and

subsequent work by Taylor, 2013 #1645; Elling et al., 2014; Qin et al., 2014; Elling et al., 2015; Kim et al., 2015; Qin et al., 2015; Hurley et al., 2016; Zhang et al., 2016). This work has delivered new constraints on the ecology of Thaumarchaeota, the dominant depth at which they reside in the ocean and from which depth their isoGDGTs are exported towards the sea floor. It also identified potential confounding factors such as variation in dominant isoGDGT export depth (e.g., Taylor et al., 2013; Kim et al., 2015), the input of non-Thaumarchaeotal-derived isoGDGTs (e.g., Weijers et al., 2011; Zhang et al., 2011), growth phase (Elling et al., 2014), and environmental ammonium and oxygen concentrations (Qin et al., 2015; Hurley et al., 2016). Moreover, several indicators to detect such anomalies have been developed. Improvements in the chromatography method used for GDGT analysis now allow for better separation of previously co-eluting compounds leading to enhanced analytical precision and sensitivity (Hopmans et al., 2016). Finally, recent work has described new GDGTs from oceans and sediments, notably branched glycerol monoalkyl glycerol tetraethers (brGMGTs, or 'H-shaped' brGDGTs) (e.g., Schouten et al., 2008; Liu et al., 2012), characterized by a covalent carbon-carbon bond that links the two alkyl chains. Their presence and distribution in peats and lake sediments has been linked to land air temperatures (LAT) (e.g., Naafs et al., 2018a; Baxter et al., 2019). However, these compounds have not yet been reported from ancient marine sediments.

Considering these developments and the paleoclimatological importance of the ACEX dataset, we re-analyzed the original lipid extracts for the PETM, ETM2 and the interval spanning these events (Sluijs et al., 2006; Sluijs et al., 2009), according to the latest chromatography protocols. We also compile published and generate new GDGT data from modern and Paleogene terrestrial deposits and use these to better assess the

potential confounding influence of isoGDGTs from terrestrial sources, which was already recognized as a potential problem in the early work (Sluijs et al., 2006).

2. GDGT-based SST indices, calibration and confounding factors

2.1 TEX_{86} and its calibration to SST

TEX_{86} is based on the relative abundance of 4 different GDGTs (Figure 2), following (Schouten et al., 2002):

$$TEX_{86} = \frac{([GDGT-2]+[GDGT-3]+[Crenarchaeol\ isomer])}{([GDGT-1]+[GDGT-2]+[GDGT-3]+[Crenarchaeol\ isomer])} \quad \text{Eq. (1)}$$

where a higher relative abundance of cyclopentane moieties implies higher SSTs.

A number of models are used to calibrate TEX_{86} to SST (Schouten et al., 2002; Schouten et al., 2003; Schouten et al., 2007; Kim et al., 2008; Liu et al., 2009; Kim et al., 2010; Tierney and Tingley, 2014; O'Brien et al., 2017), all based on a modern ocean surface sediment database. The currently available culture and mesocosm experiments and surface sediment data suggest that the relation between SST and TEX_{86} is close to linear for a large portion of the modern ocean (Kim et al., 2010; Ho et al., 2014; Tierney and Tingley, 2014; O'Brien et al., 2017). In polar regions, the TEX_{86} response to temperature diminishes (e.g., Kim et al., 2010; Tierney and Tingley, 2014). The response of TEX_{86} to SST at the high temperature end remains subject of discussion (e.g. Cramwinckel et al., 2018; Hollis et al., 2019). Several authors prefer a linear relation (e.g., Tierney and Tingley, 2014; O'Brien et al., 2017). However, physiological considerations and multiple temperature-dependent GDGT indices might imply a non-linear relation also at the high temperature end, as can be observed at the high end of the modern ocean dataset and beyond the reach of the modern ocean in paleoclimate data (Cramwinckel et al., 2018). At higher temperatures, membrane adaptation may

144 increasingly be established using isoGDGTs not included in the TEX_{86} ratio leading to
145 a diminished TEX_{86} response at very high temperatures (Cramwinckel et al., 2018). A
146 non-linear response has thus been proposed in other calibrations (Liu et al., 2009; Kim
147 et al., 2010). The most recent non-linear calibration, TEX_{86}^{H} (Kim et al., 2010),
148 represents an exponential relation between SST and TEX_{86} (Hollis et al., 2019).
149 Unfortunately, TEX_{86}^{H} is mathematically problematic and has systematic residuals in
150 the modern ocean (Tierney and Tingley, 2014).
151 Tierney and Tingley (2014) introduced a spatially-varying Bayesian method to convert
152 TEX_{86} to SST and assumes a linear relationship (BAYSPAR). BAYSPAR extracts
153 TEX_{86} values from the modern core-top dataset that are similar to the measured TEX_{86}
154 value from the geological sample based on a tolerance defined by the user, and
155 subsequently calculates regressions based on these core-top data. The uncertainty in
156 SST reflects spatial differences in the correlation coefficient and intercept and the error
157 variance of the regression model.
158 Currently, it is generally encouraged to present results both using a linear and a non-
159 linear function (Hollis et al., 2019). The assumption of a linear or non-linear relation
160 between SST and TEX_{86} leads to very different SST reconstructions for geological
161 samples yielding TEX_{86} values >0.70 (Kim et al., 2010; Tierney and Tingley, 2014;
162 Frieling et al., 2017; O'Brien et al., 2017; Cramwinckel et al., 2018; Hollis et al., 2019).
163 However, TEX_{86} values of the early Eocene ACEX samples (0.5 – 0.7, Sluijs et al.,
164 2006; Sluijs et al., 2008b; Sluijs et al., 2009) are below this value and well above most
165 values observed in the polar regions (Kim et al., 2010; Tierney and Tingley, 2014;
166 O'Brien et al., 2017), indicating that all calibrations will yield similar absolute SST
167 values.
168

169 *2.2 Caveats and confounding factors*

170 Several confounding factors and caveats have been identified that could potentially bias
171 TEX_{86} data relative to mean annual SST. These notably relate to additions of isoGDGTs
172 that were not produced in the upper water column by Thaumarchaeota, seasonal biases,
173 and choices that are made in the calibration between SST and TEX_{86}. Below we
174 summarize methods that have been developed to assess if isoGDGT distributions might
175 have been biased by confounding factors.

176

177 *2.2.1 isoGDGTs of terrestrial origin*

178 Previous work (Sluijs et al., 2006; Sluijs et al., 2008b; Sluijs et al., 2009) recognized
179 that high contributions of terrestrially-derived isoGDGTs could compromise the TEX_{86}
180 signal for portions of the upper Paleocene to lower Eocene interval of the ACEX core.
181 This contribution can be tracked using the Branched and Isoprenoid Tetraether (BIT)
182 index, a ratio of mostly soil-derived branched GDGTs (brGDGTs; Figure 2) and
183 Crenarchaeol, which is dominantly marine-derived (Hopmans et al., 2004; Schouten et
184 al., 2013):

185 $$BIT\ index = \frac{([brGDGT-Ia]+[brGDGT-IIa]+[brGDGT-IIIa])}{([brGDGT-Ia]+[brGDGT-IIa]+[brGDGT-IIIa])+[Crenarchaeol])} \quad \text{Eq. (2)}$$

186 Most studies define a BIT value (typically 0.3 or 0.4) above which TEX_{86}-derived SST
187 are unreliable (e.g., Weijers et al., 2006). However, the threshold of 0.4 is conservative
188 in some settings and the impact of terrigenous GDGTs on reconstructed SST will
189 depend on the nature and temperature of the source catchment (Inglis et al., 2015). In
190 addition, a cut-off value based on BIT values is difficult given the relatively large
191 differences in BIT between labs, which originate from methodological differences
192 (Schouten et al., 2009). A strong linear relationship between BIT and TEX_{86} values is
193 often taken as indication of a bias in TEX_{86} through land-derived isoGDGTs to the

194 marine TEX_{86} signature (e.g., Douglas et al., 2014). An earlier study used a somewhat
195 subjective threshold of 0.3 for an interval spanning ETM2 in the ACEX core (Sluijs et
196 al., 2009).
197
198 *2.2.2 isoGDGTs of deep water origin*
199 Thaumarchaeota, the source of most isoGDGTs in marine waters (Zeng et al., 2019;
200 Besseling et al., 2020), are ammonium oxidizers (Könneke et al., 2005; Wuchter et al.,
201 2006a), making them independent of light. Although they occur throughout the water
202 column, maximum abundances occur at depths <200 m, generally around NO_2 maxima
203 (e.g., Karner et al., 2001; Pitcher et al., 2011a). In most oceans, sedimentary GDGTs
204 dominantly derive from the upper few hundred meters, based on analyses of suspended
205 particular organic matter and sediment traps (Wuchter et al., 2005; Wuchter et al.,
206 2006b; Yamamoto et al., 2012; Richey and Tierney, 2016). A deeper contribution has
207 also been inferred based on ^{14}C analysis (Shah et al., 2008), implying possible
208 contributions of isoGDGTs from thermocline. Moreover, contributions of isoGDGTs
209 produced in the deep sea have regionally been identified (e.g., Kim et al., 2015). Taylor
210 et al. (2013) also found that deep dwelling (>1000 meter) archaea might contribute to
211 the sedimentary isoGDGT assemblage. They indicate that such deep contributions can
212 be tracked using the GDGT-2/GDGT-3 ratio; high values of >5 indicate contributions
213 of archaea living deeper in the water column. Given that upper Paleocene and lower
214 Eocene ACEX sediments were deposited in a shallow shelf environment (Sluijs et al.,
215 2008b), a significant contribution of deep ocean archaeal lipids is not expected.
216

2.2.3 isoGDGTs of methanotrophic and methanogenic archaea

Contributions of isoGDGTs to the sedimentary pool might also derive from anaerobic methanotrophs and/or methanogens. Several indices have been developed to track such contributions, both based on relatively high contributions of particular isoGDGTs of these groups of archaea. The Methane Index (MI) was developed to detect the relative contribution of anaerobic methanotrophic Euryarchaeota assumed to be represented by GDGT-0 but also GDGT-1, 2 and 3 (Zhang et al., 2011) and is therefore defined as

$$MI = \frac{[GDGT-1]+[GDGT-2]+[GDGT-3]}{([GDGT-1]+[GDGT-2]+[GDGT-3]+[Crenarchaeol]+[Crenarchaeol\ isomer])} \quad \text{Eq. (3)}$$

MI values greater than 0.5 indicate significant contribution of anaerobic methanotrophy. Such values may yield unreliable TEX_{86} values. Another tracer for contributions of anaerobic methanotrophic archaea is the analogous GDGT-2/Crenarchaeol ratio (Weijers et al., 2011).

Methanogenic archaea can synthesize GDGT-0, as well as smaller quantities of GDGT-1, GDGT-2 and GDGT-3. The ratio GDGT-0/Crenarchaeol is indicative of contributions of methanogenic archaea to the isoGDGT pool (Blaga et al., 2009) where values > 2 indicate substantial contribution of methanogenic archaea. Up to now, high index values have often been observed near methane seeps or anoxic basins (e.g., Jaeschke et al., 2012) but rarely in open marine waters in the modern and paleodomains (Inglis et al., 2015; Zhang et al., 2016). Given the reducing conditions in the sediment and water column at the study site across the late Paleocene and early Eocene (Sluijs et al., 2006; Stein et al., 2006; Sluijs et al., 2008b; März et al., 2010), an influence of methane cycling might be expected.

240 *2.2.4 isoGDGTs of the 'Red Sea Type'*

241 Sedimentary isoGDGT distributions from the Red Sea are anomalous to other marine
242 settings and are characterised by the low abundance of GDGT-0 and the high abundance
243 of the Crenarchaeol isomer. Presumably, this is due to an endemic Thaumarchaeotal
244 assemblage. The Red Sea isoGDGT distribution yields a different relationship between
245 SST and TEX_{86} (Trommer et al., 2009; Kim et al., 2015). Inglis et al. (2015) attempted
246 to quantify a 'Red Sea-type' GDGT distribution in geological samples using the
247 following index:

248 $$\%\mathrm{GDGTrs} = \frac{[Crenarchaeol\ isomer]}{([GDGT{-}0] + [Crenarchaeol\ isomer])}\ x\ 100 \qquad \text{Eq. (4)}$$

249 However, as noted by Inglis et al. (2015) this ratio is also strongly SST-dependent such
250 that the Red Sea type GDGT assemblage cannot be discerned from GDGT distributions
251 that occur at high temperatures in normal open marine settings.

252

253 *2.2.5 Seasonal bias*

254 TEX_{86} is calibrated to mean annual SST. However, particularly in mid and high latitude
255 areas where production and export production is highly seasonal, the sedimentary
256 GDGT distribution might not represent annual mean conditions (Wuchter et al., 2006b;
257 Pitcher et al., 2011b; Mollenhauer et al., 2015; Richey and Tierney, 2016; Park et al.,
258 2019). This issue should partly be reflected in the calibration uncertainty of the modern
259 ocean database (several °C, depending on the calibration and method; see section 2.7).
260 Sluijs et al. (2006; 2008b; 2009) originally argued that the TEX_{86} results from the
261 ACEX core could be biased towards summer temperature because the export of organic
262 matter from the surface ocean towards the sediment likely peaked during the season of
263 highest production, i.e., the summer. However, we also note that the TEX_{86}-temperature
264 relationship is not improved when using seasonal mean ocean temperatures (Kim et al.,

2010; Tierney and Tingley, 2014) and modern observations indicate homogenization of the seasonal cycle at depth (Wuchter et al., 2006b; Yamamoto et al., 2012; Richey and Tierney, 2016), implying that seasonality has relatively limited effect on modern sedimentary TEX_{86} values.

2.2.6 Additional isoGDGT-based temperature indicators

The underlying mechanism of TEX_{86} is that isoGDGTs produced at higher SSTs contain more rings than those produced at low SSTs. Although the combination of compounds included in TEX_{86} seems to yield the strongest relation with temperature in the modern ocean (Kim et al., 2010), it implies that isoGDGT ratios other than TEX_{86} also provide insights into SST. One alternative temperature sensitive isoGDGT index is the Ring Index (RI), which represents the weighed number of cyclopentane rings of isoGDGTs 0-3, Crenarchaeol and the Crenarchaeol isomer (Zhang et al., 2016), defined as:

$$RI = 0x[\%GDGT-0] + 1\,x[\%GDGT-1] + 2\,x[\%GDGT-2] + 3\,x[\%GDGT-3] + 4\,x\,[\%Crenarchaeol + \%Crenarchaeol\ isomer] \quad \text{Eq. (5)}$$

Note that the abundance of GDGT-0 is important for determining the percentage of the other GDGTs of the total isoGDGT pool.

The close relation between TEX_{86} and RI can also be used to detect aberrant distributions, including those produced by methanogenic, methanotrophic and terrestrial sources, as these sources typically contribute disproportionate amounts of specific lipids. A RI_{TEX}, calculated from TEX using the polynomial fit of Zhang et al. (2016), is subtracted from the RI to arrive at the ΔRI. Cut-off values for sample deviation from the modern ocean calibration dataset are defined as 95% confidence limits of the RI-TEX relation, or above |0.3| ΔRI units.

290 *2.3 H-shaped branched GDGTs; brGMGTs*

291 BrGMGTs (Figure 2) were first identified by Liu et al. (2012) in marine sediments, who
292 identified a single acyclic tetramethylated brGMGT (*m/z* 1020). This compound was
293 later detected within the marine water column and appeared to be abundant within the
294 oxygen minimum zone (Xie et al., 2014). Naafs et al. (2018a) identified a larger suite
295 of brGMGTs (including *m/z* 1048 and 1034), in a quasi-global compilation of modern
296 peat samples. They argued that these compounds were preferentially produced at depth,
297 within the anoxic catotelm. Analogous to the continental paleothermometer based on
298 bacterial brGDGTs produced in surface soils, termed MBT'$_{5me}$ (Weijers et al., 2007b;
299 De Jonge et al., 2014), they showed that the degree of methylation of brGMGTs in peats
300 relates to mean annual air temperature. They calculated the degree of methylation of
301 brGDGTs without cyclopentane moieties, designed for comparison to the methylation
302 of brGMGTs, defined by H-MBT$_{acyclic}$:

303

304 $$MBTacyclic = \frac{brGDGT-Ia}{(brGDGT-Ia+brGDGT-IIa+GDGT-IIa'+brGDGT-IIIa+brGDGT-IIIa')}$$ Eq. (6)

305

306 $$H-MBTacyclic = \frac{brGMGT-H1020}{(brGMGT-H1020+brGMGT-H1034+brGMGT-1048)}$$ Eq. (7)

307

308 Based on the strong relation between MBT$_{acyclic}$ and H-MBT$_{acyclic}$ in their peat samples,
309 Naafs et al. (2018a) suggested that the brGMGTs have the same origin as the brGDGTs,
310 presumably Acidobacteria (Sinninghe Damsté et al., 2011; Sinninghe Damsté et al.,
311 2018a). In addition, they showed that the abundance of brGMGTs (relative to the total
312 amount of brGMGTs and brGDGTs) positively correlates with mean annual air
313 temperature, suggesting that the covalent bond in the brGMGTs is used to maintain
314 membrane stability at higher temperature (Naafs et al., 2018a).

315 Baxter et al. (2019) identified a total of seven different brGMGTs from a suite of
316 African lake sediments (Figure 2), and found their relative distribution to correlate to
317 mean annual air temperature. Accordingly, they proposed a proxy for mean annual air
318 temperature termed brGMGT-I (see Figure 2 for the molecular structures referred to
319 here):

320 $$brGMGT - I = \frac{[H1020c]+[H1034a]+[H1034c]}{[H1020b]+[H1020c]+[H1034a]+[H1034c]+[H1048]}$$ Eq. (8)

321

322 **3. Material and Methods**

323 We used the polar fractions previously analyzed by Sluijs et al. (2006; 2009) from the
324 PETM through ETM2 interval at IODP Expedition 302 Hole 4A. These fractions
325 originate from a total lipid extract produced using a Dionex Accelerated Solvent
326 Extractor and fraction separations by Al_2O_3 column chromatography using
327 hexane:dichloromethane (DCM) (9:1, *v/v*) and DCM:methanol (1:1; *v/v*) to yield the
328 apolar and polar fractions, respectively. Polar fractions were re-dissolved in
329 hexane:isopropanol (99:1, *v/v*)) and passed through a 0.45-µm polytetrafluoroethylene
330 filter. This fraction was then analyzed by high-performance liquid chromatography
331 (HPLC) and atmospheric pressure chemical ionization–mass spectrometry using an
332 Agilent 1260 Infinity series HPLC system coupled to an Agilent 6130 single-
333 quadrupole mass spectrometer at Utrecht University following Hopmans et al. (2016)
334 to measure the abundance of GDGTs. Based on long-term observation of the in-house
335 standard, the analytical precision for TEX_{86} calculates to ±0.3 °C in the SST domain.
336 To gain further insights into the potential impact of terrestrial isoGDGT input on TEX_{86}
337 values, we compiled isoGDGT and brGDGTs distributions from modern peats (n = 473,
338 Naafs et al., 2017) and early Paleogene lignites (n = 58, Naafs et al., 2018b). Note, the
339 fractional abundance of Crenarchaeol isomer was not reported in the early Paleogene

dataset of Naafs et al. (2018b). We therefore revisited the original chromatograms from Naafs et al. (2018b) and integrated the crenarchaeol isomer (*m/z* 1292).

4. Results

The new GDGT distributions (Supplementary Table) are consistent with the TEX_{86} and BIT index data generated over a decade ago using the older analytical HPLC setup (Hopmans et al., 2000; Hopmans et al., 2016) (Figure 3). TEX_{86} exhibits some scatter but the slope of the regression is 0.98 for the entire dataset, which is indistinguishable from the 1:1 line. The scatter is minor compared to the uncertainties inherent to calibrations that transfer these values to SST. Less scatter is apparent in the BIT record but the original BIT index values were slightly higher than recorded here (~0.5), indicated by a shallower slope of the regression (0.92). This result is consistent with previous analyses with the new analytical setup (Hopmans et al., 2016). This does not impact previous qualitative interpretations of this record (Sluijs et al., 2006; Sluijs et al., 2008b; Sluijs et al., 2009). In the discussion section, we assess indicators of potential confounding factors (section 2.2), including the influx of terrestrially-derived isoGDGTs to the sediments (Figures 4, 5 and S1) and several indices related to methane and depth of production (Figures 6).

Although we did not detect significant amounts of isoprenoid GMGTs, high abundances of various brGMGTs are present in the ACEX samples, in total between 10 and 45% of the total brGDGT assemblage (Figure 7). We consistently identify at least five brGMGTs across the three different mass-to-charge ratios (*m/z* 1020, 1034 and 1048). Based on their (relative) retention times and overall distribution we were able to apply the nomenclature of Baxter et al. (2019) to five of these and assign individual peaks to previously identified compounds (Figure S2). The abundance of brGMGTs

relative to brGDGTs increase during the PETM. The proposed temperature indicators based on brGMGTs show mixed results, with some showing a clear response to the PETM (Figure 7e) while others do not (Figure 7d).

5. Discussion

5.1 IsoGDGT provenance

5.1.1 Contributions of soil-derived isoGDGTs

As noted by Sluijs et al. (2006), late Paleocene samples yield anomalously high abundances of GDGT-3, likely derived from a terrestrial source. We therefore consider the late Paleocene temperature estimates unreliable. To assess the temperature change during the PETM, Sluijs et al. (2006) developed a TEX_{86} calibration without this moiety, termed TEX'_{86}. However, TEX'_{86} has not been widely used outside the Paleogene Arctic because the anomalous abundances of GDGT-3 have not been recorded elsewhere. High contributions of GDGT-3 from terrestrial input would also be associated with an increase in the abundance of other isoGDGTs. Indeed, recent TEX_{86}-based global SST compilations and comparison to climate simulations for the PETM excluded the Paleocene ACEX data because the TEX_{86}' calibration complicates the comparison to other regions where it has not been applied (Frieling et al., 2017; Hollis et al., 2019).

Input of soil organic matter is consistent with Willard et al. (2019) who established that the brGDGT assemblage is dominantly soil-derived as opposed to being produced in the coastal marine environment. This observation is based upon the weighted average number of rings in the tetramethylated brGDGTs ($\#rings_{tetra}$) which generally does not exceed 0.4 to 0.7 in the global soil calibration dataset (Sinninghe Damsté, 2016). In the ACEX record, $\#rings_{tetra}$ is < 0.21 (Willard et al., 2019), consistent with a dominant soil

source. This indicates that 1) brGDGT abundances, 2) brGDGT distributions and 3) the BIT index are reliable indicators of the relative supply of terrestrially-derived isoGDGTs into the marine basin. The Paleocene section of the dataset also stands out regarding its relation between BIT index and TEX_{86} (Figure 4), which confirms its anomalous nature.

During the PETM, TEX_{86} values are higher (due to warming) and BIT values lower. This was attributed to sea level rise during the hyperthermals resulting in a more distal position relative to the terrestrial GDGT source (Sluijs et al., 2006; Sluijs et al., 2008a). The interval between 371.0 and 369.0 mcd (i.e. above the PETM and below ETM2) stands out. This interval was previously recognized by Sluijs et al. (2009) to reflect an open marine environment, with a dominance of marine palynomorphs and algal biomarkers. They also found that high BIT values correspond to low TEX_{86} values within that interval and therefore implemented a subjective threshold value of 0.3, above which TEX_{86}-derived SSTs were considered unreliable. Although the relation between BIT and TEX_{86} exhibits considerable much scatter, the new analyses supports the notion that higher influx of terrestrial isoGDGTs lowers TEX_{86} values. The linear regression (Figure 4; excluding the one outlier with high TEX_{86} and BIT values in the top right of the plot because it has highly anomalous distributions ($\Delta RI = 0.61$)), yields an R^2 of 0.26 so explains a portion of the variation (Figure 4). The nature of this influence is determined by the relative abundance of terrestrial isoGDGTs and their TEX_{86} value. The TEX_{86} value at the terrestrial endmember of BIT = 1, assuming various types of regressions, centers around 0.5. The remainder of the data does not show a clear relation between BIT and TEX_{86} although some of the lowest TEX_{86} values correspond to high BIT values, suggesting that the terrestrial endmember

414 contributed isoGDGT assemblages with relatively low TEX_{86} values in other intervals
415 as well.
416 The relatively low degree of cyclization in the early Eocene contrasts starkly with high
417 degree of cyclisation during the late Paleocene (Figure 6). This implies that the
418 distribution of terrestrial isoGDGTs varies strongly between the latest Paleocene and
419 early Eocene within our studied section.
420 The impact of soil-derived isoGDGTs also emerges from the Ring Index approach of
421 Zhang et al. (2016, see section 2.6 and Figure 6). The difference between the Ring Index
422 and TEX_{86} at the onset of the PETM is mainly controlled by Crenarchaeol, which is
423 comparatively low in abundance in the Paleocene but highly abundant in the PETM.
424 This increase is likely associated with sea level rise during the PETM because
425 Crenarchaeol is predominantly produced in the marine realm. It is also consistent with
426 a drop in BIT index values and the relative abundance of terrestrial palynomorphs
427 (Sluijs et al., 2008a). The approach of Zhang et al. (2016) also confirms that many
428 isoGDGT distributions exhibit an anomalous relation between TEX_{86} and the Ring
429 Index relative to the modern core top dataset, with ΔRI values >0.3 (Figure 6).
430 Importantly, all samples with ΔRI values >0.3 have BIT values above 0.35, indicating
431 that contributions of soil-derived iso-GDGTs dominate non-temperature effects in the
432 distributions. We therefore discard TEX_{86}-derived SSTs for samples with BIT values
433 >0.35.
434 We also develop a crude model to further constrain the potential contribution of
435 terrestrially-derived isoGDGTs. First, we determine the abundance of isoGDGTs
436 relative to brGDGTs in modern peat samples (Naafs et al., 2017) and early Paleogene
437 lignites (fossil peat) (Naafs et al., 2018b, the isoGDGT data are published here).
438 Although there is no reason to assume that peat was a major component of the

hinterland (Willard et al., 2019) , the aforementioned datasets can provide an estimate of the potential contribution from terrestrial isoGDGTs to our study site. The raw signal intensity of brGDGTs in the ACEX samples are used to estimate the potential contribution of terrestrially-derived isoGDGTs to the samples. To this end, we use the fractional abundance of the various isoGDGTs in the modern peat and Paleogene lignite datasets (Figure 5). Then, we estimate the abundance of these terrestrially-derived isoGDGTs in our ACEX samples by scaling this fraction to the measured abundances of brGDGTs and isoGDGTs in our ACEX samples, following

$$Terrestrial\ fraction\ of\ isoGDGT\ \mathrm{x} = \left(Fraction\ of\ isoGDGT\mathrm{x}\ in\ terrestrial\ test\ dataset * \frac{sum(brGDGTs))}{abundance\ of\ isoGDGT\ x}\right) \quad \text{Eq. (9)}$$

where x represents the specific analyzed GDGT (see Supplementary Data File for an example of these calculations).

This leads to estimates of the potential relative contributions of the individual isoGDGTs derived from land in the ACEX samples based on the entire modern peat dataset (Naafs et al., 2017), modern peats from regions with MAT exceeding 15°C (Naafs et al., 2017) and Paleogene lignites (Naafs et al., 2018b, this paper, Figures 5 and S1). This approach implies that Crenarchaeol and the Crenarchaeol-isomer are almost exclusively from the marine realm. However, GDGT-1, GDGT-2 and GDGT-3 in our study site may be derived from the terrestrial realm (Figure 5), especially in specific stratigraphic intervals (Figure S1). In the most extreme cases, the modeled contributions of terrestrial isoGDGTs is higher than the measured isoGDGT abundances (i.e., terrestrial fraction > 1). This is principally seen in iGDGT-2 and GDGT-3, especially when we employ the Paleogene lignite database. This particular assumption clearly overestimates the abundance of terrestrially sourced isoGDGTs in our setting. However, the temporal trends obtained using modern peats, subtropical

464 modern peats and Paleogene lignites are essentially identical and give some indication
465 which isoGDGTs are most likely to be impacted by terrestrial input and across which
466 intervals. Interestingly, this approach also suggests that particularly GDGT-3 is shown
467 to be strongly affected (Figure 5), which qualitatively matches the distributions in the
468 ACEX samples. This is principally because GDGT-3 is the least abundant marine
469 isoGDGT included in our analyses, whereas it is often as abundant as GDGT-1 and 2
470 in terrestrial settings (Fig. 5).
471
472 *5.1.2 Contributions of methanotrophic or methanogenic archaea?*
473 The depositional environment at the study site included ample (export) production,
474 sediment organic matter content, and low oxygen conditions at the sediment-water
475 interface (Sluijs et al., 2006; Stein et al., 2006; Stein, 2007; Sluijs et al., 2008b; Sluijs
476 et al., 2009; März et al., 2010). This may have been suitable for abundant methanogenic
477 and methanotrophic archaea, potentially contributing to the sedimentary isoGDGT
478 assemblage. However, our GDGT-2/Crenarchaeol values (<0.23; Figure 6) are far
479 below values that suggest significant isoGDGT contributions of methanotrophic
480 Euryarchaeota as described by Weijers et al. (2011). MI values (maximum observed
481 0.31) are also generally below proposed cut off values (0.3-0.5, Zhang et al., 2011) that
482 suggest such contributions. Finally, GDGT-0/Crenarchaeol ratios (<1.4) remain below
483 the cut-off value of 2 throughout the section (Figure 6), also making a significant
484 isoGDGT contribution from methanogens highly unlikely (Blaga et al., 2009).
485 Collectively, relative contributions of isoGDGTs from methanogenic and
486 methanotrophic archaea seem low despite the low-oxygen environment, suggesting a
487 relatively high flux of pelagic isoGDGTs.
488

5.1.3 Contributions of deep-dwelling archaea?

Taylor et al. (2013) showed that GDGT-2/GDGT-3 ratios correspond to depth of production, with high values (>5) in deep waters (>1000 m). We record low values (1-4) between ~390 and ~371.2 mcd (Figure 6), which supports a dominant production in the surface ocean based on the modern calibration data set (Taylor et al., 2013). However, the overlying interval (~371 to ~368.3 mcd) has much higher (average 7.4) and variable GDGT-2/GDGT-3 values with peak values of 10-14. Such values suggest significant contributions of isoGDGTs produced at water depths of several kilometers according to the analyses by Taylor et al. (2013).

However, all paleoenvironmental information generated based on the sediments as well as tectonic reconstructions of Lomonosov Ridge – a strip of continental crust that disconnected from the Siberian margin in the Paleocene - has indicated a neritic setting of the drill site at least up to the middle Eocene (e.g., O'Regan et al., 2008; Sangiorgi et al., 2008; Sluijs et al., 2008a; Sluijs et al., 2009). At ~371.2 mcd a drop in BIT index and a change in the palynological assemblages corresponds to an interval of greenish sediment, suggestive of pronounced amounts of glauconite. These changes are consistent with local relative sea level rise, causing a somewhat more distal position relative to the shoreline. However, the sediment remains dominantly siliciclastic and organic terrestrial components, particularly pollen and spores, remain abundant still indicating a shallow setting (Sluijs et al., 2008a; Sluijs et al., 2008b). Increased contributions of isoGDGTs produced at depth would be expected to have caused a systematic cold bias but based on linear regression analysis the large variability in GDGT-2/GDGT-3 ratios is unrelated to the recorded variability in TEX_{86} values. The high GDGT-2/GDGT-3 ratio values can therefore not be explained by contributions of deep dwelling archaea.

In a study of the last 160 kyr in the South China Sea, Dong et al. (2019) found that very high GDGT-2/GDGT-3 ratios (~9 but up to 13) correspond with high values in nitrogen isotope ratios, interpreted to reflect low contributions in diazotroph N_2 fixation and enhanced upwelling. In our record, the high GDGT-2/GDGT-3 ratios are associated with normal marine conditions and the dinocyst assemblages are not indicative of upwelling conditions (Sluijs et al., 2009). Unfortunately, the available nitrogen isotope record (Knies et al., 2008) does not cover this interval in sufficient resolution to assess a relation with diazotroph activity. The increase in GDGT-2/GDGT-3 ratio correlates to a strong drop in BIT index values and an increase in normal marine dinocyst species (Sluijs et al., 2009), but a shift to more open marine environment does not explain the high ratio values. As such, the cause of the high GDGT-2/GDGT-3 ratios in this interval remains unclear but we consider it highly unlikely to relate to contributions of deep dwelling Thaumarchaeota.

5.1.4 Oxygen concentrations and ammonium oxidation rates

A variety of non-thermal factors can impact TEX_{86} values, including ammonium and oxygen concentrations and growth phase (Elling et al., 2014; Qin et al., 2014; Hurley et al., 2016). Across the studied interval of the ACEX core, several intervals of seafloor and water column anoxia have been identified based on organic and inorganic proxies, notably during the PETM and ETM2 (Sluijs et al., 2006; Stein et al., 2006; Sluijs et al., 2008b; Sluijs et al., 2009; März et al., 2010).

Particularly suspect is an interval of low TEX_{86} values that marks the middle of the ETM2 interval, directly following a ~4 °C warming at its onset (Sluijs et al., 2009). This interval is also marked by the presence of sulfur-bound isorenieratane (Sluijs et al., 2009), a derivative of isorenieratene. This biomarker is produced by the brown

strain of green sulfur bacteria that require light for photosynthesis and free sulfide, indicating euxinic conditions in the (lower) photic zone (Sinninghe Damsté et al., 1993). We also record a concomitant shift in several methane-related indicators, GDGT-2/GDGT-3 ratio values and the ΔRI. A mid-ETM2 cooling signal has not been recorded at other study sites and this interval marks the occurrence of pollen of thermophilic plants such as palms and baobab (Sluijs et al., 2009; Willard et al., 2019). Therefore, the low TEX_{86} values were suggested to reflect thaumarcheotal depth migration to the deeper chemocline due to euxinic conditions (Sluijs et al., 2009), similar to the modern Black Sea (Coolen et al., 2007; Wakeham et al., 2007) and the Mediterranean Sea during sapropel formation (Menzel et al., 2006).

More recent work has indicated that the isolated marine Thaumarchaeotal species *Nitrosopumilus maritimus* produces lower TEX_{86} values with higher ammonia oxidation rates (Hurley et al., 2016) and O_2 concentrations (Qin et al., 2015). Although this observation is difficult to extrapolate to the total response of the Thaumarcheotal community in the marine environment on geological time scales, lower O_2 availability should lower oxidation rates leading to higher TEX_{86} values (Qin et al., 2015; Hurley et al., 2016). However, we record a drop in TEX_{86} values with the development of anoxia during ETM2. The nature of the anomalously low cyclization in the ETM2 isoGDGT assemblage, which passes all quality tests regarding GDGT distribution (Figure 6), remains therefore elusive.

5.2 Origin and environmental forcing of brGMGTs

The relative abundances of brGMGTs in our samples are surprisingly high. On average, they comprise 25% of the total branched GDGT and GMGT assemblage. The limited literature on modern occurrences implies that both terrestrial and marine sources may

have contributed to the brGMGT assemblage. Data from marine sediments (Liu et al., 2012) and the water column (Xie et al., 2014), clearly shows production within the marine realm. Their occurrence in modern peats (Naafs et al., 2018a), lake sediments (Baxter et al., 2019) and Paleogene lignites (Inglis et al., 2019) might also imply transport from land to marine sediments. A soil-derived source is currently unsupported, as they were most often below detection limit in recent studies of geothermally heated soils (De Jonge et al., 2019) and a soil transect from the Peruvian Andes (Kirkels et al., 2020). The brGMGT abundances we record are close to the maximum abundance found in modern peats (Naafs et al., 2018a). However, significant input of peat-derived organic matter into our study site is inconsistent with the low input of peat-derived *Sphagnum* spores (Willard et al., 2019). Alternatively, the high abundance of brGMGTs could also be related to subsurface production in marine sediments. An analogous process was invoked by Naafs et al. (2018a) to explain very high abundance of brGMGTs in an early Paleogene lignite. Collectively, however, we surmise that production in the marine realm may be an important contributor to the brGMGT pool in our setting.

Several factors may contribute to the rise in the abundance of brGMGTs relative to brGDGTs across the PETM. Higher relative abundances of brGMGTs in modern peats generally occur at higher mean annual air temperatures (Naafs et al., 2018a) and so this signal could relate to warming during the PETM if their origin at the study site is terrestrial. However, since we consider it likely that a large part of the brGMGTs assemblage is of marine origin, the rise in brGMGT abundance likely relates to the previously recorded (Sluijs et al., 2006; Sluijs et al., 2008b) sea level rise during the PETM at the study site. This is consistent with the increase in marine brGMGT production relative to terrestrial brGDGT supply to the study site (Figure 7b). This is

589 consistent with the inverse correlation between brGMGT abundance and the BIT index
590 (Figure 7b). Lastly, if the production of marine brGMGTs was focused in oxygen
591 minimum zones (Xie et al., 2014), the development of low oxygen conditions in the
592 water column based on several indicators, such as the presence of isorenieratane (Sluijs
593 et al., 2006), might have increased the production of brGMGTs in the water column. It
594 is also possible that all of these factors contributed to the changes in abundance of
595 brGMGTs relative to brGDGTs across the PETM.
596 The brGMGT-I proxy does not produce temperature trends similar to those seen in
597 TEX_{86} or MBT'_{5me} (Figure 7d). If the majority of the brGMGTs are of marine origin,
598 this indicates that brGMGTs produced in the marine realm do not respond to
599 temperature as was hypothesized based on the African Lake dataset by Baxter et al.
600 (2019).
601 Also the application of the $H\text{-}MBT_{acyclic}$ index (equation 7) appeared problematic
602 because, similar to Baxter et al. (2019), we identified several more isomers than Naafs
603 et al. (2018a, who developed this index) detected in their peat samples. It therefore
604 remains unclear which of our peaks should be used to calculate the $H\text{-}MBT_{acyclic}$ index
605 values. We therefore show the two plausible options. For the first, we use all peaks with
606 *m/z* 1020, 1034 and 1048 (*H-MBT-all* in Figure 7e) within the expected retention time
607 window. However, based on our chromatography, we consider it more likely that the
608 dominant peaks identified by Naafs et al. (2018a) at *m/z* 1020 and 1034 represent
609 H1020c and H1034b, respectively, and therefore use only those in addition to the single
610 identifiable peak at *m/z* 1048 as a second option (H-*MBT* (H1020*c*, *H1034*) in Figure
611 7e. Both options show a clear rise across the PETM, although the HMBT (H1020c,
612 H1034a) shows a larger signal and somewhat better correspondence in absolute values
613 to $MBT_{acyclic}$, though with more scatter. A close correspondence between MBT*acyclic*

614 and HMBT has also been found in a lignite that has been assigned to the PETM (Inglis
615 et al., 2019).
616 If the dominant source of the brGMGTs was marine throughout the record, the increase
617 in methylation possibly relates to warming. This would not be unprecedented as marine-
618 produced brGDGTs show an increase in methylation as a function of temperature
619 (Dearing Crampton-Flood et al., 2018). Sollic et al. (2017) also suggest that archaeal-
620 derived isoprenoid GMGTs produced in marine sediments incorporate additional
621 methyl groups at higher sediment temperatures. Water column oxygen concentrations
622 and pH also changed at our site during the PETM, which potentially affected
623 distributions. Extensive evaluation of brGMGT distributions in modern samples is
624 therefore required to assess the proxy potential.
625
626 *5.3 Uncertainty on TEX_{86}-based SST estimates.*
627 *5.3.1 Uncertainty based on calibration dataset*
628 To calculate SSTs, we use 1) the BAYSPAR method (Tierney and Tingley, 2014),
629 which assumes a linear relationship between TEX_{86} and SST, and 2) TEX_{86}^{H} (Kim et
630 al., 2010), which assumes a non-linear relationship between TEX_{86} and SST.
631 Differences between these calibrations are smaller than the calibration errors (Figure 6)
632 because the TEX_{86} values in the ACEX dataset all fall within the range of the modern
633 core top calibration. Taken together, both indices imply that mean annual SSTs varied
634 between 18 °C and 28 °C in the early Eocene, providing strong evidence for remarkable
635 early Eocene warmth in the Arctic region.
636 The TEX_{86}^{H} calibration has a calibration error of 2.5 °C (residual mean standard error;
637 RSME) (Kim et al., 2010). The BAYSPAR method yields possible values that range
638 ~6 °C from the most probable value (Figure 6), but these uncertainty estimates are more

639 comparable than is immediately apparent, as this analysis takes a 90% confidence
640 interval compared to the 68% probability of RSME. All of the calibrations and methods
641 to obtain values and uncertainties are based on a modern core-top dataset and thus
642 implicitly include potential confounding factors such as seasonality and depth of
643 production and export. However, there is no (quantitative) constraint on any of these
644 parameters in the calibration data set. This is particularly important for the studied
645 region because it represents a polar endmember of the marine environment with highly
646 seasonal production and export and potentially high seasonality in temperature. In the
647 modern ocean, relations between SST and TEX_{86} in the Arctic and ice-proximal
648 Southern Ocean settings differ from the global ocean. This is attributed to a change in
649 viscoelastic adaptation to temperature at the low end and/or a change in the
650 Thaumarchaeotal community (Kim et al., 2010; Ho et al., 2014; Tierney and Tingley,
651 2014). This may mask potential confounding factors that may be relevant specifically
652 to polar environments. This is important here, where the polar regions were ice free and
653 the functioning of physical, chemical and biological ocean systems were fundamentally
654 different from present day. This uncertainty is not accounted for using traditional
655 regression analyses or Bayesian techniques and quantification of uncertainty in non-
656 analogue climates remains extremely difficult.
657
658 *5.3.2 Constraints from independent proxy data*
659 Independent proxy data may provide additional constraints. The appearance of the
660 dinoflagellate cyst genus *Apectodinium* during the PETM and ETM2 in the Arctic basin
661 (Sluijs et al., 2006; Sluijs et al., 2009; Harding et al., 2011) provide qualitative support
662 for pronounced warming and apparent subtropical conditions. Recent efforts to quantify
663 the paleoecological affinities of this now extinct genus have suggested a required

minimum temperature of ~20°C (Frieling et al., 2014; Frieling and Sluijs, 2018). Although this value is partly based on TEX_{86} data from the ACEX cores, it is supported by data from an epicontinental site in Siberia (Frieling et al., 2014).

A second line of independent proxy evidence includes vegetation reconstructions. As indicated above, the TEX_{86} results are qualitatively consistent with the ample evidence for thermophilic plants and animals in the Arctic (e.g., Heer, 1869; Schweitzer, 1980; Greenwood and Wing, 1995; Uhl et al., 2007; Suan et al., 2017). Particularly valuable are minimum winter temperature tolerances for specific plant species. Palynological analyses have indicated the presence of palm and baobab pollen within the PETM and ETM2 intervals in the ACEX cores (Sluijs et al., 2009; Willard et al., 2019). Modern palms are unable to tolerate sustained intervals of frost and sexual reproduction is limited to regions where the coldest month mean temperature (CMMT) is significantly above freezing (Van der Burgh, 1984; Greenwood and Wing, 1995). This threshold was was recently quantified to be ≥ 5.2 °C (Reichgelt et al., 2018). The presence of baobab within the PETM interval and ETM2 also indicate mean winter air temperatures of at least 6 °C (Willard et al., 2019). Importantly, these plants were not encountered in the intervals outside the PETM and ETM2, suggesting background coldest month mean air temperatures were potentially too low (<6ºC) to support megathermal vegetation.

Pollen of palms and *Avicennia* mangroves were recently identified in time-equivalent sections in Arctic Siberia (Suan et al., 2017). Although the details of stratigraphic framework for these records may be somewhat problematic, these findings indicate elevated CMMT estimates on land (>5.5 °C) and in the surface ocean (>13 °C) during the late Paleocene and early Eocene (Suan et al., 2017).

Apparently conflicting evidence comes from the occurrence of glendonites and erratics in specific stratigraphic levels in Paleocene and Eocene strata in Spitsbergen,

689 interpreted to reflect ‘cold snaps’ in climate (Spielhagen and Tripati, 2009). Some of
690 these stratigraphic levels are very close to (or even potentially within) the PETM,
691 considering the local stratigraphic level of the PETM (Cui et al., 2011; Harding et al.,
692 2011). However, glendonites and erratics have not been found at the exact same
693 stratigraphic levels as thermophilic biota (Spielhagen and Tripati, 2009). The formation
694 and stability of ikaite (the precursor mineral of the diagenetic glendonites) in
695 Spitsbergen was dependent on relatively low temperature, arguably persistent near-
696 freezing sea water temperatures in the sediment (Spielhagen and Tripati, 2009).
697 However, glendonite occurrences in other settings (e.g. Mesozoic sediments in mid-
698 latitude regions, Teichert and Luppold, 2013) have recently also been linked to methane
699 seeps (Morales et al., 2017). Therefore, the specific temperature constraints implied by
700 glendonites under such conditions are subject of debate. Future work should apply
701 temperature reconstructions based on the geochemical composition of the glendonites,
702 and biomarkers or biota on corresponding strata to assess whether glendonite
703 occurrence is related to colder climates.
704 The estimate on seasonal minima provides an important constraint on Arctic
705 climatology during the PETM and ETM2. Most likely, the palms and baobabs grew
706 close to the shore, where the relative heat of the ocean kept atmospheric temperatures
707 relatively high during the winter. If minimum winter SSTs were in the range of the SST
708 reconstructions based on the nearby *Avicennia* mangrove pollen (Suan et al., 2017),
709 which for open ocean settings would perhaps amount to ~10 °C, then summer SST must
710 have soared to at least 30 °C in summer if TEX_{86}–based SST reconstructions of ~20 °C
711 truly reflects the annual mean. It would imply an SST seasonality of ~20 °C, much
712 higher than any modern open marine setting. In the present day Arctic Ocean, heat is
713 seasonally stored and released in sea ice melting and freezing, and sea ice cover

714 insulates the ocean and reflects much sunlight, resulting in a seasonal cycle of not more
715 than 1.5 °C, even in ice-free regions (Chepurin and Carton, 2012). However, coupled
716 model simulations have indicated that the future loss of sea ice will greatly enhance the
717 seasonal SST range to up to 10 °C in 2300 given unabated CO_2 emissions (Carton et
718 al., 2015). With year-round snow and ice-free conditions, even stronger summer
719 stratification during the Eocene due to higher greenhouse gas concentrations and fresh-
720 water supply through an enhanced hydrological cycle (Pierrehumbert, 2002;
721 Carmichael et al., 2017), a near-shore 20 °C seasonal cycle in Arctic Ocean SST may
722 not be unrealistic, although it remains inconsistent with current-generation fully
723 coupled, relatively low resolution, model simulations (e.g., Frieling et al., 2017).
724 Constraints from the total pollen assemblages in the ACEX cores based on a nearest
725 living relative approach suggest Arctic mean annual temperatures on land of 13-18 °C,
726 and summer temperatures significantly exceeding 20 °C during the PETM and ETM2
727 (Willard et al., 2019). Although these estimates come with much larger uncertainty than
728 winter temperatures and may suffer from the non-analogous setting, they are generally
729 lower than our TEX_{86} values. The brGDGT-based paleothermometer MBT'_{5me} (De
730 Jonge et al., 2014) also indicates lower mean annual air temperatures than reported from
731 TEX_{86} (Willard et al., 2019, Figure 7). These data, derived from the same UHPLC/MS
732 analyses as the isoGDGT data presented here, indicate mean annual air temperatures
733 averaging ~18 °C during the PETM, with a residual mean calibration error of 4.8 °C.
734 This value is ~7 °C lower than earlier estimates based on a slightly different method,
735 analytical procedure and a smaller modern calibration dataset (Weijers et al., 2007a).
736

5.4 State of constraints on Paleocene-Eocene Arctic temperatures

To unlock the unique premise of Eocene climates for testing the skill of current-generation fully coupled climate models under high greenhouse gas forcing, proxy data and models are ideally approached separately. Among the most important implications of the Arctic temperature estimates are reconstructions of the meridional temperature gradients. Importantly, not a single simulation using an IPCC-class model of early Paleogene climate has produced Arctic annual mean sea surface temperatures close to the ACEX TEX_{86}-based reconstructions without unrealistically high tropical SSTs (Lunt et al., 2012). Recent simulations using the Community Earth System Model (CESM) versions 1 (Frieling et al., 2017; Cramwinckel et al., 2018) and 1.2 (Zhu et al., 2019) using Eocene boundary conditions produced climates that correspond to SST reconstructions in many ocean regions based on several proxies, but still produced cooler mean annual SSTs for the Arctic Ocean than suggested by TEX_{86} (Frieling et al., 2017; Cramwinckel et al., 2018; Zhu et al., 2019). TEX_{86} also indicates SSTs higher than in these model simulations at several sites along the Antarctic margin (Bijl et al., 2009; Bijl et al., 2013). The question thus remains if the conversion of TEX_{86} values towards mean annual SST using any modern core-top calibration for high latitude Paleogene locations is valid, or if the climate models still significantly underestimate polar temperatures. Certainly, if interpreted as mean annual SST, TEX_{86}-based estimates are high compared to the few available additional estimates, notably based on vegetation, but the latter also suffer from similar uncertainties (e.g., Hollis et al., 2019). A few biases might lead to underestimates of meridional temperature gradients as indicated from TEX_{86}. First, the flat Eocene temperature gradient implied by TEX_{86} was suggested to result from erroneously calibrating the proxy to SST rather than to the temperature of the subsurface (Ho and Laepple, 2016). The rationale is that the

meridional temperature gradient is smaller in deeper waters than it is in the surface. However, the idea was contested for multiple reasons, including the fact that sediments at most Eocene study sites, such as the ACEX site, were deposited at a depth of less than 200m, making the application of a deep subsurface (>1000m) calibration inappropriate (Tierney et al., 2017). Moreover, recent analyses have indicated that the TEX_{86} signal dominantly reflects temperature of top 200 m of the water column (Zhang and Liu, 2018).

Secondly, as suggested previously (Sluijs et al., 2006), if TEX_{86} were biased towards any season in the non-analogue Arctic Ocean, it would be the summer, the dominant season of organic matter export towards the seafloor through fecal pelleting or marine snow aggregates. Vegetation suggests very high winter continental coldest month mean air temperatures of at least 6-8 °C (Sluijs et al., 2009; Suan et al., 2017; Willard et al., 2019), coastal coldest month mean SSTs of >13 °C (Suan et al., 2017), and terrestrial mean annual and warmest month mean temperature on land of 13-21 °C and >20°C, respectively (Suan et al., 2017; Willard et al., 2019) (see section 5.3.2). These estimates are closer to the most recent model simulations and lower than the existing TEX_{86} (e.g., Frieling et al., 2017; Zhu et al., 2019). If TEX_{86}-implied SST of ~25 °C is skewed towards a summer estimate, this would decrease the model-data bias regarding the meridional temperature gradient estimates. Given the current uncertainties in the use of TEX_{86} for the non-analogue Arctic Ocean, we however cannot independently constrain this.

6. Conclusions

We analyzed isoGDGT and brGMGT (H-shaped brGDGT) distributions in sediments recovered from the Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma) to Eocene

Thermal Maximum 2 (ETM2; ~54 Ma) interval on Lomonosov Ridge, Arctic Ocean using state-of-the-art analytical procedures, compare them to the original dataset (Sluijs et al., 2006; Sluijs et al., 2009) and interpret the results following the currently available TEX_{86} proxy constraints.

Although contributions of isoGDGTs from land complicate TEX_{86} paleothermometry in some stratigraphic intervals, temperature was the dominant variable controlling TEX_{86} values. Background early Eocene SSTs exceed ~20 °C and peak warmth occurred during the PETM and ETM2. However, uncertainty estimates of these SSTs based on the non-analogue modern ocean, remains complex. Temperature constraints from terrestrial vegetation support remarkable warmth in the study section and elsewhere in the Arctic basin, notably coldest month mean temperatures around 10 °C at least within the PETM and ETM2. If TEX_{86}-derived SSTs of ~20 °C truly represent mean annual SSTs, the seasonal range of Arctic SST might have been in the order of 20 °C. If SST estimates are entirely skewed towards the summer season, seasonal ranges in the order of 10 °C may be considered comparable to those simulated in future ice-free Arctic Ocean scenarios.

We find abundant brGMGTs, which appear predominantly produced in the marine realm at the study site. Their abundance increases during the PETM, likely due to sea level rise and perhaps due to warming and a drop in seawater oxygen concentrations. Although speculative, an increase in brGMGT methylation during the PETM may be a function of temperature, but a relation between brGMGT distribution and environmental parameters including temperature is yet to be confirmed.

6. Data Availability

All data is provided in the Supplement Table and will be included in the PANGAEA database upon publication of this paper.

7. Sample Availability

Requests for materials can be addressed to A.Sluijs@uu.nl

8. Author Contributions

AS initiated the study, KGJN generated the data, JF modeled terrestrial contributions of isoGDGTs based on published information and the new Crenarchaeol data of the modern peat dataset, which was contributed by GNI. All authors contributed to the interpretation of the data and AS wrote the paper with input from all authors.

9. Competing Interests

The authors declare no competing interests

10. Acknowledgments

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Figure 1. Location of ACEX Hole 4A within a paleogeographic reconstruction of the Arctic region at the time of the PETM. Reconstruction made using gplates (Müller et al., 2018), with the tectonic reconstruction of Seton et al. (2012, red shape is Lomonosov Ridge in this reconstruction and grey lines are structural features including spreading ridges), the paleomagnetic reference frame of Torsvik et al., (2012), and modern coastlines.

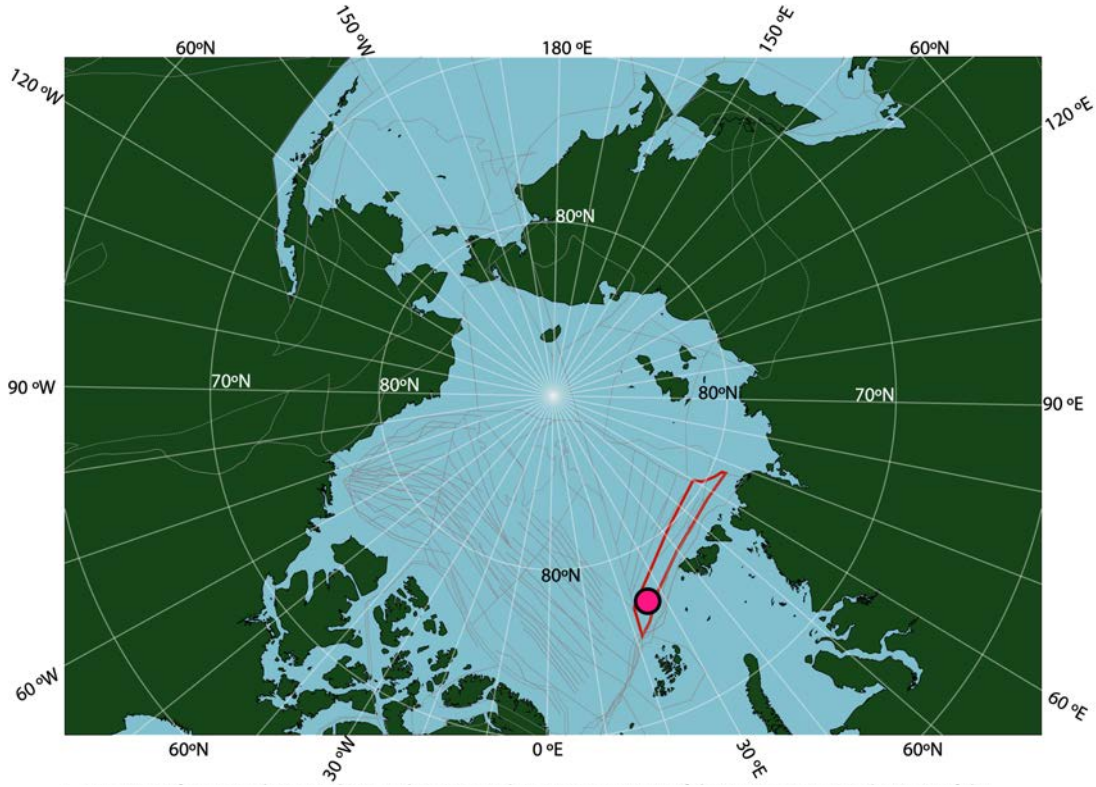


Figure 2. Molecular structures of the relevant isoGDGTs, brGDGTs and brGMGTs and their terminology as described in this study. Crenarchaeol isomer (not shown) differs from Crenarchaeol in the stereochemistry of the cyclopentane moiety adjacent to the cyclohexyl moiety (Sinninghe Damsté et al., 2018b). For the terminology of the brGMGTs, for which the exact chemical structure is still unclear, we follow Baxter et al. (2019), since we identify the same isomers (see Figure S2 for a chromatogram).

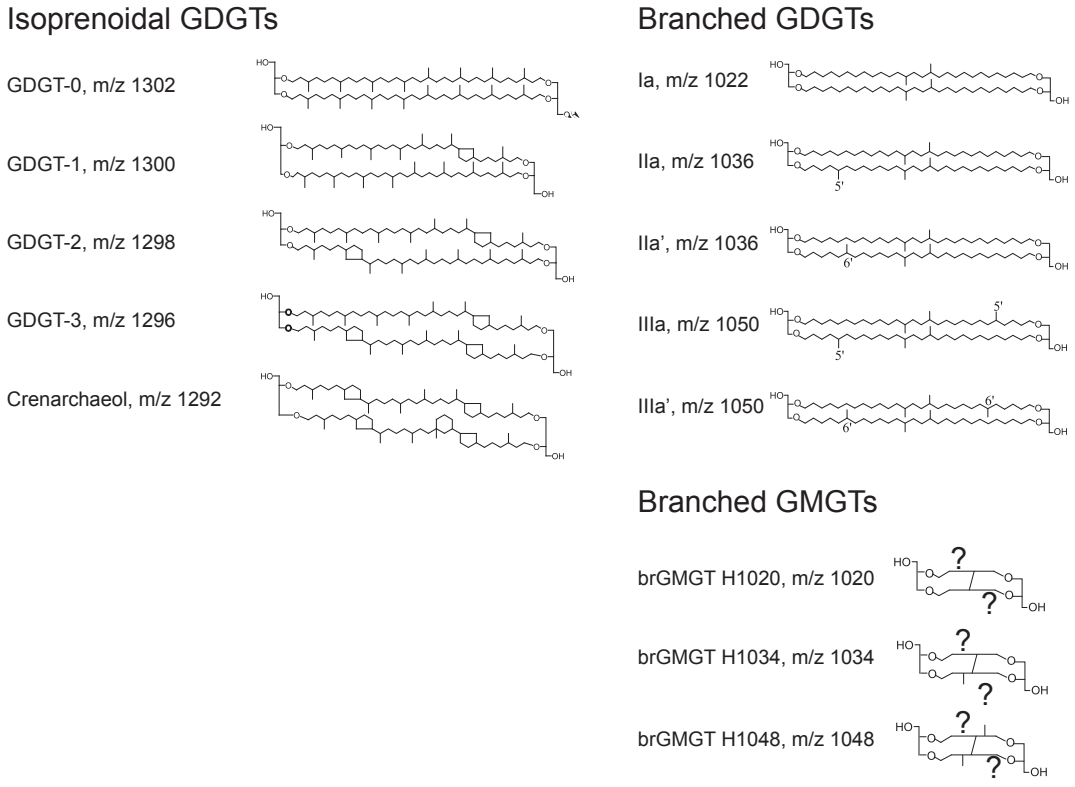
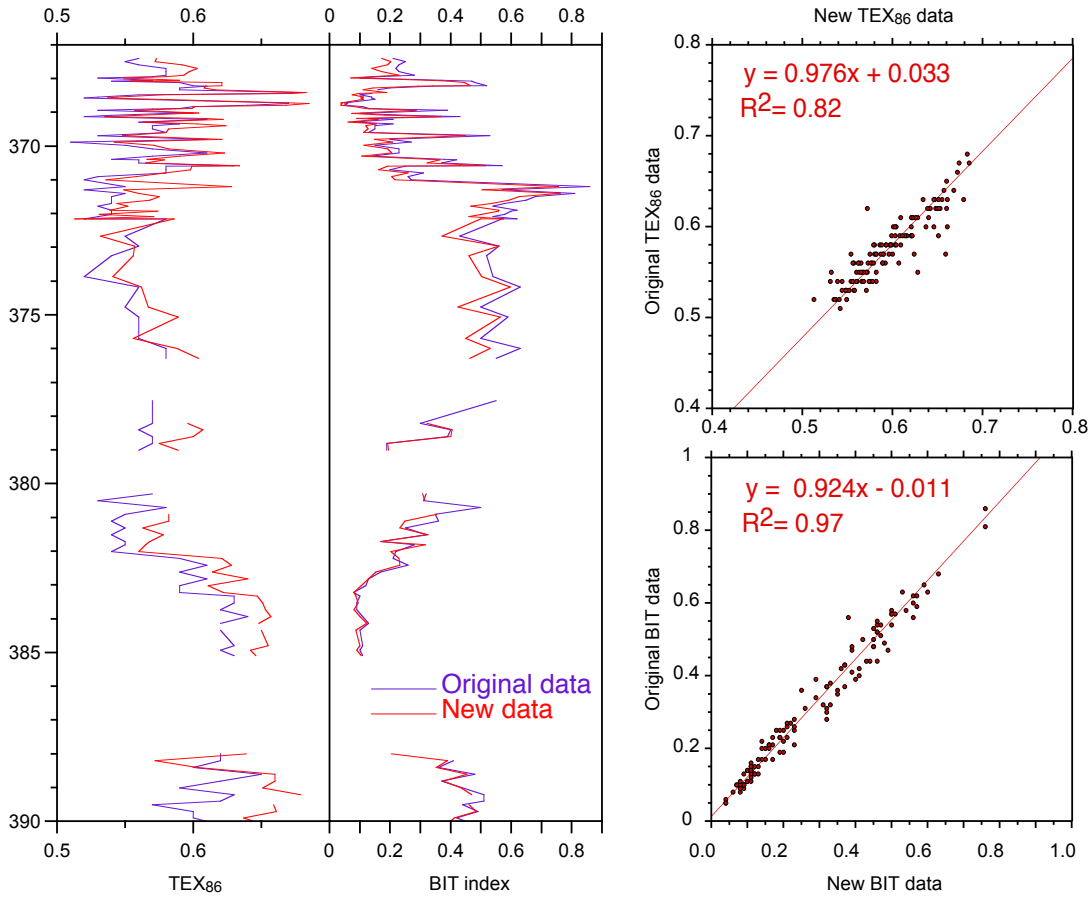
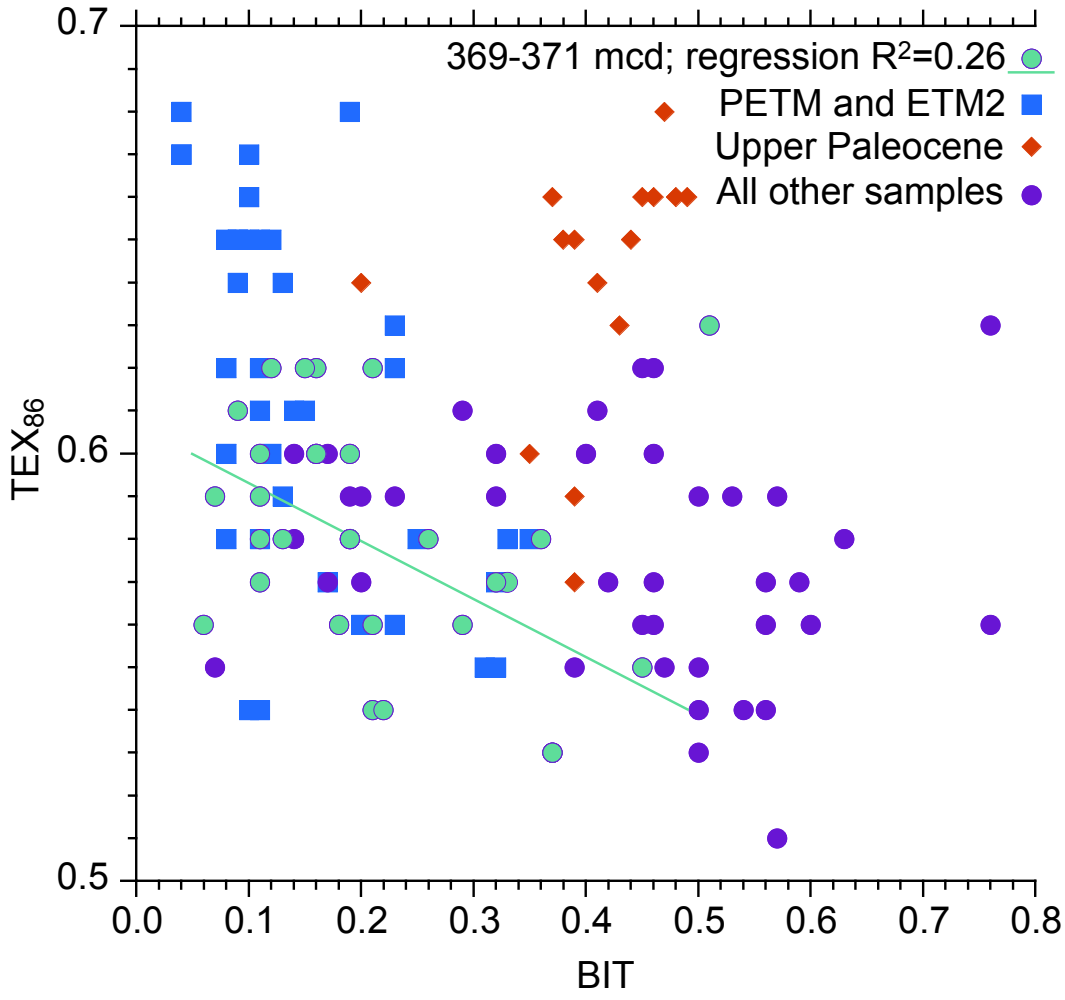


Figure 3. Comparison of the original GDGT dataset of the upper Paleocene and lower Eocene of ACEX Hole 4A (Sluijs et al., 2006; Sluijs et al., 2009) and the new data generated according to the latest chromatography protocols.



1342 **Figure 4.** Comparison between BIT index values and TEX_{86} for various intervals

1343 spanning the upper Paleocene and lower Eocene of ACEX Hole 4A.



1344

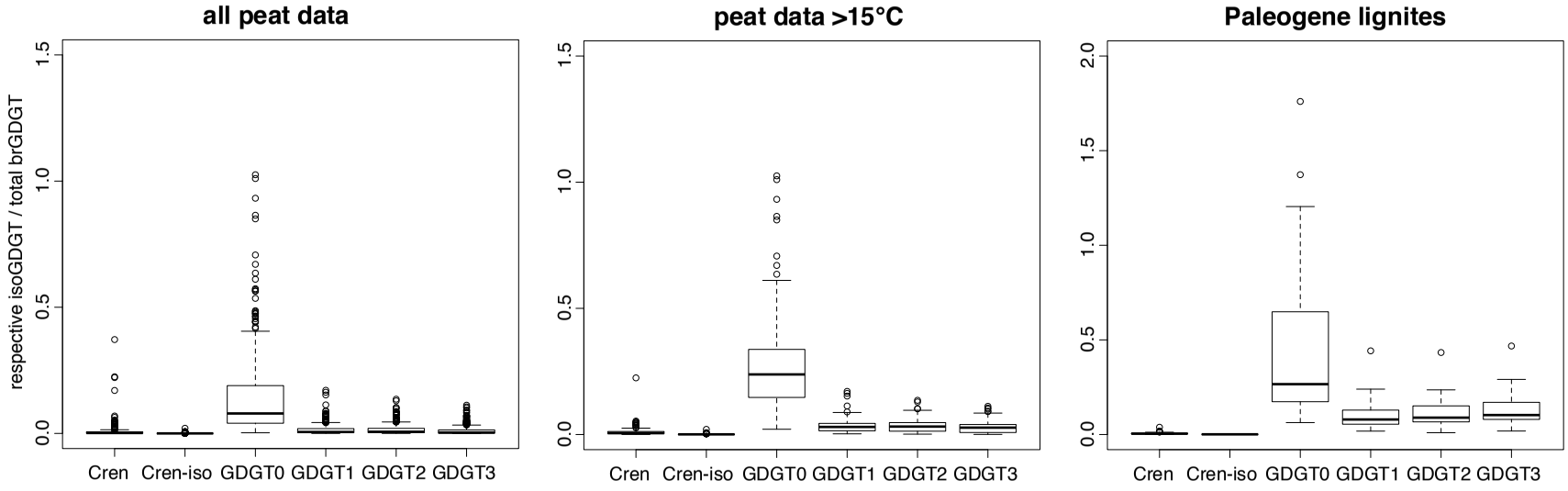


Figure 5. The abundance of various isoGDGTs relative to the total brGDGT abundance in modern peats (left 2 panels) and Paleogene lignites (right panel; Equation 9), used to assess potential isoGDGT contributions to the ACEX samples. The box is standard 25%-50%-75% quantiles, whiskers represent box limits plus/minus 1.5 x the interquartile range (IQR). Any data outside that range is given as circles. Number of measurements per dataset: Modern peats = 473 (most isoGDGTs have been identified in ±430 of those; Modern peats above 15ºC = 141 (all except one of there have isoGDGT data; Lignites = 58 (allof which have isoGDGT data but only 29 have available (quantifiable) crenarchaeol isomer data).

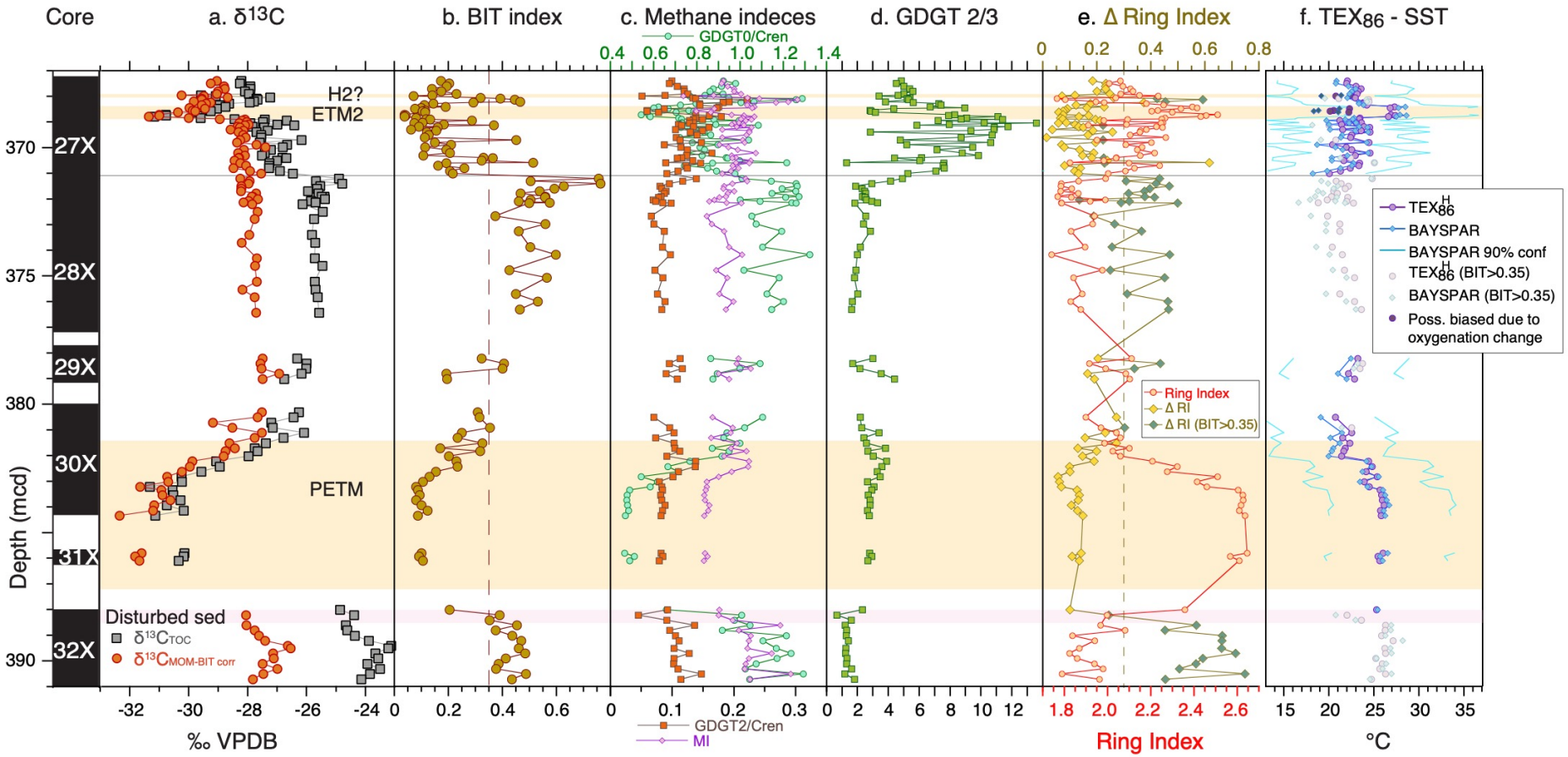


Figure 6. Branched and Isoprenoid GDGT records across the upper Paleocene and lower Eocene of ACEX Hole 4A. a. carbon isotope stratigraphy (total organic carbon record from Sluijs et al., 2006 and 2009; marine organic matter record from Sluijs and Dickens (2012)), b. BIT index (equation 2), c. indices indicative of anaerobic archaeal methanotrophy (MI index (equation 3) and GDGT-2/Crenarchaeol), and methanogenesis (GDGT-0/Crenarchaeol), d. GDGT2-GDGT3 ratio, e. Ring index (equation 5) and Δ Ring Index, f. TEX_{86} (equation 1) calibrated to sea surface temperature using a non-linear calibration TEX_{86}^{H} calibration (Kim et al., 2010) and the BAYSPAR method, which is based on a linear calibration (Tierney and Tingley, 2014).

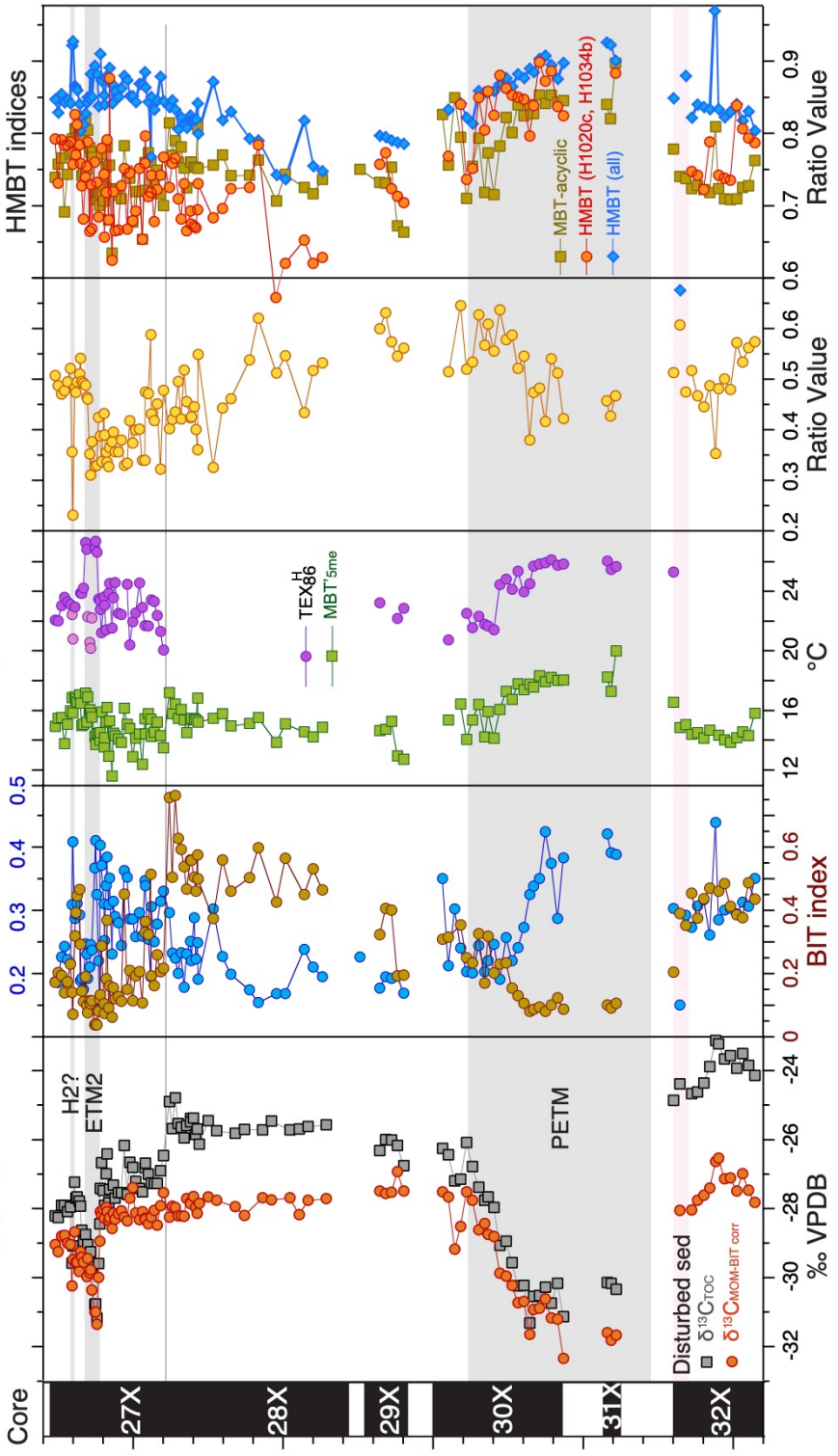


Figure 7. Branched GMGT records across the upper Paleocene and lower Eocene of ACEX Hole 4A. a. carbon isotope stratigraphy (total organic carbon record from Sluijs et al., 2006 and 2009; marine organic matter record from Sluijs and Dickens (2012)), b. fraction of brGMGTs of the total branched GDGTs and GMGTs and BIT index (equation 2), c. MBT'$_{5me}$ record (Willard et al., 2019) and TEX^{H}_{86}, d. MBT*acyclic* (equation 6) and H-MBT based on all isomers detected with m/z 1020 and m/z 1034 (H-MBT all; equation 7) and based on H1020a and H1034b (H-MBT H1020a, H1034c), e. brGMGT-1 record (equation 8).