

Reviewer #1 Prof. Andrew S. Gale

Reviewer's Comment: This is an important paper, as it uses a multidisciplinary approach in order to tease out the respective controls of temperature and hydrology through OAE2, in relation to the orbital signal. The results are convincing and interesting, and attribute much of the anoxia to variation in the hydrological cycle driven by precession, separate from a cooling event. There are however unanswered questions surrounding the Plenus Cold Event, which could be usefully addressed. Firstly, the precise timing of this event is in some doubt; the original description was based on rather sound isotopic (heavy d18O excursion) and faunal evidence, and showed the event extending from Bed 4-8 of the Plenus Marl, exactly coincident with the range of the boreal belemnite *Actinocamax*. However, Jarvis et al. 2012, fig. 8 used rather poor quality (probably diagenetically compromised) oxygen isotope data (Eastbourne, Grobern) to extend the event down to the lower part of the carbon excursion. I know that one of your authors is unhappy about this. I see that your sampling around this level is a bit sparse (Fig. 6), but it looks as if the 86 Tex cold event is entirely above the Plenusbank. Some discussion of this would be really useful. A few more samples would be even better, but beyond the scope of this paper. The precision of timing is quite critical to interpretation.

Author's Reply: Determining precise correlations of the Plenus Cold Event between sites remains a challenge. In three more complete, published TEX₈₆ records across the Plenus Cold Event, ODP 1260 (Forster et al., 2007), ODP 1276 (Sinninghe Damsté et al., 2010) and Bass River (van Helmond et al., 2014) the cooling in TEX₈₆-based SSTs starts before the first maximum in the carbon isotope excursion. At Bass River the termination of this cooling phase is concurrent with the first maximum in the carbon isotope excursion, while for ODP 1260 and 1276, the cooling event continues till after the first maximum in the carbon isotope excursion (i.e., the isotopic-plateau phase). In Wunstorf the cooling event seems to take place after this first maximum, exclusively.

During our study, we analyzed more samples across this interval at Wunstorf; unfortunately we had to exclude most of the resulting data, as the samples did not yield sufficient molecular fossils to generate reliable TEX₈₆-based sea-surface temperature reconstructions (SSTs; Section 4.1.1). None of the generated data (including the excluded analyses) indicates that cooling was associated with the lower part of the carbon isotope excursion. As you indicate,

the cooling, as far as high-resolution correlations are feasible, seems to correlate to a level above the Plenusbank (47.30–46.85 mbs), which seems to be conflicting with the extension of the Plenus Event to the lower part of the carbon isotope excursion by Jarvis et al. (2012; Fig. 8). On the other hand we have no trustworthy SST data for the interval from 47.73 to 46.21 mbs, so it is very difficult to determine the precise start of the cooling event. We will incorporate the above discussions in the revised manuscript.

The heading of paragraph 4.1.2. now reads: “*Trends, stratigraphic correlation and absolute values*” (Page 23, Line 31)

We additionally explain our low sample resolution around the Plenus Cold Event as follows: “*The Wunstorf SST-record does show, despite being supported by predominantly one data point (resulting from the removal of samples with a BIT-index > 0.15), a ~5°C cooling pulse during the early stages of OAE2 (Fig. 6c). Six consecutive samples following our data point with lowest SST support a subsequent warming trend, following a colder phase, however.*” (Page 24, Lines 5-9)

The stratigraphic position of the Plenus Cold Event at Wunstorf and its correlation to other sites is detailed as follows: “*Based on its stratigraphic position within the early stages of the CIE, we attribute this cooling pulse to the Plenus Cold Event (PCE; Gale and Christensen, 1996). The PCE, an event first recognized as an incursion of boreal fauna in the shelf seas of NW Europe (e.g., Jefferies, 1962; Gale and Christensen, 1996; Voigt et al., 2004), represents a substantial cooling event based on TEX₈₆-based paleo-SST records throughout the proto-North Atlantic basin (Forster et al., 2007; Sinninghe Damsté et al., 2010; van Helmond et al., 2014). At Wunstorf the data point with lowest SST correlates to a level above the Plenusbank, located at 47.30–46.85 mbs (Voigt et al., 2008) after the maximum in the CIE. The lack of reliable SST data for the interval between 47.74 and 46.21 mbs complicates precise determination of the onset of the PCE at Wunstorf, however. In three more “complete”, previously published TEX₈₆-based paleo-SST records across the PCE, i.e., ODP Site 1260 (Forster et al., 2007), ODP Site 1276 (Sinninghe Damsté et al., 2010) and Bass River (van Helmond et al., 2014) the cooling in TEX₈₆-based SSTs starts before the first maximum in the CIE, prior to the occurrence of boreal fauna in the shelf seas of NW Europe (Gale and Christensen, 1996), suggesting that faunal migrations lagged the cooling event as*

1 *reconstructed by TEX₈₆. Therefore precise correlations of the PCE between sites remains*
2 *challenging.” (Page 24, Lines 10-26)*

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4 **Reviewer’s Comment:** You should also refer to Zheng et al. 2013 EPSL
5 .doi.org/10.1016/j.epsl.2013.05.053i, who described a negative neodymium isotope excursion
6 also coincident with the Plenus Cold Event, and attribute this to the incursion of a northerly
7 water mass. Discussion of this paper in the light of your results would be helpful and
8 interesting.

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10 **Author’s Reply:** In the revised version we discuss the incursion of a northerly sourced water
11 mass as derived from the negative neodymium isotope excursion by Zheng et al. (2013), and
12 the trace-metal anomaly that has been linked to the incursion of a boreal water mass by
13 Eldrett et al. (2014) as follows: *“The PCE is related to changes in ocean circulation,*
14 *recorded by the incursion of a northerly sourced water mass as derived from a negative*
15 *neodymium isotope excursion in the English Chalk at Eastbourne (Zheng et al., 2013) and a*
16 *trace-metal anomaly in the Western Interior Seaway (Eldrett et al., 2014). This northerly*
17 *sourced water mass may have been instrumental for the dispersion of boreal fauna in the*
18 *shelf seas of NW Europe, in line with the observed differences in timing between TEX₈₆-based*
19 *cooling in SSTs and the occurrence of boreal fauna.” (Page 24-25, Lines (33 (p. 24)-6 (p. 25)*

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30 **Reviewer #2 Dr. B. David Naafs**

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32 **Reviewer’s Comment:** The main issue is that the authors base their first (and main)
33 conclusion on the high concentration of pollen and spores in black shales. Although they
34 argue that preferential degradation is driving their BIT-index and complicates their TEX₈₆

record (which I concur), the influence of degradation on their palynological records is discarded based on the presence of a thin-walled dinocyst (*Paleohystrichophora infusorioides*). I find it hard to believe that BIT is (completely) driven by preservation, but that this had no impact on the pollen and spores, which we know can be heavily influenced by preferential degradation (see various papers of G. Versteegh). I am not an expert in dinoflagellates, but is this thin-walled dinocyst a commonly used indicator of preservation in the Cretaceous? The authors don't give a reference that would justify the use of this dino as preservation indicator. As far as I can see their main conclusions relies on this single line of evidence against preservation so I strongly urge the authors to provide additional evidence that preferential preservation is not primarily driving the observed changes in pollen and spores accumulation across OAE 2.

Author's Reply: The difference in preservation between biomarkers and palynomorphs (pollen and spores and dinocysts) has never been fully quantified. Based on our record from the Wunstorf section, we suggest that oxidation had a larger effect on the GDGTs as compared to the palynomorphs. This view is supported by data from other paleosettings, where palynomorphs are still present while GDGTs (and some other biomarkers) have already degraded (e.g., Ruhl et al., 2011). Moreover, studies on the Madeira Abyssal Plain F-turbidite (a 140 kyr old, ~4 m thick, turbidite rich in organic matter, with 40–50 cm oxidized sediment on top of the unoxidized turbidite, equivalent to ca. 10 kyr of oxidation) show that only 7–20% of the branched GDGTs and 0.2–3% of the isoprenoid GDGTs were preserved in the oxidized part of the turbidite (Huguet et al., 2008). A different study on the same turbidite shows that most (50–90%) of the oxygen-resistant dinocysts were preserved in the oxidized part, while 100% of the oxygen-sensitive dinocysts were degraded (Zonneveld et al., 2008). This implies that the effect of oxidation depends on the types of palynomorphs (i.e., oxygen-sensitive or not) looked at.

The work of Dr. G. Versteegh is not so much focused on pollen and spores, but rather on the selective preservation among dinoflagellate cysts. In fact, part of our reasoning why our palynological assemblage has not been altered by differential preservation is based on some of the studies he has co-authored. These studies (e.g., Zonneveld et al., 1997, 2001), which focus on Quaternary sediments, show that cysts of (proto)peridinioid dinoflagellates are most sensitive to oxygen, and thus are affected strongest by differential preservation. No consensus exists in the field if this differential preservation is imprinted in the sedimentary record (see,

e.g., Reichart & Brinkhuis, 2003). At present, there is also no published information that suggests that the selective preservation of dinocysts plays any role in described assemblages from the Cretaceous. If there were a ‘prime suspect’ dinocyst taxon potentially 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. The presence of *Paleohystrichophora infusorioides* throughout the record supports our reasoning that the palynological assemblage is little (or not) influenced by preferential preservation of palynomorphs.

We have include these discussions in the revised manuscript: “Among modern dinoflagellate cysts, members of the family Protoperidiniaceae, are most sensitive to oxidation, and thus may potentially be affected by differential preservation (e.g., Zonneveld, et al., 1997, Zonneveld et al., 2001; Versteegh and Zonneveld, 2002). No consensus exists in the field whether this differential preservation is imprinted in the sedimentary record (e.g., Reichart and Brinkhuis, 2003). At present, there is no published information that suggests that the selective preservation of dinocysts plays a role in assemblages described from the Cretaceous. If there were one dinocyst taxon potentially 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-preserved representatives of *P. hystrichophora* are, however, commonly present in the organic lean marls and limestones.” (Page 26, Lines 8-22)

Reviewer’s Comment: In addition, the evidence/reasoning in favor of fluvial input versus aeolian is also weak (lines 12-18 on page 3770). Is there any other evidence that could favor one of the two mechanisms? If not, based on the current data I don’t think you can rule-out aeolian input, especially because you are pretty far away from land.

Author’s Reply: We assume that the reviewer refers to lines 12-18 on page 3769 instead of 3770. In that paragraph we explain that pollen and spores are transported into the marine realm by a mixture of different processes, e.g., fluvial and eolian transport. Saccate gymnosperm pollen may be transported predominantly by eolian processes. In Wunstorf we encountered a mixed assemblage of pollen and spores, but saccate gymnosperm pollen were generally in the minority, suggesting that most pollen and spores were transported by fluvial processes.

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2 We have clarified this as follows: *“Pollen and spores are transported to the marine*
3 *environment by a wide range of processes, with river discharge and wind being the most*
4 *important factors (e.g., Traverse and Ginsburg, 1966; Thomson, 1986; Feinsinger and Busby,*
5 *1987). Particularly saccate gymnosperm pollen (bisaccates) may be transported by eolian*
6 *pathways (e.g., Heusser, 1988). Palynological assemblages at Wunstorf are a mixture of*
7 *saccate gymnosperm pollen and non-saccate gymnosperm pollen and spores, suggesting a*
8 *mixture of eolian and fluvial input of pollen and spores. However, most of the analyzed*
9 *samples contain relatively low amounts of saccate gymnosperm pollen (Fig. 6e; Prauss,*
10 *2006), suggesting that a substantial amount of the pollen and spores encountered at Wunstorf*
11 *was transported to the marine realm by fluvial processes. The relatively high amounts of*
12 *pollen and spores with respect to marine palynomorphs (T/M-ratio; Fig. 6e) in the black*
13 *shales at Wunstorf are therefore interpreted to represent phases of enhanced run-off. This*
14 *was previously also shown for other Cretaceous Oceanic Anoxic Events (e.g., Herrle et al.,*
15 *2003).”* (Page 26-27, Lines (27 (p. 26) – 6 (p. 27))

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17 **Reviewer’s Comment:** The authors state that they can disentangle the impact of warming,
18 hydrology, and productivity (lines 2-6), but their results indicate it’s hydrology combined
19 with productivity that led to black shale formation (lines 22-25) (and their TEX data also
20 indicates a super greenhouse climate). So they don’t really disentangle the individual
21 contribution of these parameters to OAE 2. I suggest rephrasing the beginning of the abstract.

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23 **Author’s Reply:** We agree, and rephrased this part of the abstract, which now reads: *“In an*
24 *attempt to separate these forcing factors, we generated palynological and organic*
25 *geochemical records using a core spanning the OAE2 from Wunstorf...”* (Page 15, Lines 27-
26 29)

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28 **Reviewer’s Comment:** Page 3578 Line 25: rephrase sentence.

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30 **Author’s Reply:** We assume that the reviewer is referring to Page 3758 Line 25, we
31 rephrased the sentence: *“which reduced the solubility of oxygen in surface waters.”* (Page 17,
32 Line 5)

Reviewer's Comment: Page 3760: Line 20: TOC of 2.8 % is not rich in TOC. Elevated TOC levels would a better phrasing.

Author's Reply: We have adjusted the sentence as suggested by the reviewer: *"The Hesseltal Formation consists of rhythmically alternating couplets of finely laminated black shales with elevated levels of relatively rich in total organic carbon (TOC; max. 2.8%; Hetzel et al., 2011; Fig. 2b)..."* (Page 18, Line 20)

Reviewer's Comment: Page 3761: Line 20: change organic molecules into biomarkers.

Author's Reply: We adjusted the sentence as suggested.

Reviewer's Comment: Page 3762: Line 1: Which solvent volumes were used for the columns? Line 2: What was the selection for apolar samples based on? And how many samples? Line 18: Rephrase Line 18: Give the m/z's.

Author's Reply: Line 1: We used three column volumes of solvent per fraction. Line 2: The selection of apolar samples was based on the yield of the apolar fractions. We only analyzed two samples (WUN 41,14m and WUN 42,81m), since our results were comparable with Blumenberg and Wiese, 2012 – BG, who performed the same analyses on a larger sample set from the same interval of the Wunstorf core. Line 18 is now rephrased and m/z's are provided.

We have incorporated the above as follows in the revised manuscript:

"The TLEs were separated by Al₂O₃ column chromatography, into apolar, ketone, 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 DCM/methanol(1:1, v/v), respectively." (Page 19, Lines 17-20)

"The apolar fractions of two samples (41.14 mbs and 42.81 mbs), selected based on their high yield, were measured using gas chromatography-mass spectrometry (GC–MS), to determine the thermal maturity of the sediments based on the degree of isomerisation of hopanes." (Page 19, Lines 21-24)

1 “GDGTs (m/z 1018-1302) were detected using selective ion monitoring. For this method it
2 was exhibited that for samples with a high TEX_{86} value...” (Page 20, Lines 2-3)

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4 **Reviewer’s Comment:** Page 3763 Line 1-2: It is an assumption that crenarchaeol mainly
5 originates from marine thaumarchaeota. It is also found in soils and the usage of the BIT-
6 index is complicated by many factors. Please elaborate a bit more on the limitations of BIT.

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8 **Author’s Reply:** Crenarchaeol is indeed also produced by thaumarchaeota in soil. Many
9 studies have indicated, however, that BIT is still a useful tracer for continental organic matter
10 (e.g., Schouten et al., 2013; review).

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12 We have briefly elaborated on the limitations of the BIT-index in the revised manuscript:
13 “Application of the BIT index may be complicated by in situ production of brGDGTs in the
14 marine water column and in marine sediments and the ubiquitous presence of crenarchaeol in
15 soils. Nonetheless many studies have shown that BIT is still a useful tracer for continental
16 organic matter in marine environments (Schouten et al., 2013).” (Page 20, Lines 15-18)

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18 **Reviewer’s Comment:** Page 3764: Line 5: Again, how was this selection made and how
19 many samples did you look at? Why weren’t all samples used for TEX_{86} measured on the
20 GC-MS to infer the thermal maturity for each TEX_{86} data point? Some sections are
21 characterized by large variations in hopane distributions across OAEs. You have the fractions,
22 so I don’t understand why not all samples were run on the GC-MS to assess the maturity. Did
23 I miss something? I urge the authors to measure all samples on the GC-MS. Or at least plot
24 the C31 hopane $\beta\beta/(\alpha\beta+\beta\alpha+\alpha\alpha)$ of all the measured samples in figure 2 and 6. Also show the
25 S/R ratio. Are the samples all immature enough to be confident in your TEX_{86} estimates?
26 Line 5: C31 17 β (H), 21 β (H) hopane. Line 7: Even if you don’t have detectable amounts of $\alpha\beta$
27 -hopanes (but see next comment), the $\beta\beta/(\alpha\beta+\beta\alpha+\alpha\alpha)$ ratio can still be $\ll 1$ if you have $\beta\alpha$ -
28 hopanes. Line 8: Blumenberg and Wiese (2012) do report (C31) $\alpha\beta$ (and $\beta\alpha$) -hopanes in their
29 samples (Fig. 6 of their manuscript). So do you really only have $\beta\beta$ -hopanes in your samples
30 and if so, why are the results different from the previous study?

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32 **Author’s Reply:** We measured the degree of isomerization of the C31 hopanes to check if the
33 degree of thermal maturity was not too high for TEX_{86} palaeothermometry (cf. Schouten et
34 al., 2004) in two samples. We only could identify C31 $\beta\beta$ -hopanes and consequently the

1 isomerization ratio is 1. We only checked two samples because typically the degree of thermal
2 maturation will be similar throughout a section like this. Distribution of hopane biomarkers
3 was not the target of the study; therefore, we only analyzed two samples. We don't really see
4 the added value of analyzing the hopanes in all of the samples analyzed as requested by the
5 referee.

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8 **Reviewer's Comment:** Page 3767 Line 20: In my opinion, there is no significant cooling if
9 you take out the one data point at ~47 m from figure 6c. So the whole story of a ~5°C cooling
10 during the Plenus cold event is based on one single data point. I suggest deleting the
11 section(s) that deal with cooling during the Plenus cold event or at least mention that this is
12 based on very few data points. I concur with the other reviewer that a few more TEX₈₆
13 datapoints during the event would be ideal to confidently identify a cooling, although I'm not
14 sure whether the high BIT values prevents the authors from doing this.

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16 **Author's Reply:** We agree with the reviewer that our cold event is based on one data point.
17 However, the observed trend does fit to other TEX₈₆ records from other locations (ODP Site
18 1260 - Forster et al., 2007; ODP Site 1276 - Sinninghe Damsté et al., 2010; Bass River - van
19 Helmond et al., 2014). Unfortunately, the other samples surrounding this interval did not yield
20 sufficient isoprenoid GDGTs to produce a reliable signal. If we, however, would consider the
21 SST estimates derived from these excluded samples, five samples would have supported this
22 ~5°C cooling during the Plenus cold event (fig. 2). Furthermore, the samples following our
23 coldest data point support a warming trend (following a colder phase).

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25 We have explained this in our revised manuscript as follows: *"The Wunstorf SST-record does*
26 *show, despite being supported by predominantly one data point (resulting from the removal of*
27 *samples with a BIT-index > 0.15), a ~5°C cooling pulse during the early stages of OAE2*
28 *(Fig. 6c). Six consecutive samples following our data point with lowest SST support a*
29 *subsequent warming trend, following a colder phase, however."* (Page 24, Lines 5-9)

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31 **Reviewer's Comment:** Page 3768 Line 19: Can you elaborate a bit on the possible TEX₈₆
32 errors you mention.

Author's Reply: The modern core-top calibration only ranges to 30°C, so SSTs exceeding this value will always be based on extrapolation, although mesocosm studies have revealed that TEX₈₆ also shows a positive response with increasing temperatures, in the 30-40°C range (Schouten et al., 2007). The logarithmic TEX₈₆^H-index, used in this study, has a calibration maximum of 38.6°C, i.e., when TEX₈₆ = 1 the reconstructed SST is 38.6°C. SSTs reconstructions for samples with a TEX₈₆-value >0.9 may therefore be relatively conservative.

We have added the above to our revised manuscript: *“Reconstructions of absolute temperatures based on TEX₈₆ at values significantly exceeding the modern calibration may yield significant errors, since the modern core-top calibration only ranges to 30°C (Kim et al., 2010). Therefore SSTs exceeding this value will always be based on extrapolation, although mesocosm studies have revealed that TEX₈₆ also shows a positive response with increasing temperatures, in the 30-40°C range (Schouten et al., 2007b). Furthermore the logarithmic TEX₈₆^H-index (Kim et al., 2010), used in this study, has a calibration maximum of 38.6°C, i.e., when TEX₈₆ = 1 the reconstructed SST is 38.6°C. SSTs reconstructions for samples with a TEX₈₆-value >0.9 may therefore be relatively conservative.”* (Page 25, Lines 21-29)

Reviewer's Comment: Page 3770: Line 12-14: Could your P/G ratio also be driven by preferential degradation, just as the BIT-index is?

Author's Reply: P cysts are considered more prone to oxidation than G cysts (e.g., Zonneveld et al., 2008). However, we record high relative proportions of P cysts in samples with low TOC content around 49,5 and between 35 and 30 meters. Hence, the signal goes the wrong way to be explained by selective degradation. This preferential preservation among dinocysts was discussed after the first comment of the reviewer.

Reviewer's Comment: Page 3771 Line 8: Did anybody ever imply that SSTs were driving the cyclic deposition of organic matter?

Author's Reply: Higher SSTs decrease the potential of oxygen to dissolve in seawater, thereby contributing to decreasing dissolved oxygen levels and ultimately anoxia. In this study we show, that SST is not the primary driver of anoxia, hence black shale deposition, during OAE2.

We clarified the above in the following sentence: *“This implies that, although higher temperatures must have had an effect on the solubility of oxygen in seawater, surface temperature was not the critical factor for the cyclic deposition of organic matter.”*

(Page 28, Lines 13-15)

Reviewer’s Comment: Lastly, I’m wondering why the proposed forcing for black shale deposition (precession) leads to black shale deposition during OAE 2 alone. Wouldn’t orbital forcing by a “constant” forcing, independent of the occurrence of an OAE? What is special to OAE 2 that the orbital forcing triggers black shale deposition and not before or after the event? I urge the authors to discuss this issue in the revised version.

Author’s Reply: We fully agree that orbital forcing is a constant factor. During specific intervals, however, the entire system becomes more prone to anoxia, for example through tectonics (basinal restriction) or climatic changes (warming - greenhouse conditions), hence the formation of anoxia, e.g., sapropels in the Eastern Mediterranean or OAEs. Orbital forcing is then, all of a sudden, controlling the formation of anoxia at certain locations. During OAE2 this is particularly observed in the mid-latitudes, e.g., Wunstorf (this study), DSDP Site 530 (Forster et al., 2008), and DSDP Sites 105 and 603 (Kuypers et al., 2004). In the equatorial proto-North Atlantic, on the other hand, there is no evidence for orbital forcing of black shale formation (e.g., Kuypers et al., 2002).

We have explained this in the revised manuscript: *“A combination of continental configuration and extensive volcanism, intensifying greenhouse conditions around the CTB, resulted in an epicontinental shelf sea prone to black shale deposition as a consequence of precession-driven climate change at Wunstorf (Voigt et al., 2008).”*

(Page 28, Lines 25-28)

Review by the editor (after revised submission):

Editorial comment: As you acknowledge, TEX₈₆ can be significantly affected (e.g. result in lower SSTs) by changes in thermal maturity of organic matter (Schouten et al., 2004; 2013). One way to check for the influence of thermal maturity is by using the distribution of hopanes (a type of biomarker). You determine the hopane ratio in (only) two samples, which according to your results are thermally very immature (only the immature BB hopanes are found). Based on these two data points you argue that thermal maturity is constantly low throughout the section ("We only checked two samples because typically the degree of thermal maturation in a section like this will be similar") and hence TEX₈₆ can be applied with confidence.

However, (and as highlighted in the original comments of the reviewer), this is directly contradicting previously published results from the same section (Blumenberg and Wiese, 2012). That study did detect the thermally more mature ab and ba hopanes. Together this suggests changes in thermal maturity between samples (from samples with only immature bb hopanes as measured and presented in your work to samples with significant amounts of the more mature ab hopanes as shown by Blumenberg and Wiese (2012). Based on the results of Blumenberg and Wiese (2012) it is difficult to judge whether the thermal maturity is significantly high enough to affect TEX₈₆, but the reviewer requests that you should

acknowledge 1) the Blumenberg and Wiese (2012) study that suggests higher thermal maturity in parts of the section, 2) indicate that thermal maturity is changing in the section and 3) that this might affect TEX₈₆ (but as you do not want to measure the hopane distributions in all samples used for TEX₈₆ it is impossible to know which samples might be affected).

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 biomarkers) a wide variety of biomarkers including functionalized hopanoids and steroids, which are only present in thermally immature sediments. Accordingly, they report that various types of hopanoids are dominated by the 17 β , 21 β (H)-stereochemistry. This is in excellent agreement with our results. In the same paper, Blumenberg and Wiese (2012) also report much higher degrees of thermal maturity based upon isomerization ratios of biomarkers in hydropyrolysates generated from the kerogen. However, to obtain these pyrolyzates these kerogens were heated by temperatures up to 500°C. It is well known that during such experiments the degree of isomerization of biomarkers alters towards a thermodynamic equilibrium mixture depending on time of the experiment and temperature applied (e.g., see Koopmans et al., 1996; Figure 4). Accordingly, the data of Blumenberg and Wiese (2012) obtained from the hydropyrolysates are not relevant to assess the *natural* level of thermal 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 TEX₈₆ palaeothermometry. In addition, 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.

We have added two sentences to the methods (Page 7, Lines 21-24): “*Only two samples were analyzed because 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.*”

We have rephrased the results section reporting on thermal maturity as follows (Page 9, Lines 13-29): “*For two selected samples the hopane distribution was determined. C₃₁17 β ,21 β (H)*

1 *hopane was the dominant hopane. No $\alpha\beta$ -hopanes were encountered, so the $(\beta\beta)/(\beta\beta+\beta\alpha+\alpha\alpha)$*
2 *of hopane biomarkers was 1. This is in perfect agreement with Blumenberg and Wiese (2012),*
3 *who report that various types of hopanoids, for the same core, are dominated by the 17 β , 21 β*
4 *(H)-stereochemistry. This indicates that the thermal maturity of the sedimentary organic*
5 *matter was sufficiently low for the application of TEX₈₆ paleothermometry (cf. Schouten et al.,*
6 *2004).*
7 *Blumenberg and Wiese (2012) also report much higher degrees of thermal maturity based*
8 *upon isomerization ratios of biomarkers in hydropyrolysates generated from the kerogen.*
9 *However, to obtain these pyrolysates, kerogens were heated by temperatures up to 500°C. It*
10 *is well known that during such experiments the degree of isomerization of biomarkers alters*
11 *towards a thermodynamic equilibrium mixture depending on time of the experiment and*
12 *temperature applied (e.g., Koopmans et al., 1996). Accordingly, the data of Blumenberg and*
13 *Wiese (2012) obtained from the hydropyrolysates are not relevant to assess the natural level*
14 *of thermal maturity. Therefore there is no conflict between the data of Blumenberg and Wiese*
15 *(2012) and the data presented in this study.”*

References

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Freshwater discharge controlled deposition of Cenomanian-Turonian black shales on the NW European epicontinental shelf (Wunstorf, North Germany)

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Abstract

Global warming, changes in the hydrological cycle and enhanced marine primary productivity all have been invoked to have contributed to the occurrence of widespread ocean anoxia during the Cenomanian-Turonian Oceanic Anoxic Event (OAE2; ~94 Ma), but disentangling these factors on a regional scale has remained problematic. [In an attempt to separate these forcing factors, we](#) generated palynological and organic geochemical records [that allow the separation of these forcing factors in using](#) a core spanning the OAE2 from Wunstorf, Lower Saxony Basin (LSB; North Germany), which exhibits cyclic black shale – marl alternations related to the orbital precession cycle.

Despite the widely varying depositional conditions complicating the interpretation of the obtained records, TEX₈₆^H indicates that sea-surface temperature (SST) evolution in the LSB

during OAE2 resembles that of previously studied sites throughout the proto-North Atlantic. Cooling during the so-called Plenus Cold Event interrupted black shale deposition during the early stages of OAE2. However, TEX₈₆ does not vary significantly across marl-black shale 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 abundances of pollen and spores are elevated during phases of black shale deposition, indicative of enhanced precipitation and run-off. High abundances of cysts from inferred heterotrophic and euryhaline dinoflagellates supports high run-off, which likely introduced additional nutrients to the epicontinental shelf resulting in elevated marine primary 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.

1 Introduction

Dark, often laminated marine sediments that are usually devoid of fossil traces of benthic life and exhibit a total organic carbon (TOC) content of >1% (Creaney and Passey, 1993), were episodically deposited during Jurassic and Cretaceous times. The deposition of these sediments, generally referred to as black shales, has typically been taken to indicate ancient episodes of dys- or anoxic bottom water conditions (Schlanger and Jenkyns, 1976). During some of these episodes, anoxia developed widespread in one or more ocean basins; such episodes were termed Oceanic Anoxic Events (OAEs; Schlanger and Jenkyns, 1976). One of the most prominent, best-constrained and best-studied of these OAEs formed across the Cenomanian-Turonian boundary (CTB; ~94 Ma) and became known as OAE2 (e.g., Jenkyns, 2010). The widespread enhanced organic carbon burial in marine sediments during OAE2 is expressed by a worldwide documented >2‰ positive [carbon isotopic excursion \(CIE\)](#) ~~in the carbon isotopic composition~~ of carbonate ($\delta^{13}\text{C}_{\text{carb}}$) and organic matter ($\delta^{13}\text{C}_{\text{org}}$), with an estimated duration of 450-600 kyr (e.g., Voigt et al., 2008; Meyers et al., 2012). This [CIE excursion](#) likely resulted from enhanced burial of $\delta^{13}\text{C}$ -depleted organic matter (Arthur et al., 1988; Tsikos et al., 2004) and therefore provides a C-isotopic signature of the global exogenic carbon pool, making it a proper tool to confidently 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, 2008) has been linked to high levels of atmospheric CO₂ (e.g., Schouten et al., 2003; Sinninghe Damsté et al., 2008; Barclay et al., 2010), raising the temperatures of already warm oceans towards a maximum at the onset of OAE2 (e.g., Bice et al., 2006; Forster et al., 2007), which reduced thereby diminishing the solubility of oxygen solubility in the surface waters. This warming caused an enhanced hydrological cycle (van Helmond et al., 2014), which would likely have contributed to increased rates of continental weathering and runoff (Blätter et al., 2011; Pogge von 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 may also have directly contributed to ocean fertilization (Kerr et al., 1998; Snow et al., 2005), while changes in proto-Atlantic circulation may have increased the strength of upwelling (e.g., Poulsen et al., 2001; Junium and Arthur, 2007). Enhanced regeneration of sedimentary phosphorus from dysoxic and anoxic sediments (e.g., Kuypers et al., 2004b; Mort et al., 2007) combined with abundant nitrogen-fixing cyanobacteria (Kuypers et al., 2004b) may have sustained high levels of primary productivity. All of the above factors would conspire to expansion of oxygen minimum zones and oxygen depletion of bottom waters, leading to enhanced organic carbon burial.

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

The complete OAE2-interval has been recovered from the LSB through coring at Wunstorf (Erbacher et al., 2007; North Germany; Fig. 1). Application of an orbital cycle-based age model has shown that black shale deposition in the Wunstorf core sediments is consistent with precession forcing (Voigt et al., 2008). This implies that climate change resulting from orbital fluctuations was directly related to phases of black shale deposition. The robust cyclostratigraphy and biostratigraphic zonation of the Wunstorf core allows for a high-resolution study of astronomically-induced climate change. Here we aim to reconstruct mean annual sea surface temperature (SST), hydrological changes and marine primary productivity, to determine the dominant control on decreasing oxygen concentrations during OAE2 on the

European shelf. To this end, we combined organic geochemical (TEX₈₆; BIT index) and palynological proxies, notably organic-walled dinoflagellate cysts (dinocysts) and pollen and spore abundances, across the CTB for the Wunstorf core.

2 Material and methods

2.1 Site description, depositional setting and age model

The Wunstorf core was drilled in 2006 ~25 km west of Hannover, Germany (52°24.187'N, 9°29.398'E, Voigt et al., 2008; Fig.1). Approximately 76 m of middle Cenomanian to middle Turonian sediments, comprising a ~13.5 m thick CTB succession, were retrieved. During the 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 (Hancock and Kauffman, 1979). The sediments at Wunstorf were deposited at an estimated water depth of 100-150 m based on sequence stratigraphy, sedimentological analysis and (micro)fossil content (Wilmsen, 2003). The most proximal exposed land, the Rheno-Bohemian Massif, was located ~150 km to the south and formed a barrier towards the Western Tethys. 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). 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 alternating couplets of finely laminated black shales with elevated levels of~~relatively rich in~~ total organic carbon (TOC; max. 2.8%; Hetzel et al., 2011; Fig. 2b), grey to green marls, and light-grey (marly) limestones (Fig. 2; Erbacher et al., 2007; Voigt et al., 2008). The cyclic lithology results from a depositional system greatly influenced by precession (Voigt et al., 2008). Biostratigraphic zonation for the Hesseltal Formation relies on inoceramids, ammonites, acme 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 ammonite *Metoicoceras geslinianum* at 49.6 mbs, consistent with the English Chalk (Voigt et al., 2008). At 47.8 mbs, the onset of the characteristic positive shift in $\delta^{13}\text{C}_{\text{carb}}$ (~2‰) and $\delta^{13}\text{C}_{\text{org}}$ (~2.5‰) was recognized (Voigt et al., 2008; Du Vivier et al., 2014; Fig. 2a). The termination of the OAE2 interval at Wunstorf was placed at 36 mbs (Voigt et al., 2008). The 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 $\delta^{13}\text{C}_{\text{org}}$, respectively (Voigt et al., 2008; Du Vivier et al., 2014).

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.%).

2.3 Organic geochemistry

For 48 samples, ~~biomarkers organic molecules~~ were extracted from 10-15 g of powdered and freeze-dried sediments with a Dionex accelerated solvent extractor (ASE) using dichloromethane (DCM)/ methanol mixture (9:1, v/v). Total lipid extracts (TLEs) were evaporated to near dryness using rotary evaporation. Subsequently, remaining solvents were removed under a nitrogen flow. The TLEs were separated by Al_2O_3 column chromatography, into apolar, ketone, 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 DCM/methanol(1:1, v/v), respectively. The apolar and GDGT fractions were dried under a nitrogen flow and weighed. ~~Selected-The~~ apolar fractions of two samples (41.14 mbs and 42.81mbs), selected based on their high yield, were measured using gas chromatography-mass spectrometry (GC-MS), to determine the thermal maturity of the sediments based on the degree of isomerisation of hopanes. Only two samples were analyzed because 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. 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 range of m/z 50–800 and a cycle time of 3 scans s^{-1} . The temperature program and column conditions resemble that of Sinninghe Damsté et al. (2008). To quantify the GDGT abundances a known amount of C_{46} GDGT-standard was added (Huguet et al., 2006), after which the GDGT-fractions were re-dissolved in hexane/propanol (99:1, v/v) and filtered over a 0.45 μm mesh PTFE filter. The filtered GDGT fractions were analysed using high performance liquid chromatography - atmospheric

pressure chemical ionization/ mass spectrometry (HPLC-APCI/MS) according to the method described in Schouten et al. (2007a). Analysis were performed on an Agilent 1290 infinity series coupled to a 6130 single 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 μ m; Alltech). ~~Selective ion monitoring was used to detect the~~ GDGTs (m/z 1018-1302) ~~were detected using selective ion monitoring.~~ For which ~~it~~ this method it was exhibited that for samples with a high TEX₈₆ value, a concentration of 0.1 ng of injected GDGTs on the LC column was still sufficient to yield trustworthy TEX₈₆ values (Schouten et al., 2007a). The minimum GDGT concentration injected on the LC column per measurement in this study was ~0.3 ng. TEX₈₆-index values were calculated after Schouten et al. (2002), and converted to absolute annual average sea surface temperatures (SSTs) using the TEX₈₆^H Kim et al. (2010) modern core top calibration, which has a calibration error of 2.5°C. Analytical reproducibility was generally better than 0.3°C.

The Branched and Isoprenoid Tetraether (BIT) index was used to estimate the relative abundance of soil organic matter in marine sediments (Hopmans et al., 2004). The BIT index is based on the amount of predominantly soil-derived branched GDGTs (brGDGTs) relative to the isoprenoid GDGT (iGDGT) crenarchaeol, which is chiefly derived from marine Thaumarchaeota. Application of the BIT index may be complicated by in situ production of 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 tracer for continental organic matter in marine environments (Schouten et al., 2013).

2.4 Palynology

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

3 Results

3.1 Total organic carbon

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

3.2 Thermal maturity

For ~~two~~ selected samples the hopane distribution was determined. $C_{31}17\beta,21\beta(H)$ hopane was the dominant hopane. No $\alpha\beta$ -hopanes were encountered, so the $(\beta\beta/(\beta\beta+\beta\alpha+\alpha\alpha))$ of hopane 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 β , 21 β (H)-stereochemistry. in agreement with results on sediments from this core presented by Blumenberg and Wiese (2012). This indicates that the thermal maturity of the sedimentary organic matter was sufficiently low for the application of TEX₈₆ paleothermometry (cf. Schouten et al., 2004).

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

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 $\mu\text{g/g}$ organic carbon (OC). Crenarchaeol concentrations vary by three orders of magnitude, whereas brGDGT concentrations vary by one to two orders of magnitude. High GDGT concentrations coincide with the organic carbon-rich black shales (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-derived brGDGTs, to 0.56, evidencing substantial soil-derived input of brGDGTs. The BIT-index (Fig. 2d) is relatively high in the organic-poor intervals and generally low (i.e. <0.10) for the organic-rich black-shale intervals. Values for TEX_{86} fluctuate between 0.71 and 0.99 (Fig. 2e).

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.

Dinocyst assemblages are dominated by multiple species of the Peridiniaceae family, i.e., *Paleohystrichophora infusorioides*, *Subtilisphaera pontis-mariae*, *Eurydinium saxoniense*, *Isabelidinium* spp., and *Gingidinium* spp.. Members of this family have repeatedly been shown to be derived of low-salinity tolerant dinoflagellates in Late Cretaceous and Paleogene successions and likely represent heterotrophic, euryhaline dinoflagellates (e.g., Harland, 1973; Sluijs and Brinkhuis, 2009; Powell et al., 1990; Lewis et al., 1990; Fig. 3c). Other quantitatively important taxa include *Spiniferites* spp. (Fig. 3d) and *Impagidinium* spp. (Fig.

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 *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. Discussion

4.1 SST reconstruction

4.1.1 Input of terrestrially derived GDGTs and post-depositional oxidation

Small quantities of iGDGTs as used for determination of TEX₈₆ values, are also produced in soils. High input of soil-derived iGDGTs, reflected by elevated BIT index values, might therefore bias TEX₈₆-derived SST reconstructions (Weijers et al., 2006). TEX₈₆ and BIT index values for the OAE2-record of the Wunstorf core exhibit a negative linear relation (R^2 -value of 0.43; Fig. 4), which may be the result of relatively high input of soil-derived iGDGTs, potentially affecting TEX₈₆ values. Previous work has recommended a cut-off value of the BIT index to exclude this effect from TEX₈₆-based paleotemperature reconstructions (Weijers et al., 2006).

Low-TOC sediments have high BIT index values and low TOC-normalized concentrations for brGDGTs and, to a larger extent, iGDGTs (Fig. 5). This is similar to results from TOC-rich turbidites that are affected by post-depositional oxidation (e.g., Huguet et al., 2008; Lengger et al., 2013). This was explained by preferential preservation of soil-derived brGDGTs over marine-derived iGDGTs upon post-depositional oxidation of the turbidites. For the Wunstorf section, the marls and limestones represent depositional phases during which the water column and pore waters of surface sediments contained relatively high concentrations of oxygen, as is evident from bioturbation, low TOC content (Fig. 2b), and low levels of redox-sensitive trace elements (Hetzl et al., 2011). Diagenetic effects caused by the oxidation of biomarkers in the water column and pore waters most likely played a substantial role in this depositional setting. Preferential preservation of brGDGTs is therefore likely responsible for the observed pattern in the BIT-index. Although Lengger et al. (2013) did not find a bias in TEX₈₆ values for sediments that suffered post-depositional oxidation, other studies have shown that there can be a considerable post-depositional oxidation effect on TEX₈₆ values and thus the paleo-SST reconstructions derived from it (e.g., Huguet et al., 2009). The linear

correlation between TEX₈₆ and BIT-index values for the analyzed sediments of the Wunstorf core, is in line with the latter.

Based on the relation between TOC and the BIT-index (Fig. 5a) and the concentrations of the sum of the brGDGTs and crenarchaeol (Fig. 5b), we decided to remove reconstructed paleo-SST data with a BIT-index > 0.15. This changes the linear correlation between TEX₈₆ and BIT-index, suggesting that samples with a BIT-index > 0.15 are affected by post-depositional oxidation. This results in a dataset in which samples with a BIT-index value between 0.02 and 0.12 are considered for paleo-SST reconstructions, removing the impact of soil derived iGDGTs on the paleo-SST reconstructions.

4.1.2 Trends, stratigraphic correlation and absolute values

Trends and values of the reconstructed SSTs at Wunstorf using the TEX₈₆^H-calibration of Kim et al. (2010; Fig. 6c) are similar to previous TEX₈₆-based SST reconstructions for OAE2. Previously studied sites were located in the equatorial Atlantic (DSDP Site 367 and ODP Site 1260; Forster et al., 2007) and the mid-latitudes (ODP Site 1276 – Sinninghe Damsté et al., 2010; Bass River – van Helmond et al., 2014; Fig. 1). Potentially due to a lack of reliable TEX₈₆ values at the onset of the OAE2-interval (Fig. 6b), ~~the~~ the Wunstorf SST record does not capture the rapid increase in SST at the onset of OAE2, previously attributed to a rise in atmospheric CO₂ released by extensive volcanism (e.g., Forster et al., 2007). The Wunstorf SST-record does show, despite being supported by predominantly one data point (resulting from the removal of samples with a BIT-index > 0.15) ~~however~~, a ~5°C cooling pulse during the early stages of OAE2 (Fig. 6c). Six consecutive samples following our data point with lowest SST support a subsequent warming trend, following a colder phase, however. Based on its stratigraphic position within the early stages of the CIE ~~carbon isotope excursion~~, we attribute this cooling pulse to the Plenus Cold Event (PCE; Gale and Christensen, 1996). The PCE, The Plenus Cold Event, previously an event first recognized as an incursion of boreal fauna in the shelf seas of NW Europe (e.g., Jefferies, 1962; Gale and Christensen, 1996; Voigt et al., 2004), represents a substantial cooling event based on TEX₈₆-based paleo-SST records throughout the proto-North Atlantic basin (Forster et al., 2007; Sinninghe Damsté et al., 2010; van Helmond et al., 2014). At Wunstorf the data point with lowest SST correlates to a level above the Plenusbank, located at 47.30–46.85 mbs (Voigt et al., 2008) after the maximum in the CIE. The lack of reliable SST data for the interval between 47.74 and 46.21 mbs complicates precise determination of the onset of the PCE at Wunstorf, however. In three more “complete”, previously published TEX₈₆-based paleo-SST records

across the PCE, i.e., ODP Site 1260 (Forster et al., 2007), ODP Site 1276 (Sinninghe Damsté et al., 2010) and Bass River (van Helmond et al., 2014) the cooling in TEX₈₆-based SSTs starts before the first maximum in the CIE, prior to the occurrence of boreal fauna in the shelf seas of NW Europe (Gale and Christensen, 1996), suggesting that faunal migrations lagged the cooling event as reconstructed by TEX₈₆. Therefore precise correlations of the PCE between sites remains challenging. The identification of the PCE at ~~has by now been identified as a substantial cooling event in TEX₈₆-based paleo-SST records at DSDP Site 367, ODP Site 1260, ODP Site 1276, Bass River (all proto-North Atlantic basin; Forster et al., 2007; Sinninghe Damsté et al., 2010; van Helmond et al., 2014) and Wunstorf, alongside the previous identifications of the PCE throughout the proto-North Atlantic basin, suggesting~~ suggest that ~~the PCE~~ was a hemisphere-wide and perhaps even a global ~~-event~~ signal. This supports the hypothesis that enhanced global carbon burial temporarily suppressed atmospheric CO₂ levels during OAE2 (Arthur et al., 1988; Sinninghe Damsté et al., 2010). The PCE is related to changes in ocean circulation, recorded by the incursion of a northerly sourced water mass as derived from a negative neodymium isotope excursion in the English Chalk at Eastbourne (Zheng et al., 2013) and a trace-metal anomaly in the Western Interior Seaway (Eldrett et al., 2014). This northerly sourced water mass may have been instrumental for the dispersion of boreal fauna— in the shelf seas of NW Europe, in line with the observed differences in timing between TEX₈₆-based cooling in SSTs and the occurrence of boreal fauna.

Interestingly, ~~this—the~~ interval of the PCE marks the occurrence of the *Cyclonephelium compactum-membraniphorum* complex (*C. comp.-memb. cplx.*) within the OAE2 interval in the Wunstorf core (Fig. 6c,d). This is in accordance with previous records from the Bass River section (van Helmond et al., 2014) and the Shell Iona-1 core (Eldrett et al., 2014). Although the biogeographic distribution of this complex is still partly unclear, this suggests that the introduction of *C. comp.-memb. cplx.* at mid-latitude sites in both northwest Europe and the east coast of North-America was quasi-instantaneous and linked to the ~~-PCE~~ Plenus Cold Event.

No significant difference in the reconstructed SSTs is recorded between the black shales and the more TOC-lean marls and limestones. This suggests that the cyclic deposition of black 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 Shelf), DSDP Site 367 (Cape Verde Basin), ODP Site 1260 (Demarara Rise), and Site 1276 (North Atlantic; Table 1), which may perhaps be an artefact of the low resolution achieved for

the Plenus Cold Event at Wunstorf. Reconstructions of absolute temperatures based on TEX₈₆ at values significantly exceeding the modern calibration may yield significant errors, since the modern core-top calibration only ranges to 30°C (Kim et al., 2010). Therefore SSTs exceeding this value will always be based on extrapolation, although mesocosm studies have revealed that TEX₈₆ also shows a positive response with increasing temperatures, in the 30-40°C range (Schouten et al., 2007b). Furthermore the logarithmic TEX₈₆^H-index (Kim et al., 2010), used in this study, has a calibration maximum of 38.6°C, i.e., when TEX₈₆ = 1 the reconstructed SST is 38.6°C. SSTs reconstructions for samples with a TEX₈₆-value >0.9 may therefore be relatively conservative. Nonetheless, the warm and relatively stable background 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).

4.2 Hydrology

Although pollen rank among the most resistant groups of palynomorphs (Traverse, 1994), there is evidence that pollen grains are degraded relatively rapidly (<10 kyr) in the presence of diffusively introduced oxygen (e.g., Keil et al., 1994). This may perhaps explain why absolute pollen and spores concentrations are higher in the black shales, deposited under anoxic conditions. This contrasts with the organic lean marls and limestones deposited during ~~in~~ phases in which pore waters of surface sediments contained relatively high concentrations of oxygen, explaining the low absolute pollen and spores concentrations. Among modern dinoflagellate cysts, members of the family Protoperidiniaceae, are most sensitive to oxidation, and thus may potentially be affected by differential preservation (e.g., Zonneveld, et al., 1997, Zonneveld et al., 2001; Versteegh and Zonneveld, 2002). No consensus exists in the field whether this differential preservation is imprinted in the sedimentary record (e.g., Reichart and Brinkhuis, 2003). ~~Despite evidence for some preferential preservation of some groups of dinocysts in Quaternary sediments (e.g., Zonneveld, et al., 1997; Versteegh and Zonneveld, 2002), in general the same holds for dinocysts, explaining higher dinocyst concentrations in the black shales.~~ At present, there is no published information that suggests that the selective preservation of dinocysts plays a role in assemblages described from the Cretaceous. If there were one dinocyst taxon potentially 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. ~~Thin-walled dinocysts, e.g., *Paleohystrichophora infusorioides*, which would be expected to be lost from~~

~~sediments upon oxidation most rapidly, are~~ Well-preserved representatives of *P. hystrichophora* are, however, commonly present in the organic lean marls and limestones. ~~This shows that the preferential preservation of palynomorphs, and dinocysts in particular, may not be so straightforward in older sediments, e.g., the Cretaceous, as previously reported for some Quaternary sediments (e.g., Zonneveld, et al., 1997; Versteegh and Zonneveld, 2002).~~

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 ~~ranging from river discharge, wind, to birds and insects~~ (e.g., Traverse and Ginsburg, 1966; Thomson, 1986; Feinsinger and Busby, 1987). Particularly saccate gymnosperm pollen (bisaccates) may be transported by eolian pathways (e.g., Heusser, 1988). Palynological assemblages at Wunstorf are a mixture of saccate gymnosperm pollen and non-saccate gymnosperm pollen and spores, suggesting a mixture of eolian and fluvial input of pollen and spores. However, most of the analyzed samples contain relatively low amounts of saccate gymnosperm pollen (Fig. 6e; Prauss, 2006), suggesting that a substantial amount of the ~~most~~ pollen and spores encountered at Wunstorf ~~were was~~ transported to the ~~ocean~~ marine realm by fluvial processes. The relatively high amounts of pollen and spores with respect to marine palynomorphs (T/M-ratio; Fig. 6e) in the black shales at Wunstorf are therefore interpreted to represent phases of enhanced run-off. This was previously also shown for other Cretaceous Oceanic Anoxic Events (e.g., Herrle et al., 2003). Enhanced run-off most likely resulted from increased (seasonal) precipitation over north and mid-European landmasses, assuming that these yielded significant vegetation cover. Regarding the distance to the coring site, non-saccate pollen and spores most likely originated from the Rheno-Bohemian Massif (e.g., Falcon-Lang et al., 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 could well have stratified the water column, leading to low-oxygen levels in bottom waters. This is also indicated by high abundances of bacterivorous ciliates (Blumenberg and Wiese, 2012), which graze on the interfaces of stratified water bodies (Sinninghe Damsté et al., 1995), supporting the presence of a chemocline in the water column. A persistent stratification of the water column ultimately leads to bottom water anoxia and the formation of black shales in the deeper parts of the LSB. The coupling of the rhythmical occurrence of the black shale layers to the precession cycle (Voigt et al., 2008) suggests that changes in the hydrological cycle were controlled by Earth's orbital parameters.

4.3 Marine Productivity

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

5. Conclusions

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

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

6 [A combination of continental configuration and extensive volcanism, intensifying greenhouse](#)
7 [conditions around the CTB, resulted in an epicontinental shelf sea prone to black shale](#)
8 [deposition as a consequence of precession-driven climate change for the OAE2 interval](#) at
9 Wunstorf, ~~relied on precession-driven changes~~ (Voigt et al., 2008). We conclude, based on
10 relatively high numbers of terrestrially derived pollen and spores and freshwater tolerating
11 dinocysts in the black shale intervals, that precession ~~was driving~~ [drove](#) variations in the
12 hydrological cycle. This caused (seasonal) freshwater stratification of the water column and
13 likely enhanced primary production, ultimately culminating in bottom water anoxia and black
14 shale formation. An orbitally controlled hydrological cycle may have been a critical factor
15 ~~triggering mechanism~~ for other cyclic OAE2 sites located in the proto-Atlantic and Western
16 Interior Seaway at similar latitudes as well.

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Table 1. Overview of the different sites for which TEX₈₆-paleothermometry was applied over the OAE2-interval, and TEX₈₆ values and paleo-SST ranges and averages.

Site	Estimated paleolatitude	TEX ₈₆ range (average)	Reconstructed paleo-SST ^a range (average)
ODP Site 367 ^b	5°N	0.84-0.95 (0.90)	33-37°C (36°C)
ODP Site 1260 ^b	0°	0.85-0.95 (0.92)	34-37°C (36°C)
ODP Site 1276 ^c	30°N	0.74-0.96 (0.90)	30-37°C (36°C)
Bass River ^d	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)

^a Based on the TEX₈₆^H calibration by Kim et al., 2010, ^b Forster et al., 2007, ^c Sinninghe Damsté et al., 2010, ^d van Helmond et al., 2014

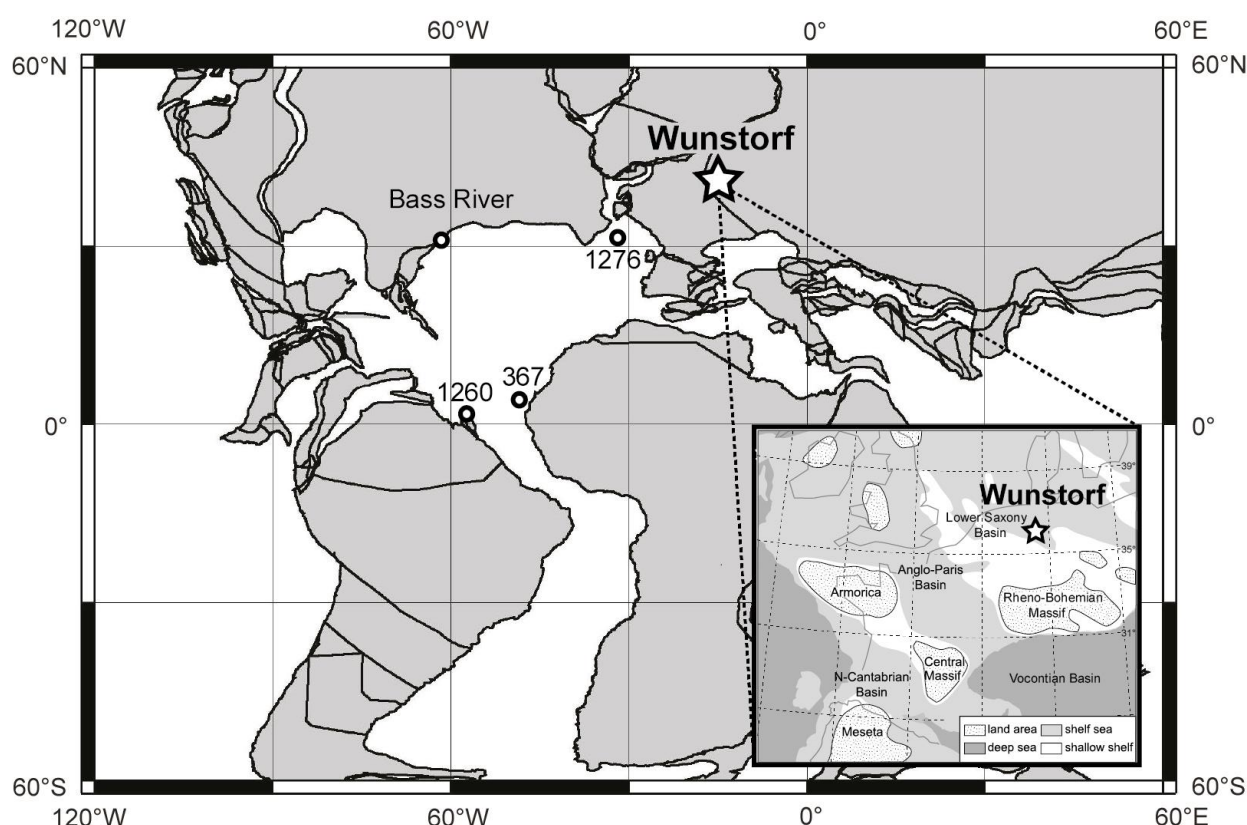


Figure 1. Paleotectonic reconstruction for the Cenomanian/Turonian boundary time interval, with the location of the Wunstorf core and sections with previously published TEX₈₆-based SST-records: Bass River, DSDP site 367, ODP sites 1260 and 1276 indicated (map generated at <http://www.odsn.de/odsn/services/paleomap/paleomap.html>). 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).

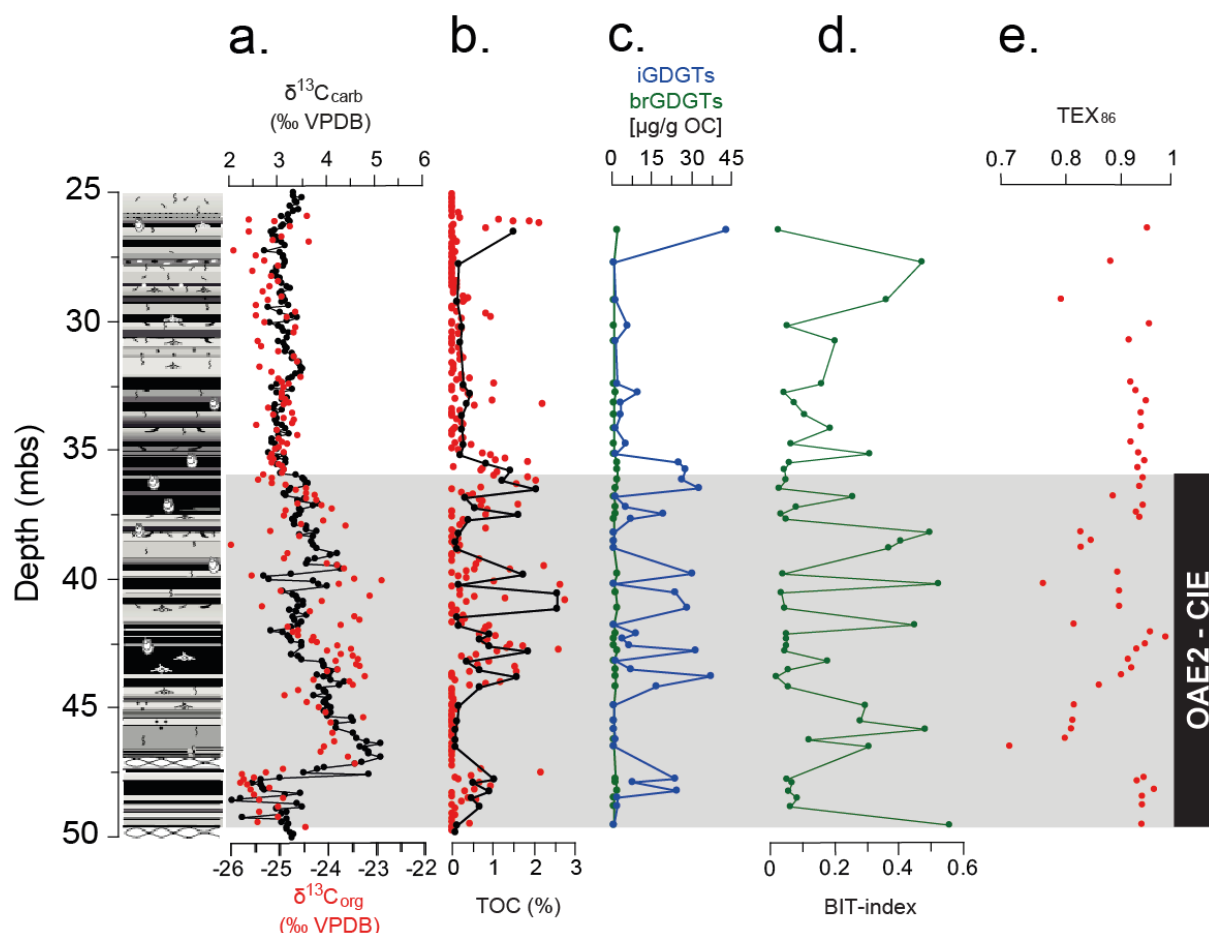
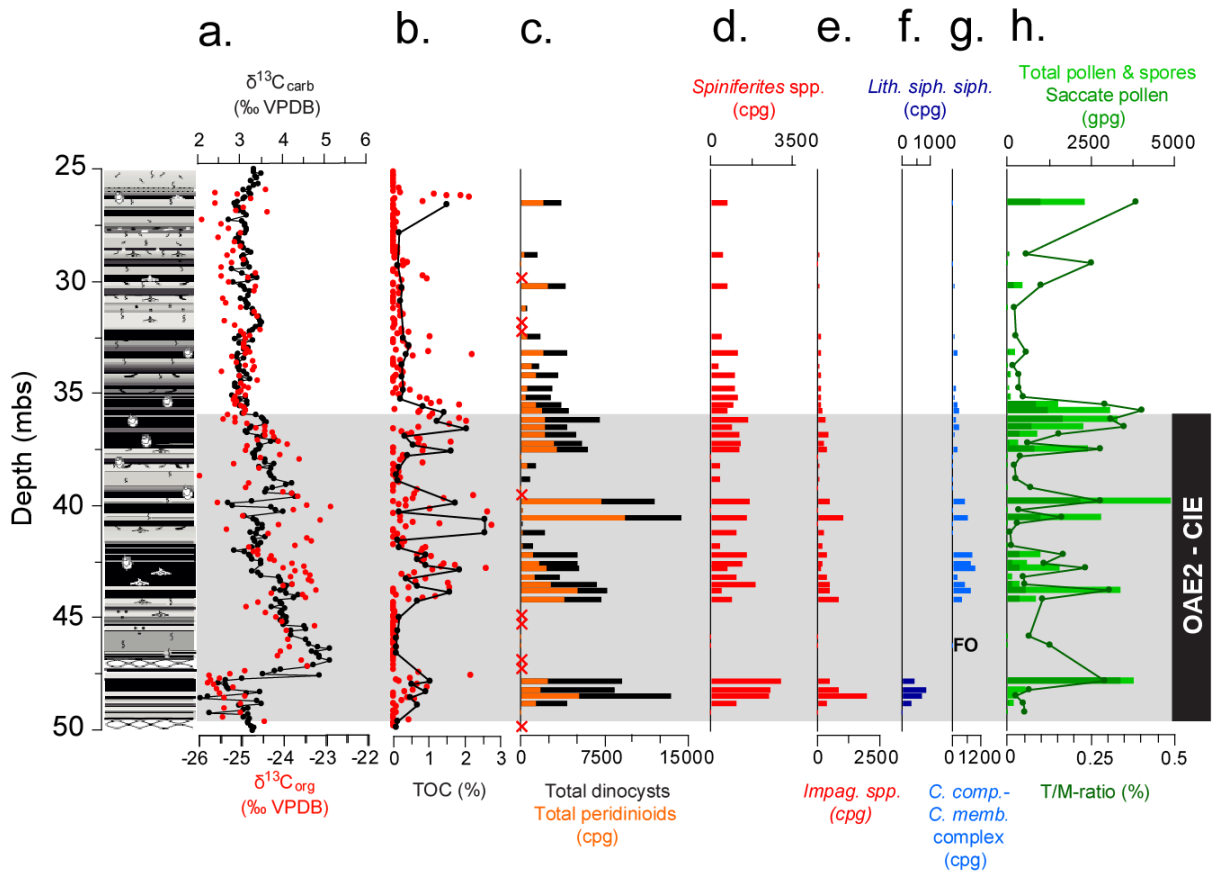
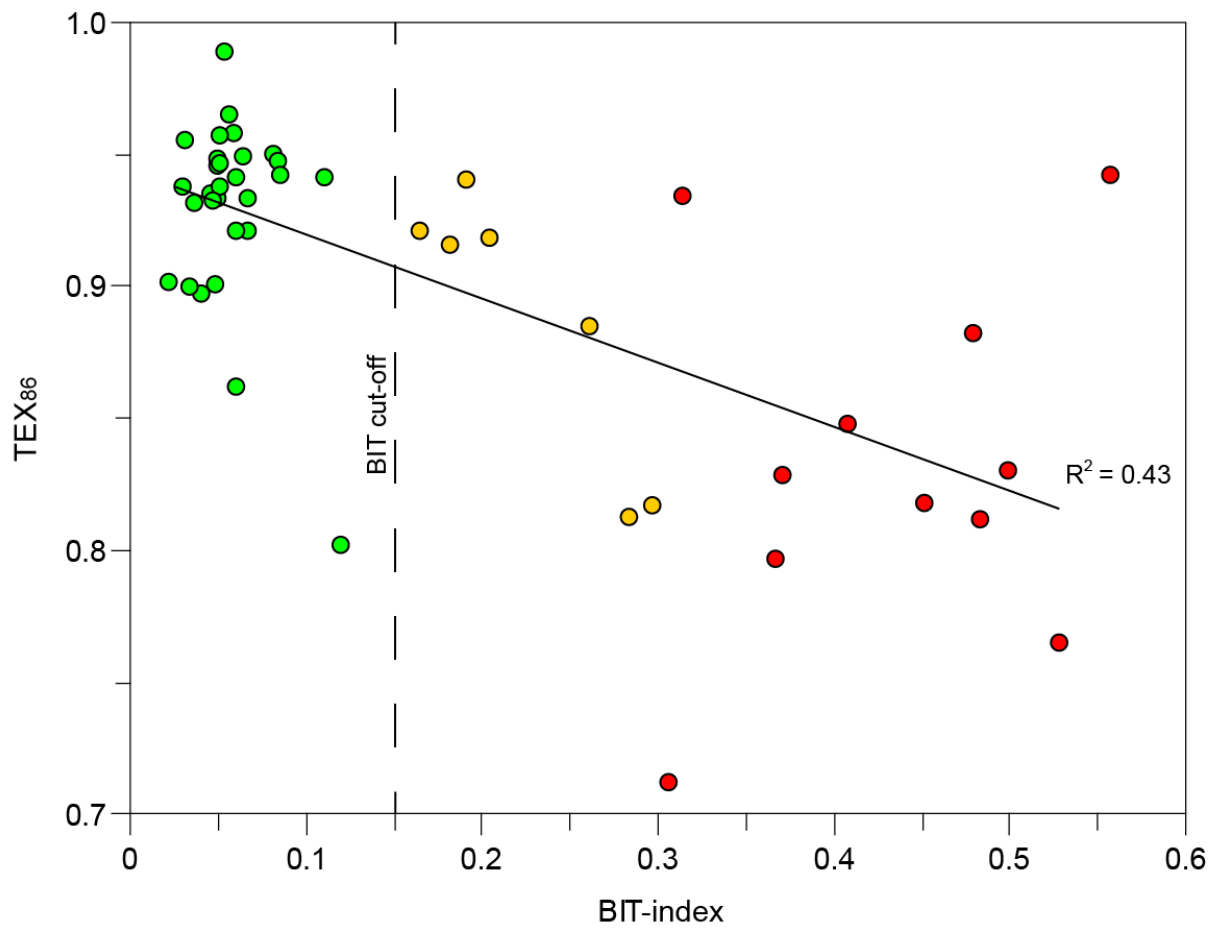


Figure 2. Geochemical results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al.(2008). (a) $\delta^{13}\text{C}_{\text{carb}}$ (Voigt et al., 2008) and $\delta^{13}\text{C}_{\text{org}}$ (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this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



1 Figure 3. Geochemical and palynological results for the Cenomanian-Turonian transition of
2 the Wunstorf core. Stratigraphy from Voigt et al. (2008). (a) $\delta^{13}\text{C}_{\text{carb}}$ (Voigt et al., 2008) and
3 $\delta^{13}\text{C}_{\text{org}}$ (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 peridinioid 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.



1
2 Figure 4. Cross plot of TEX₈₆ versus BIT-index values.

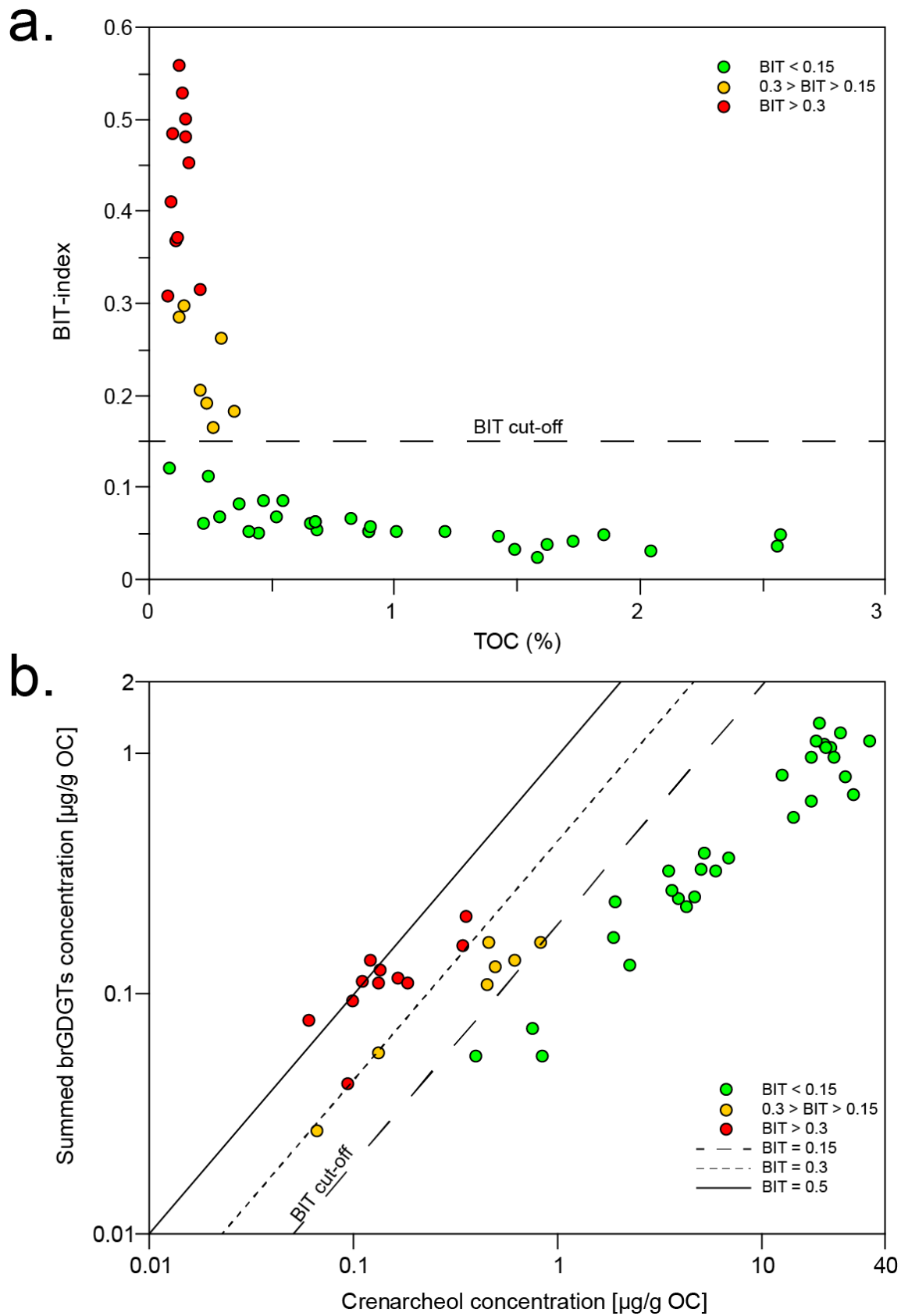


Figure 5. (a) Cross plot of summed brGDGTs ($\mu\text{g/g OC}$) versus crenarcheol ($\mu\text{g/g OC}$) on a logarithmic axis. (b) Cross plot of BIT-index values versus total organic carbon (TOC).

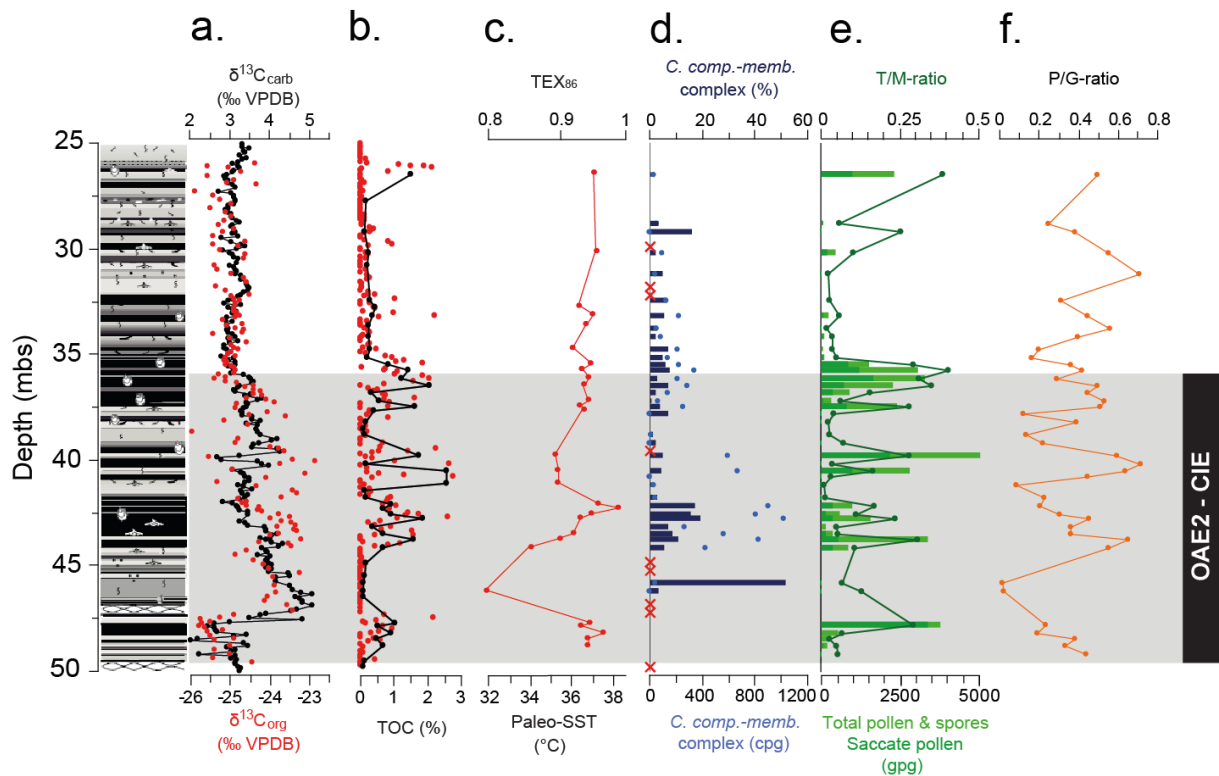


Figure 6. Geochemical and palynological results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al. (2008). (a) $\delta^{13}\text{C}_{\text{carb}}$ (Voigt et al., 2008) and $\delta^{13}\text{C}_{\text{org}}$ (du Vivier et al., 2014; red). (b) Total organic carbon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