- 1 Review by the editor (after revised submission):
- 2

3 Editorial comment: As you acknowledge,  $TEX_{86}$  can be significantly affected (e.g. result in lower 4 SSTs) by changes in thermal maturity of organic matter (Schouten et al., 2004; 2013). One way to 5 check for the influence of thermal maturity is by using the distribution of hopanes (a type of 6 biomarker). You determine the hopane ratio in (only) two samples, which according to your results are 7 thermally very immature (only the immature BB hopanes are found). Based on these two data points 8 you argue that thermal maturity is constantly low throughout the section ("We only checked two 9 samples because typically the degree of thermal maturation in a section like this will be similar") and 10 hence  $\text{TEX}_{86}$  can be applied with confidence.

11

12 However, (and as highlighted in the original comments of the reviewer), this is directly contradicting 13 previously published results from the same section (Blumenberg and Wiese, 2012). That study did 14 detect the thermally more mature ab and ba hopanes. Together this suggests changes in thermal 15 maturity between samples (from samples with only immature bb hopanes as measured and presented 16 in your work to samples with significant amounts of the more mature ab hopanes as shown by 17 Blumenberg and Wiese (2012). Based on the results of Blumenberg and Wiese (2012) it is difficult to 18 judge whether the thermal maturity is significantly high enough to affect TEX<sub>86</sub>, but the reviewer 19 requests that you should acknowledge 1) the Blumenberg and Wiese (2012) study that suggests higher 20 thermal maturity in parts of the section, 2) indicate that thermal maturity is changing in the section and 21 3) that this might affect  $TEX_{86}$  (but as you do not want to measure the hopane distributions in all 22 samples used for  $TEX_{86}$  it is impossible to know which samples might be affected).

23

24 Author's reply: We evaluated the Blumenberg and Wiese (2012) study once more and we do not see how this conflicts our results. Blumenberg and Wiese (2012) report for the bitumen (extractable 25 26 biomarkers) a wide variety of biomarkers including functionalized hopanoids and steroids, which are 27 only present in thermally immature sediments. Accordingly, they report that various types of 28 hopanoids are dominated by the  $17\beta$ ,  $21\beta$ (H)-stereochemistry. This is in excellent agreement with our 29 results. In the same paper, Blumenberg and Wiese (2012) also report much higher degrees of thermal 30 maturity based upon isomerization ratios of biomarkers in hydropyrolysates generated from the 31 kerogen. However, to obtain these pyrolyzates these kerogens were heated by temperatures up to 32 500°C. It is well known that during such experiments the degree of isomerization of biomarkers alters 33 towards a thermodynamic equilibrium mixture depending on time of the experiment and temperature 34 applied (e.g., see Koopmans et al., 1996; Figure 4). Accordingly, the data of Blumenberg and Wiese 35 (2012) obtained from the hydropyrolysates are not relevant to assess the *natural* level of thermal 36 maturity and, therefore, there is no conflict between the Blumenberg and Wiese (2012) data and our data, and the sediments studied can be confidently applied for TEX<sub>86</sub> palaeothermometry. In addition, 37

we would like to stress that it is very unlikely that the degree of thermal maturity will change over a distance of 25 m (difference in depth of the studied section). This relates to the relatively modest geothermal gradient of 2.5°C per 100 m. Therefore, we feel that the examination of two samples from the studied section suffices to determine the degree of thermal maturity of the studied section.

5

6 We have added two sentences to the methods (Page 7, Lines 21-24): "Only two samples were analyzed
7 because it is very unlikely that the degree of thermal maturity will change over a distance of 25 m
8 (difference in depth of the studied section). This relates to the relatively modest geothermal gradient of
9 2.5°C per 100 m."

10

11 We have rephrased the results section reporting on thermal maturity as follows (Page 9, Lines 13-29): 12 "For two selected samples the hopane distribution was determined.  $C_{31}17\beta,21\beta(H)$  hopane was the 13 dominant hopane. No  $\alpha\beta$ -hopanes were encountered, so the  $(\beta\beta/(\beta\beta+\beta\alpha+\alpha\alpha))$  of hopane biomarkers 14 was 1. This is in perfect agreement with Blumenberg and Wiese (2012), who report that various types 15 of hopanoids, for the same core, are dominated by the  $17\beta$ ,  $21\beta$  (H)-stereochemistry. This indicates 16 that the thermal maturity of the sedimentary organic matter was sufficiently low for the application of 17 *TEX*<sub>86</sub> paleothermometry (cf. Schouten et al., 2004). 18 Blumenberg and Wiese (2012) also report much higher degrees of thermal maturity based upon 19 isomerization ratios of biomarkers in hydropyrolysates generated from the kerogen. However, to 20 obtain these pyrolysates, kerogens were heated by temperatures up to 500°C. It is well known that 21 during such experiments the degree of isomerization of biomarkers alters towards a thermodynamic 22 equilibrium mixture depending on time of the experiment and temperature applied (e.g., Koopmans et 23 al., 1996). Accordingly, the data of Blumenberg and Wiese (2012) obtained from the hydropyrolysates 24 are not relevant to assess the natural level of thermal maturity. Therefore there is no conflict between

- 25 the data of Blumenberg and Wiese (2012) and the data presented in this study."
- 26

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discharge controlled deposition Freshwater of 1 Cenomanian-Turonian black shales on the NW European 2 epicontinental shelf (Wunstorf, North Germany) 3 4 5 N.A.G.M. van Helmond<sup>1</sup>, A. Sluijs<sup>1</sup>, J.S. Sinninghe Damsté<sup>2,3</sup>, G.-J. Reichart<sup>2,3</sup>, S. Voigt<sup>4</sup>, J. Erbacher<sup>5</sup>, J. Pross<sup>6</sup>, H. Brinkhuis<sup>1,3</sup> 6 7 8 [1]{Marine Palynology and Paleoceanography, Laboratory of Palaeobotany and Palynology, 9 Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Budapestlaan 4, 10 3584 CD Utrecht, Netherlands} 11 [2] {Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Budapestlaan 12 4, 3584 CD Utrecht, Netherlands} [3]{NIOZ, Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg, 13 14 Texel, Netherlands} [4] [Institute of Geosciences, Goethe-University Frankfurt, Altenhöferallee 1, 60438 15 16 Frankfurt, Germany} 17 [5] Bundesanstalt für Geowissenschaften und Rohstoffe, P.O. Box 51 01 53, Alfred-Benz-18 Haus, Stilleweg 2, 30641 Hanover, Germany} 19 [6] {Paleoenvironmental Dynamics Group, Institute of Earth Sciences, University of 20 Heidelberg, Im Neuenheimer Feld 234, 69120 Heidelberg, Germany} 21 Correspondence to: N.A.G.M. van Helmond (n.vanhelmond@uu.nl) 22 23 Abstract 24 Global warming, changes in the hydrological cycle and enhanced marine primary productivity 25 all have been invoked to have contributed to the occurrence of widespread ocean anoxia 26 during the Cenomanian-Turonian Oceanic Anoxic Event (OAE2; ~94 Ma), but disentangling 27 these factors on a regional scale has remained problematic. In an attempt to separate these

forcing factors, we generated palynological and organic geochemical records using a core spanning the OAE2 from Wunstorf, Lower Saxony Basin (LSB; North Gemany), which

- 30 exhibits cyclic black shale marl alternations related to the orbital precession cycle.
- 31 Despite the widely varying depositional conditions complicating the interpretation of the 32 obtained records,  $\text{TEX}_{86}^{\text{H}}$  indicates that sea-surface temperature (SST) evolution in the LSB
- 33 during OAE2 resembles that of previously studied sites throughout the proto-North Atlantic.

1 Cooling during the so-called Plenus Cold Event interrupted black shale deposition during the 2 early stages of OAE2. However, TEX<sub>86</sub> does not vary significantly across marl-black shale 3 alternations, suggesting that temperature variations did not force the formation of the cyclic black shale horizons. Relative (i.e., with respect to marine palynomorphs) and absolute 4 5 abundances of pollen and spores are elevated during phases of black shale deposition, 6 indicative of enhanced precipitation and run-off. High abundances of cysts from inferred 7 heterotrophic and euryhaline dinoflagellates supports high run-off, which likely introduced 8 additional nutrients to the epicontinental shelf resulting in elevated marine primary 9 productivity.

We conclude that orbitally-forced enhanced precipitation and run-off, in tandem with elevated marine primary productivity, were critical in cyclic black shale formation on the northwest European epicontinental shelf and potentially for other OAE2 sections in the proto-Atlantic and Western Interior Seaway at similar latitudes as well.

14

### 15 **1** Introduction

16 Dark, often laminated marine sediments that are usually devoid of fossil traces of benthic life 17 and exhibit a total organic carbon (TOC) content of >1% (Creaney and Passey, 1993), were 18 episodically deposited during Jurassic and Cretaceous times. The deposition of these 19 sediments, generally referred to as black shales, has typically been taken to indicate ancient 20 episodes of dys- or anoxic bottom water conditions (Schlanger and Jenkyns, 1976). During 21 some of these episodes, anoxia developed widespread in one or more ocean basins; such 22 episodes were termed Oceanic Anoxic Events (OAEs; Schlanger and Jenkyns, 1976). One of 23 the most prominent, best-constrained and best-studied of these OAEs formed across the 24 Cenomanian-Turonian boundary (CTB; ~94 Ma) and became known as OAE2 (e.g., Jenkyns, 25 2010). The widespread enhanced organic carbon burial in marine sediments during OAE2 is 26 expressed by a worldwide documented >2‰ positive carbon isotopic excursion (CIE) of carbonate ( $\delta^{13}C_{carb}$ ) and organic matter ( $\delta^{13}C_{org}$ ), with an estimated duration of 450-600 kyr 27 28 (e.g., Voigt et al., 2008; Meyers et al., 2012). This CIE likely resulted from enhanced burial of  $\delta^{13}$ C-depleted organic matter (Arthur et al., 1988; Tsikos et al., 2004) and therefore provides a 29 30 C-isotopic signature of the global exogenic carbon pool, making it a proper tool to confidently 31 correlate OAE2 sections.

Over the past decades, many studies have been conducted to unravel the processes responsible for this massive burial of organic carbon during OAEs, and OAE2 in particular. Extensive volcanism close to the CTB (e.g. Snow et al., 2005; Kuroda et al., 2007; Turgeon and Creaser,

1 2008) has been linked to high levels of atmospheric CO<sub>2</sub> (e.g., Schouten et al., 2003; 2 Sinninghe Damsté et al., 2008; Barclay et al., 2010), raising the temperatures of already warm 3 oceans towards a maximum at the onset of OAE2 (e.g., Bice et al., 2006; Forster et al., 2007), 4 which reduced the solubility of oxygen in surface waters. This warming caused an enhanced 5 hydrological cycle (van Helmond et al., 2014), which would likely have contributed to 6 increased rates of continental weathering and runoff (Blätter et al., 2011; Pogge von 7 Strandmann et al., 2013). This, in turn would have led to at least seasonal stratification and enhanced nutrient supply to continental margins and epicontinental seas. Extensive volcanism 8 9 may also have directly contributed to ocean fertilization (Kerr et al., 1998; Snow et al., 2005), 10 while changes in proto-Atlantic circulation may have increased the strength of upwelling 11 (e.g., Poulsen et al., 2001; Junium and Arthur, 2007). Enhanced regeneration of sedimentary 12 phosphorus from dysoxic and anoxic sediments (e.g., Kuypers et al., 2004b; Mort et al., 2007) 13 combined with abundant nitrogen-fixing cyanobacteria (Kuypers et al., 2004b) may have 14 sustained high levels of primary productivity. All of the above factors would conspire to 15 expansion of oxygen minimum zones and oxygen depletion of bottom waters, leading to 16 enhanced organic carbon burial.

17 As a result of late Cenomanian sea level rise (e.g., Erbacher et al., 1996; Voigt et al., 2006), 18 large parts of continents became flooded, greatly expanding the extent of epicontinental shelf 19 seas where sediments recording the OAE2 were deposited. Particularly the Lower Saxony 20 Basin (LSB; northwest Germany) exhibits expanded and complete OAE2-succesions 21 (Wilmsen, 2003) containing several cyclic alternations of organic-poor marls, limestones and 22 organic-rich black shales (Voigt et al., 2008). Organic matter accumulation on the European 23 shelf was relatively modest, however, compared with other cyclic OAE2-sections in the 24 proto-Atlantic (Kuypers et al, 2004a; Forster et al., 2008).

25 The complete OAE2-interval has been recovered from the LSB through coring at Wunstorf 26 (Erbacher et al., 2007; North Germany; Fig. 1). Application of an orbital cycle-based age 27 model has shown that black shale deposition in the Wunstorf core sediments is consistent with 28 precession forcing (Voigt et al., 2008). This implies that climate change resulting from orbital 29 fluctuations was directly related to phases of black shale deposition. The robust 30 cyclostratigraphy and biostratigraphic zonation of the Wunstorf core allows for a high-31 resolution study of astronomically-induced climate change. Here we aim to reconstruct mean 32 annual sea surface temperature (SST), hydrological changes and marine primary productivity, 33 to determine the dominant control on decreasing oxygen concentrations during OAE2 on the 34 European shelf. To this end, we combined organic geochemical (TEX<sub>86</sub>; BIT index) and

palynological proxies, notably organic-walled dinoflagellate cysts (dinocysts) and pollen and
 spore abundances, across the CTB for the Wunstorf core.

3

4

### 2 Material and methods

## 5 2.1 Site description, depositional setting and age model

6 The Wunstorf core was drilled in 2006 ~25 km west of Hannover, Germany (52°24.187'N, 7 9°29.398''E, Voigt et al., 2008; Fig.1). Approximately 76 m of middle Cenomanian to middle 8 Turonian sediments, comprising a ~13.5 m thick CTB succession, were retrieved. During the 9 Late Cretaceous, the drill site was located in the LSB, which was part of the expanded epicontinental shelf sea that covered most of Eurasia after the Cenomanian transgression 10 11 (Hancock and Kauffman, 1979). The sediments at Wunstorf were deposited at an estimated 12 water depth of 100-150 m based on sequence stratigraphy, sedimentological analysis and 13 (micro)fossil content (Wilmsen, 2003). The most proximal exposed land, the Rheno-Bohemian 14 Massif, was located ~150 km to the south and formed a barrier towards the Western Tethys. 15 The Armorican and British massifs formed a barrier towards the Atlantic, while the Fennoscandian Shield formed a barrier to the open ocean in the north (Fig.1; Wilmsen, 2003). 16 17 The OAE2-interval at Wunstorf is part of the Hesseltal Formation and occurs between 49.6 and 23.1 meters below surface (mbs). The Hesseltal Formation consists of rhythmically 18 19 alternating couplets of finely laminated black shales with elevated levels oftotal organic carbon (TOC; max. 2.8%; Hetzel et al., 2011; Fig. 2b), grey to green marls, and light-grey 20 21 (marly) limestones (Fig. 2; Erbacher et al., 2007; Voigt et al., 2008). The cyclic lithology 22 results from a depositional system greatly influenced by precession (Voigt et al., 2008). 23 Biostratigraphic zonation for the Hesseltal Formation relies on inoceramids, ammonites, acme 24 occurrences of macrofossils and planktonic foraminifera that can be reliably correlated

regionally and globally (Ernst et al., 1984; Voigt et al., 2008, and references therein).

The onset of the OAE2-interval is primarily based on the first occurrence (FO) of the 26 ammonite Metoicoceras geslinianum at 49.6 mbs, consistent with the English Chalk (Voigt et 27 al., 2008). At 47.8 mbs, the onset of the characteristic positive shift in  $\delta^{13}C_{carb}$  (~2‰) and 28  $\delta^{13}C_{org}$  (~2.5‰) was recognized (Voigt et al., 2008; Du Vivier et al., 2014; Fig. 2a).The 29 30 termination of the OAE2 interval at Wunstorf was placed at 36 mbs (Voigt et al., 2008). The 31 duration of the OAE2 for the Wunstorf core was estimated at ~435 kyr or ~500 kyr based on spectral analyses of the lithological cyclicity and  $\delta^{13}C_{org}$ , respectively (Voigt et al., 2008; Du 32 33 Vivier et al., 2014).

34

#### 1 **2.2** Total organic carbon analysis

About 0.3 g of freeze-dried and powdered sediment sample was decalcified using 1M HCl, followed by rinsing with demineralized water and drying again. Total Organic Carbon (TOC) concentrations were measured using a Fisons Instruments CNS NA 1500 analyzer and corrected for weight loss during decalcification. Results were normalized to in-house standards, acetanilide, atropine and nicotinamide. The average analytical uncertainty based on duplicate analyses of sediment samples was 0.04 weight percent (wt.%).

8

## 9 2.3 Organic geochemistry

10 For 48 samples, biomarkers were extracted from 10-15 g of powdered and freeze-dried 11 sediments with a Dionex accelerated solvent extractor (ASE) using dichloromethane (DCM)/ 12 methanol mixture (9:1, v/v). Total lipid extracts (TLEs) were evaporated to near dryness 13 using rotary evaporation. Subsequently, remaining solvents were removed under a nitrogen 14 flow. The TLEs were separated by  $Al_2O_3$  column chromatography, into apolar, ketone, 15 glycerol dialkyl glycerol tetraether (GDGT) and polar fractions using three column volumes of the eluents hexane/DCM (9:1, v/v), ethyl acetate (v), DCM/methanol (95:5, v/v) and 16 17 DCM/methanol(1:1, v/v), respectively. The apolar and GDGT fractions were dried under a 18 nitrogen flow and weighed. The apolar fractions of two samples (41.14 mbs and 42.81 mbs), 19 selected based on their high yield, were measured using gas chromatography-mass 20 spectrometry (GC-MS), to determine the thermal maturity of the sediments based on the 21 degree of isomerisation of hopanes. Only two samples were analyzed because it is very 22 unlikely that the degree of thermal maturity will change over a distance of 25 m (difference in 23 depth of the studied section). This relates to the relatively modest geothermal gradient of 24 2.5°C per 100 m. -Analyses were performed on a Thermo Finnigan Trace Gas Chromatograph (GC) Ultra connected to a Thermofinnigan DSQ mass spectrometer operated at 70 eV, with a 25 range of m/z 50–800 and a cycle time of 3 scans  $s^{-1}$ . The temperature program and column 26 27 conditions resemble that of Sinninghe Damsté et al. (2008). To quantify the GDGT abundances a known amount of C<sub>46</sub> GDGT-standard was added (Huguet et al., 2006), after 28 29 which the GDGT-fractions were re-dissolved in hexane/propanol (99:1, v/v) and filtered over 30 a 0.45 µm mesh PTFE filter. The filtered GDGT fractions were analysed using high 31 performance liquid chromatography - atmospheric pressure chemical ionization/ mass 32 spectrometry (HPLC-APCI/MS) according to the method described in Schouten et al. 33 (2007a). Analysis were performed on an Agilent 1290 infinity series coupled to a 6130 single 34 quadrupole MSD, equipped with auto-injection system and HP-Chemstation software.

Separation was achieved on a Prevail Cyano column (150 mm x 2.1 mm, 3 µm; Alltech). 1 2 GDGTs (m/z 1018-1302) were detected using selective ion monitoring. For this method it was exhibited that for samples with a high TEX<sub>86</sub> value, a concentration of 0.1 ng of injected 3 4 GDGTs on the LC column was still sufficient to yield trustworthy TEX<sub>86</sub> values (Schouten et 5 al., 2007a). The minimum GDGT concentration injected on the LC column per measurement 6 in this study was ~0.3 ng. TEX<sub>86</sub>-index values were calculated after Schouten et al. (2002), and converted to absolute annual average sea surface temperatures (SSTs) using the  $TEX_{86}^{H}$ 7 8 Kim et al. (2010) modern core top calibration, which has a calibration error of 2.5°C. 9 Analytical reproducibility was generally better than 0.3°C.

The Branched and Isoprenoid Tetraether (BIT) index was used to estimate the relative 10 11 abundance of soil organic matter in marine sediments (Hopmans et al., 2004). The BIT index 12 is based on the amount of predominantly soil-derived branched GDGTs (brGDGTs) relative 13 to the isoprenoid GDGT (iGDGT) crenarchaeol, which is chiefly derived from marine 14 Thaumarchaeota. Application of the BIT index may be complicated by in situ production of 15 brGDGTs in the marine water column and in marine sediments and the ubiquitous presence of crenarchaeol in soils. Nonetheless many studies have shown that the BIT index is still a useful 16 17 tracer for continental organic matter in marine environments (Schouten et al., 2013).

18

#### 19 2.4 Palynology

20 In total 51 samples were prepared for quantitative palynological analysis. In general between 21 5 and 10 g, and for samples low in organic carbon up to ~20 g, of freeze-dried sediment 22 sample were crushed to pieces smaller than 5 mm. Subsequently a known amount of 23 Lycopodium marker spores was added to allow for quantitative analysis. After reaction with 24 ~30% HCl and twice with ~38% HF, to dissolve carbonates and silicates respectively, 25 ultrasonic separation was employed. Finally, samples were sieved over a 15 µm nylon mesh. 26 Residuals were mounted on slides for microscopic analysis. Approximately 250 dinocysts per 27 sample were counted using a light microscope at 500x magnification. Taxonomy follows that 28 of Fensome and Williams (2004). Pollen and spores were counted as one group, except for 29 saccate gymnosperm pollen. All samples and slides are stored in the collection of the 30 Laboratory of Palaeobotany and Palynology, Utrecht University, the Netherlands.

- 31
- 32 3 Results

### **33 3.1 Total organic carbon**

Trends in, and absolute values of TOC (Fig. 2) are generally in agreement with results 1 2 reported by Hetzel et al. (2011), i.e., relatively high for black shales and low for marls and 3 limestones. The background TOC content is <0.3%, somewhat higher than reported by Hetzel 4 et al. (2011). Within the OAE2, four intervals with elevated TOC content are identified. The 5 first interval is between 49 and 47.5 m and contains the first black shale, at the onset of the 6 CIE. A second organic-rich cluster is recognized between ~44 and 42 mbs, with the maximum 7 TOC content approaching 2%. The third organic-rich interval is from 41 to 39.5 mbs, with a maximum TOC content just over 2.5%. The last organic-rich cluster ranges from 37.5 to 35.5 8 9 mbs, with a maximum TOC content just above 2%. For the remainder of the record, only the 10 youngest sample (26.51 mbs) has an elevated TOC content (close to 1.5%).

11

# 12 3.2 Thermal maturity

13 For two selected samples the hopane distribution was determined.  $C_{31}17\beta$ ,  $21\beta$ (H) hopane was 14 the dominant hopane. No  $\alpha\beta$ -hopanes were encountered, so the  $(\beta\beta/(\beta\beta+\beta\alpha+\alpha\alpha))$  of hopane 15 biomarkers was 1. This is in perfect agreement with Blumenberg and Wiese (2012), who report that various types of hopanoids, for the same core, are dominated by the  $17\beta$ ,  $21\beta$  (H)-16 17 stereochemistry.; in agreement with results on sediments from this core presented by 18 Blumenberg and Wiese (2012). This indicates that the thermal maturity of the sedimentary 19 organic matter was sufficiently low for the application of TEX<sub>86</sub> paleothermometry (cf. 20 Schouten et al., 2004).

21 Blumenberg and Wiese (2012) also report much higher degrees of thermal maturity based 22 upon isomerization ratios of biomarkers in hydropyrolysates generated from the kerogen. 23 However, to obtain these pyrolysates, kerogens were heated by temperatures up to 500°C. It is 24 well known that during such experiments the degree of isomerization of biomarkers alters 25 towards a thermodynamic equilibrium mixture depending on time of the experiment and 26 temperature applied (e.g., Koopmans et al., 1996). Accordingly, the data of Blumenberg and 27 Wiese (2012) obtained from the hydropyrolysates are not relevant to assess the natural level 28 of thermal maturity. Therefore there is no conflict between the data of Blumenberg and Wiese 29 (2012) and the data presented in this study.

30

## 31 **3.3 GDGT-based proxies**

Except for Sample 41.45 mbs, all samples yielded quantifiable GDGT abundances, although with orders of magnitude differences in concentration (Fig. 2c). Total GDGT concentrations are in the range of 0.13-43  $\mu$ g/g organic carbon (OC). Crenarchaeol concentrations vary by

1 three orders of magnitude, whereas brGDGT concentrations vary by one to two orders of 2 magnitude. High GDGT concentrations coincide with the organic carbon-rich black shales 3 (Figs. 2b,c), while low GDGT concentrations coincide with organic-poor sediments (Figs. 2b,c). Values for the BIT-index range from 0.02, indicating low relative abundances of soil-4 5 derived brGDGTs, to 0.56, evidencing substantial soil-derived input of brGDGTs. The BIT-6 index (Fig. 2d) is relatively high in the organic-poor intervals and generally low (i.e. <0.10) 7 for the organic-rich black-shale intervals. Values for TEX<sub>86</sub> fluctuate between 0.71 and 0.99 8 (Fig. 2e).

9

### 10 **3.4 Palynology**

Nine samples were barren of palynomorphs (Fig. 3c). For the remaining 42 samples, dinocyst concentrations range from ~35 to 15000 cysts per gram, and pollen and spores concentrations range from 10> to 5000 grains per gram, with highest concentrations in the organic-rich black shales (Fig. 3c).

Palynological assemblages are dominated by dinocysts, ~85% on average (max. >99%).
Summed pollen and spores, and hence the terrestrially derived fraction, comprises on average ~15% of the assemblage (max. ~40%). The terrestrial over marine palynomorph ratio (T/M-ratio) was calculated by dividing terrestrial palynomorphs (pollen and spores) by aquatic palynomorphs (dinocysts and acritarchs). In general T/M-values are elevated in the organic-rich intervals (Fig. 3h), while minima in the T/M-ratio correspond to organic-poor intervals.
Age-diagnostic dinocyst species include *Lithosphaeridium siphoniphorum siphoniphorum*, a

marker species for the CTB interval in the northwest European reference section at Eastbourne (Pearce et al., 2009). The last occurrence of *L.siphoniphorum siphoniphorum* is at 47.81 mbs (Fig. 3f), confirming a latest Cenomanian age.

25 Dinocyst assemblages are dominated by multiple species of the Peridiniaceae family, i.e., 26 Paleohystrichophora infusorioides, Subtilisphaera pontis-mariae, Eurydinium saxoniense, 27 Isabelidiniumspp., and Ginginodinium spp.. Members of this family have repeatedly been 28 shown to be derived of low-salinity tolerant dinoflagellates in Late Cretaceous and Paleogene 29 successions and likely represent heterotrophic, euryhaline dinoflagellates (e.g., Harland, 1973; 30 Sluijs and Brinkhuis, 2009; Powell et al., 1990; Lewis et al., 1990; Fig. 3c). Other 31 quantitatively important taxa include Spiniferites spp. (Fig.3d) and Impagidinium spp. (Fig. 32 3e), which are generally associated with outer shelf to oceanic environments (e.g., Wall et al., 1977; Harland, 1983; Brinkhuis, 1994). Commonly present are representatives of 33 34 Odontochitina, Oligosphaeridium, Exochosphaeridium, Downiesphaeridium,

*Cyclonephelium, Lithosphaeridium, Achomosphaera*, and *Florentinia* spp., which are, like
 most encountered pollen and spores, typical for Late Cretaceous dinocyst shelf to bathyal
 assemblages (e.g., Dodsworth, 2004; Pearce et al., 2009; Peyrot et al., 2012).

4 5

#### 4. Discussion

## 6 4.1 SST reconstruction

### 7 4.1.1 Input of terrestrially derived GDGTs and post-depositional oxidation

8 Small quantities of iGDGTs as used for determination of TEX<sub>86</sub> values, are also produced in 9 soils. High input of soil-derived iGDGTs, reflected by elevated BIT index values, might 10 therefore bias TEX<sub>86</sub>-derived SST reconstructions (Weijers et al., 2006). TEX<sub>86</sub> and BIT 11 index values for the OAE2-record of the Wunstorf core exhibit a negative linear relation ( $R^2$ -12 value of 0.43; Fig. 4), which may be the result of relatively high input of soil-derived 13 iGDGTs, potentially affecting TEX<sub>86</sub> values. Previous work has recommended a cut-off value 14 of the BIT index to exclude this effect from TEX<sub>86</sub>-based paleotemperature reconstructions 15 (Weijers et al., 2006).

16 Low-TOC sediments have high BIT index values and low TOC-normalized concentrations for 17 brGDGTs and, to a larger extent, iGDGTs (Fig. 5). This is similar to results from TOC-rich 18 turbidites that are affected by post-depositional oxidation (e.g., Huguet et al., 2008; Lengger 19 et al., 2013). This was explained by preferential preservation of soil-derived brGDGTs over 20 marine-derived iGDGTs upon post-depositional oxidation of the turbidites. For the Wunstorf 21 section, the marls and limestones represent depositional phases during which the water 22 column and pore waters of surface sediments contained relatively high concentrations of 23 oxygen, as is evident from bioturbation, low TOC content (Fig. 2b), and low levels of redox-24 sensitive trace elements (Hetzel et al., 2011). Diagenetic effects caused by the oxidation of 25 biomarkers in the water column and pore waters most likely played a substantial role in this 26 depositional setting. Preferential preservation of brGDGTs is therefore likely responsible for 27 the observed pattern in the BIT-index. Although Lengger et al. (2013) did not find a bias in TEX<sub>86</sub> values for sediments that suffered post-depositional oxidation, other studies have 28 29 shown that there can be a considerable post-depositional oxidation effect on  $TEX_{86}$  values and 30 thus the paleo-SST reconstructions derived from it (e.g., Huguet et al., 2009). The linear correlation between TEX<sub>86</sub> and BIT-index values for the analyzed sediments of the Wunstorf 31 32 core, is in line with the latter. 33 Based on the relation between TOC and the BIT-index (Fig. 5a) and the concentrations of the

Based on the relation between TOC and the BI1-index (Fig. 5a) and the concentrations of the
 sum of the brGDGTs and crenarcheol (Fig. 5b), we decided to remove reconstructed paleo-

1 SST data with a BIT-index > 0.15. This changes the linear correlation between  $TEX_{86}$  and 2 BIT-index, suggesting that samples with a BIT-index > 0.15 are affected by post-depositional 3 oxidation. This results in a dataset in which samples with a BIT-index value between 0.02 and 4 0.12 are considered for paleo-SST reconstructions, removing the impact of soil derived 5 iGDGTs on the paleo-SST reconstructions.

6

# 7 4.1.2 Trends, stratigraphic correlation and absolute values

Trends and values of the reconstructed SSTs at Wunstorf using the TEX<sub>86</sub><sup>H</sup>-calibration of Kim 8 9 et al. (2010; Fig. 6c) are similar to previous TEX<sub>86</sub>-based SST reconstructions for OAE2. 10 Previously studied sites were located in the equatorial Atlantic (DSDP Site 367 and ODP Site 11 1260; Forster et al., 2007) and the mid-latitudes (ODP Site 1276 - Sinninghe Damsté et al., 12 2010; Bass River – van Helmond et al., 2014; Fig. 1). Potentially due to a lack of reliable 13 TEX<sub>86</sub> values at the onset of the OAE2-interval (Fig. 6b), the Wunstorf SST record does not 14 capture the rapid increase in SST at the onset of OAE2, previously attributed to a rise in 15 atmospheric CO<sub>2</sub> released by extensive volcanism (e.g., Forster et al., 2007). The Wunstorf 16 SST-record does show, despite being supported by predominantly one data point (resulting 17 from the removal of samples with a BIT-index > 0.15), a ~5°C cooling pulse during the early 18 stages of OAE2 (Fig. 6c). Six consecutive samples following our data point with lowest SST 19 support a subsequent warming trend, following a colder phase, however.

20 Based on its stratigraphic position within the early stages of the CIE, we attribute this cooling 21 pulse to the Plenus Cold Event (PCE; Gale and Christensen, 1996). The PCE, an event first 22 recognized as an incursion of boreal fauna in the shelf seas of NW Europe (e.g., Jefferies, 23 1962; Gale and Christensen, 1996; Voigt et al., 2004), represents a substantial cooling event 24 based on TEX<sub>86</sub>-based paleo-SST records throughout the proto-North Atlantic basin (Forster 25 et al., 2007; Sinninghe Damsté et al., 2010; van Helmond et al., 2014). At Wunstorf the data 26 point with lowest SST correlates to a level above the Plenusbank, located at 47.30-46.85 mbs 27 (Voigt et al., 2008) after the maximum in the CIE. The lack of reliable SST data for the 28 interval between 47.74 and 46.21 mbs complicates precise determination of the onset of the 29 PCE at Wunstorf, however. In three more "complete", previously published TEX<sub>86</sub>-based paleo-SST records across the PCE, i.e., ODP Site 1260 (Forster et al., 2007), ODP Site 1276 30 31 (Sinninghe Damsté et al., 2010) and Bass River (van Helmond et al., 2014) the cooling in 32 TEX<sub>86</sub>-based SSTs starts before the first maximum in the CIE, prior to the occurrence of 33 boreal fauna in the shelf seas of NW Europe (Gale and Christensen, 1996), suggesting that 34 faunal migrations lagged the cooling event as reconstructed by TEX<sub>86.</sub> Therefore precise

1 correlations of the PCE between sites remains challenging. The identification of the PCE at 2 Wunstorf, alongside the previous identifications of the PCE throughout the proto-North 3 Atlantic basin, suggest that the PCE was a hemisphere-wide and perhaps even a global event. 4 This supports the hypothesis that enhanced global carbon burial temporary suppressed 5 atmospheric CO<sub>2</sub> levels during OAE2 (Arthur et al., 1988; Sinninghe Damsté et al., 2010). 6 The PCE is related to changes in ocean circulation, recorded by the incursion of a northerly 7 sourced water mass as derived from a negative neodymium isotope excursion in the English 8 Chalk at Eastbourne (Zheng et al., 2013) and a trace-metal anomaly in the Western Interior 9 Seaway (Eldrett et al., 2014). This northerly sourced water mass may have been instrumental 10 for the dispersion of boreal fauna in the shelf seas of NW Europe, in line with the observed 11 differences in timing between TEX<sub>86</sub>-based cooling in SSTs and the occurrence of boreal 12 fauna. Interestingly, the interval of the PCE marks the occurrence of the Cyclonephelium 13 compactum-membraniphorum complex (C. comp.-memb. cplx.) within the OAE2 interval in 14 the Wunstorf core (Fig. 6c,d). This is in accordance with previous records from the Bass 15 River section (van Helmond et al., 2014) and the Shell Iona-1 core (Eldrett et al., 2014). 16 Although the biogeographic distribution of this complex is still partly unclear, this suggests 17 that the introduction of C. comp.-memb. cplx. at mid-latitude sites in both northwest Europe 18 and the east coast of North-America was quasi-instantaneous and linked to the PCE.

19 No significant difference in the reconstructed SSTs is recorded between the black shales and 20 the more TOC-lean marls and limestones. This suggests that the cyclic deposition of black 21 shales during OAE2 in the LSB was not primarily driven by changes in SST.

Average SSTs for the OAE2-interval at Wunstorf are higher than at Bass River (New Jersey 22 23 Shelf), DSDP Site 367 (Cape Verde Basin), ODP Site 1260 (Demarara Rise), and Site 1276 24 (North Atlantic; Table 1), which may perhaps be an artefact of the low resolution achieved for 25 the Plenus Cold Event at Wunstorf. Reconstructions of absolute temperatures based on  $TEX_{86}$ 26 at values significantly exceeding the modern calibration may yield significant errors, since the 27 modern core-top calibration only ranges to 30°C (Kim et al., 2010). Therefore SSTs 28 exceeding this value will always be based on extrapolation, although mesocosm studies have revealed that TEX<sub>86</sub> also shows a positive response with increasing temperatures, in the 30-29 40°C range (Schouten et al., 2007b). Furthermore the logarithmic TEX<sub>86</sub><sup>H</sup>-index (Kim et al., 30 31 2010), used in this study, has a calibration maximum of  $38.6^{\circ}$ C, i.e., when TEX<sub>86</sub> = 1 the 32 reconstructed SST is 38.6°C. SSTs reconstructions for samples with a TEX<sub>86</sub>-value >0.9 may 33 therefore be relatively conservative. Nonetheless, the warm and relatively stable background 34 SSTs for Wunstorf (~37°C) suggest that SSTs on the European shelf were exceptionally high and supports the notion that thermal gradients were substantially reduced during the Late
 Cretaceous greenhouse world (e.g., Baron, 1983; Huber et al., 1995).

3

## 4 4.2 Hydrology

5 Although pollen rank among the most resistant groups of palynomorphs (Traverse, 1994), 6 there is evidence that pollen grains are degraded relatively rapidly (<10 kyr) in the presence 7 of diffusively introduced oxygen (e.g., Keil et al., 1994). This may perhaps explain why 8 absolute pollen and spores concentrations are higher in the black shales, deposited under 9 anoxic conditions. This contrasts with the organic lean marls and limestones deposited during 10 phases in which pore waters of surface sediments contained relatively high concentrations of 11 oxygen, explaining the low absolute pollen and spores concentrations.

12 Among modern dinoflagellate cysts, members of the family Protoperidiniaceae, are most 13 sensitive to oxidation, and thus may potentially be affected by differential preservation (e.g., 14 Zonneveld, et al., 1997, Zonneveld et al., 2001; Versteegh and Zonneveld, 2002). No 15 consensus exists in the field whether this differential preservation is imprinted in the 16 sedimentary record (e.g., Reichart and Brinkhuis, 2003). At present, there is no published 17 information that suggests that the selective preservation of dinocysts plays a role in 18 assemblages described from the Cretaceous. If there were one dinocyst taxon potentially 19 prone to be selectively degraded in the assemblages we record, it would be the thin-walled taxon Paleohystrichophora infusorioides, which also belongs to the peridinioids. Well-20 21 preserved representatives of *P. hystrichophora* are, however, commonly present in the organic 22 lean marls and limestones.

23 Pollen and spores are transported to the marine environment by a wide range of processes, with river discharge and wind being the most important factors (e.g., Traverse and Ginsburg, 24 25 1966; Thomson, 1986; Feinsinger and Busby, 1987). Particularly saccate gymnosperm pollen 26 (bisaccates) may be transported by eolian pathways (e.g., Heusser, 1988). Palynological 27 assemblages at Wunstorf are a mixture of saccate gymnosperm pollen and non-saccate 28 gymnosperm pollen and spores, suggesting a mixture of eolian and fluvial input of pollen and 29 spores. However, most of the analyzed samples contain relatively low amounts of saccate 30 gymnosperm pollen (Fig. 6e; Prauss, 2006), suggesting that a substantial amount of the pollen 31 and spores encountered at Wunstorf was transported to the marine realm by fluvial processes. 32 The relatively high amounts of pollen and spores with respect to marine palynomorphs (T/M-33 ratio; Fig. 6e) in the black shales at Wunstorf are therefore interpreted to represent phases of 34 enhanced run-off. This was previously also shown for other Cretaceous Oceanic Anoxic

1 Events (e.g., Herrle et al., 2003). Enhanced run-off most likely resulted from increased 2 (seasonal) precipitation over north and mid-European landmasses, assuming that these yielded 3 significant vegetation cover. Regarding the distance to the coring site, non-saccate pollen and 4 spores most likely originated from the Rheno-Bohemian Massif (e.g., Falcon-Lang et al., 5 2001; Herman et al., 2002), which is in accordance with the prevailing paleo-wind directions (Hay and Floegel, 2012). Enhanced (seasonal) influx of fresh, low-density, surface waters 6 7 could well have stratified the water column, leading to low-oxygen levels in bottom waters. 8 This is also indicated by high abundances of bacterivorous ciliates (Blumenberg and Wiese, 9 2012), which graze on the interfaces of stratified water bodies (Sinninghe Damsté et al., 10 1995), supporting the presence of a chemocline in the water column. A persistent 11 stratification of the water column ultimately leads to bottom water anoxia and the formation 12 of black shales in the deeper parts of the LSB. The coupling of the rhythmical occurrence of 13 the black shale layers to the precession cycle (Voigt et al., 2008) suggests that changes in the 14 hydrological cycle were controlled by Earth's orbital parameters.

15

### 16 **4.3 Marine Productivity**

17 High abundances of dinocysts and organic matter in general may result from both enhanced 18 marine primary productivity and an improved preservation potential for organic matter during 19 black shale deposition. In modern oceans, most peridinioid dinocysts are produced by heterotrophic dinoflagellates, whilst most gonyaulacoid dinocysts are derived from 20 21 autotrophic taxa (Lewis et al., 1990). As a consequence, the ratio between peridinioids and 22 gonyaulacoids (P/G-ratio) has been employed widely as a proxy for paleoproductivity (Sluijs 23 et al., 2005). In the Wunstorf OAE2-section, the P/G-ratio reaches maximum values within 24 the different black shale couplets, implying that productivity was elevated during their 25 deposition (Fig. 6f). Furthermore the peridinioids encountered at Wunstorf belong to the 26 Peridiniaceae family, which has been shown to be low-salinity tolerant (e.g., Harland, 1973; 27 Sluijs and Brinkhuis, 2009). Together, this suggests that during seasons of high precipitation 28 and run-off that introduced nutrients a low-salinity, high-productivity surface layer existed in 29 the Lower Saxony Basin. This hypothesis is supported by assemblages of calcareous 30 nannofossils, showing a shift from a generally oligotrophic ecosystem to more mesotrophic or 31 even eutrophic conditions during black shale deposition (Linnert et al., 2010).

Enhanced marine primary productivity likely contributed to the establishment of bottom water
anoxia by increasing the flux of organic matter to the seafloor, depleting bottom water oxygen
concentrations upon decay.

1

# 2 **5.** Conclusions

3 Despite differences in the preservation of organic matter throughout the OAE2 interval at 4 Wunstorf, the general trend in reconstructed SSTs, including the cooling phase associated 5 with the Plenus Cold Event, is consistent with the results of previous studies that targeted the 6 proto-North Atlantic. Hence, the SST trend recorded at Wunstorf and the other sites was of at 7 least hemispheric significance. Reconstructed SSTs do not substantially differ between black 8 shales and less organic-rich deposits. This implies that, although higher temperatures must 9 have had an effect on the solubility of oxygen in seawater, surface temperature was not the 10 critical factor for the cyclic deposition of organic matter. Absolute SSTs for the Wunstorf 11 OAE2 section show little or no difference in comparison with SST reconstructions for sites 12 located at lower latitudes, which were evaluated using the same proxy and the same 13 methodology. This confirms that thermal gradients were much reduced during the Late 14 Cretaceous (Barron, 1983; Huber et al., 1995).

The dinocyst complex *Cyclonephelium compactum–C. membraniphorum*, previously linked to the Plenus Cold Event (van Helmond et al., 2014), was encountered at the respective level at Wunstorf, suggesting that its occurrence is indeed linked to this cooling. Its continued presence in the remainder of the record suggests, however, that other paleoenviromental factors were also critical in controlling its distribution.

20 A combination of continental configuration and extensive volcanism, intensifying greenhouse 21 conditions around the CTB, resulted in an epicontinental shelf sea prone to black shale 22 deposition as a consequence of precession-driven climate change at Wunstorf, (Voigt et al., 23 2008). We conclude, based on relatively high numbers of terrestrially derived pollen and 24 spores and freshwater tolerating dinocysts in the black shale intervals, that precession was 25 driving variations in the hydrological cycle. This caused (seasonal) freshwater stratification of 26 the water column and likely enhanced primary production, ultimately culminating in bottom 27 water anoxia and black shale formation. An orbitally controlled hydrological cycle may have 28 been a critical factor for other cyclic OAE2 sites located in the proto-Atlantic and Western 29 Interior Seaway at similar latitudes as well.

30

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18	Table 1. Overview of the different sites for which $TEX_{86}$ -paleothermometry was applied over the				
19	OAE2-interval, and TEX <sub>86</sub> values and paleo-SST ranges and averages.				
	Site Estimated TEV range Deconstructed roles SST <sup>4</sup> range				

Site	Estimated	TEX <sub>86</sub> range	Reconstructed paleo-SST <sup>a</sup> range
	paleolatitude	(average)	(average)
ODP Site 367 <sup>b</sup>	5°N	0.84-0.95 (0.90)	33-37°C (36°C)
ODP Site 1260 <sup>b</sup>	0°	0.85-0.95 (0.92)	34-37°C (36°C)
ODP Site 1276 <sup>c</sup>	30°N	0.74-0.96 (0.90)	30-37°C (36°C)
Bass River <sup>d</sup>	30°N	0.84-0.95 (0.91)	33-37°C (36°C)
Wunstorf	40°N	0.80-0.99 (0.93)	32-38°C (36°C)

<sup>a</sup> Based on the TEX<sub>86</sub><sup>H</sup> calibration by Kim et al., 2010, <sup>b</sup> Forster et al., 2007, <sup>c</sup> Sinninghe Damsté et al.,

22 2010, <sup>d</sup> van Helmond et al., 2014



Figure 1. Paleotectonic reconstruction for the Cenomanian/Turonian boundary time interval, with the location of the Wunstorf core and sections with previously published TEX<sub>86</sub>-based SST-records: Bass River, DSDP site 367, ODP sites 1260 and 1276 indicated (map generated at http://www.odsn.de/odsn/services/paleomap/paleomap.html). Inset map shows a detailed paleogeographic reconstruction of central and western Europe, including the location of the Wunstorf core (modified from Voigt et al., 2004).



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Figure 2. Geochemical results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al.(2008). (a)  $\delta^{13}C_{carb}$  (Voigt et al., 2008) and  $\delta^{13}C_{org}$  (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, Hetzel et al., 2011). (c) concentrations of summed iGDGTs and summed brGDGTs [µg/g OC].(d) BIT-index. (e) TEX<sub>86</sub>-values. The grey zone indicates the OAE2 interval after Voigt et al.(2008). mbs = meters below surface.

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1 Figure 3.Geochemical and palynological results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al.(2008). (a)  $\delta^{13}C_{carb}$  (Voigt et al., 2008) and 2 3  $\delta^{13}C_{org}$  (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, 4 Hetzel et al., 2011). (c) Total dinocyst concentrations (black) and total peridinioidal cysts 5 (orange) per gram sediment dry weight (cpg). (d) Dinocyst species Spiniferites spp. (cpg). (e) 6 Dinocyst species Impagidinium spp. (cpg). (f) Dinocyst species Lithosphaeridium 7 siphoniphorum siphoniphorum (cpg). (g) Dinocyst species Cyclonephelium compactum - C. 8 membraniphorum complex (cpg). (h).Terrestrial vs. marine palynomorphs (T/M-ratio) and 9 total pollen and spores in grains per dry gram of sediment (gpg), saccate gymnosperm pollen 10 in dark green. The grey zone indicates the OAE2 interval after Voigt et al.(2008). mbs = 11 meters below surface.



2 Figure 4. Cross plot of TEX<sub>86</sub> versus BIT-index values.





2 Figure 5. (a) Cross plot of summed brGDGTs ( $\mu$ g/g OC) versus crenarcheol ( $\mu$ g/g OC) on a

3 logarithmic axis. (b) Cross plot of BIT-index values versus total organic carbon (TOC).



Figure 6. Geochemical and palynological results for the Cenomanian-Turonian transition of 2 the Wunstorf core. Stratigraphy from Voigt et al. (2008). (a)  $\delta^{13}C_{carb}$  (Voigt et al., 2008) and 3  $\delta^{13}C_{org}$  (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, 4 Hetzel et al., 2011). (c) TEX<sub>86</sub>-values and TEX<sub>86</sub><sup>H</sup>-based SST reconstruction (Kim et al., 5 6 2010) (d) Relative abundance (%) and absolute abundancein cysts per dry gram of sediment 7 (cpg), of the dinocyst species Cyclonephelium compactum- C. membraniphorum complex, 8 'X' represents barren samples.(e).Terrestrial vs. marine palvnomorphs (T/M-ratio) and total 9 pollen and spores in grains per dry gram of sediment (gpg), saccate gymnosperm pollen in 10 dark green (f) Peridiniod vs. gonyaulacoid dinocysts (P/G-ratio). The grey zone indicates the 11 OAE2 interval after Voigt et al. (2008). mbs = meters below surface.

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