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 using a core spanning the OAE2 from Wunstorf, Lower Saxony Basin (LSB; North Gemany), 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, TEX_{86}^{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, TEX_{86} 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) of carbonate ($\delta^{13}C_{carb}$) and organic matter ($\delta^{13}C_{org}$), with an estimated duration of 450-600 kyr (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 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 CO_2 (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 the solubility of oxygen in 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 (TEX_{86}; 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 oftotal 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 $\delta^{13}C_{carb}$ (~2‰) and $\delta^{13}C_{org}$ (~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 $\delta^{13}C_{org}$, 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 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. 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 µm; Alltech). GDGTs (m/z 1018-1302) were detected using selective ion monitoring. For this method it was exhibited that for samples with a high TEX_{86} value, a concentration of 0.1 ng of injected GDGTs on the LC column was still sufficient to yield trustworthy TEX_{86} values (Schouten et al., 2007a). The minimum GDGT concentration injected on the LC column per measurement in this study was ~0.3 ng. TEX_{86}-index values were calculated after Schouten et al. (2002), and converted to absolute annual average sea surface temperatures (SSTs)using the TEX_{86}^{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 µm 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}17β,21β(H) hopane was the dominant hopane. No αβ-hopanes were encountered, so the (ββ/(ββ+βα+αα)) 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 17β, 21β (H)-stereochemistry. This indicates that the thermal maturity of the sedimentary organic matter was sufficiently low for the application of TEX_{86} 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 µg/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 *Ginginodinium* 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 TEX_{86} values, are also produced in soils. High input of soil-derived iGDGTs, reflected by elevated BIT index values, might therefore bias TEX_{86}-derived SST reconstructions (Weijers et al., 2006). TEX_{86} 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 TEX_{86} values. Previous work has recommended a cut-off value of the BIT index to exclude this effect from TEX_{86}-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 (Hetzel 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 TEX_{86} values for sediments that suffered post-depositional oxidation, other studies have shown that there can be a considerable post-depositional oxidation effect on TEX_{86} values and thus the paleo-SST reconstructions derived from it (e.g., Huguet et al., 2009). The linear correlation between TEX_{86} 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 crenarcheol (Fig. 5b), we decided to remove reconstructed paleo-SST data with a BIT-index > 0.15. This changes the linear correlation between TEX_{86} 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 TEX_{86}^{H}-calibration of Kim et al. (2010; Fig. 6c) are similar to previous TEX_{86}-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 TEX_{86} values at the onset of the OAE2-interval (Fig. 6b), the Wunstorf SST record does not capture the rapid increase in SST at the onset of OAE2, previously attributed to a rise in atmospheric CO_2 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), 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, 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 TEX_{86}-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 TEX_{86}-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 TEX_{86}-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 $TEX_{86.}$ Therefore precise correlations of the PCE between sites remains challenging. The identification of the PCE at

Wunstorf, alongside the previous identifications of the PCE throughout the proto-North Atlantic basin, suggest that the PCE was a hemisphere-wide and perhaps even a global event. This supports the hypothesis that enhanced global carbon burial temporary suppressed atmospheric CO_2 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 TEX_{86}-based cooling in SSTs and the occurrence of boreal fauna. Interestingly, 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.

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 TEX_{86} 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 TEX_{86} also shows a positive response with increasing temperatures, in the 30-40°C range (Schouten et al., 2007b). Furthermore the logarithmic TEX_{86}^{H}-index (Kim et al., 2010), used in this study, has a calibration maximum of 38.6°C, i.e., when TEX_{86} = 1 the reconstructed SST is 38.6°C. SSTs reconstructions for samples with a TEX_{86}-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 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). 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.

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, 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 pollen and spores encountered at Wunstorf was transported to the 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).

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.

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). We conclude, based on relatively high numbers of terrestrially derived pollen and spores and freshwater tolerating dinocysts in the black shale intervals, that precession was driving variations in the hydrological cycle. This caused (seasonal) freshwater stratification of the water column and likely enhanced primary production, ultimately culminating in bottom water anoxia and black shale formation. An orbitally controlled hydrological cycle may have been a critical factor for other cyclic OAE2 sites located in the proto-Atlantic and Western Interior Seaway at similar latitudes as well.

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Table 1. Overview of the different sites for which TEX_{86}-paleothermometry was applied over the OAE2-interval, and TEX_{86} 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 TEX_{86}^{H} calibration by Kim et al., 2010, [b] Forster et al., 2007, [c] Sinninghe Damsté et al., 2010, [d] van Helmond et al., 2014

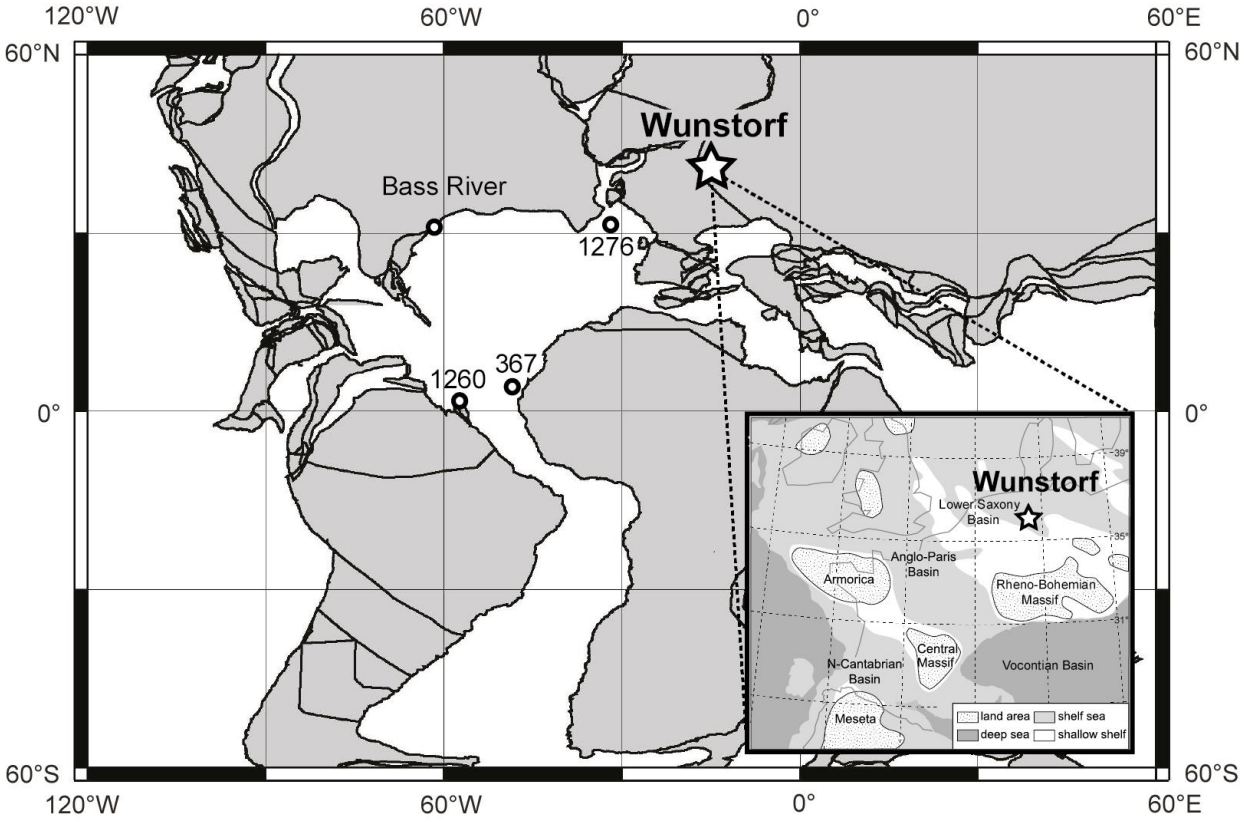

Figure 1. Paleotectonic reconstruction for the Cenomanian/Turonian boundary time interval, with the location of the Wunstorf core and sections with previously published TEX_{86}-based SST-records: Bass River, DSDP site 367, ODP sites 1260 and 1276 indicated (map generated at http://www.odsn.de/odsn/services/paleomap/paleomap.html). 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).

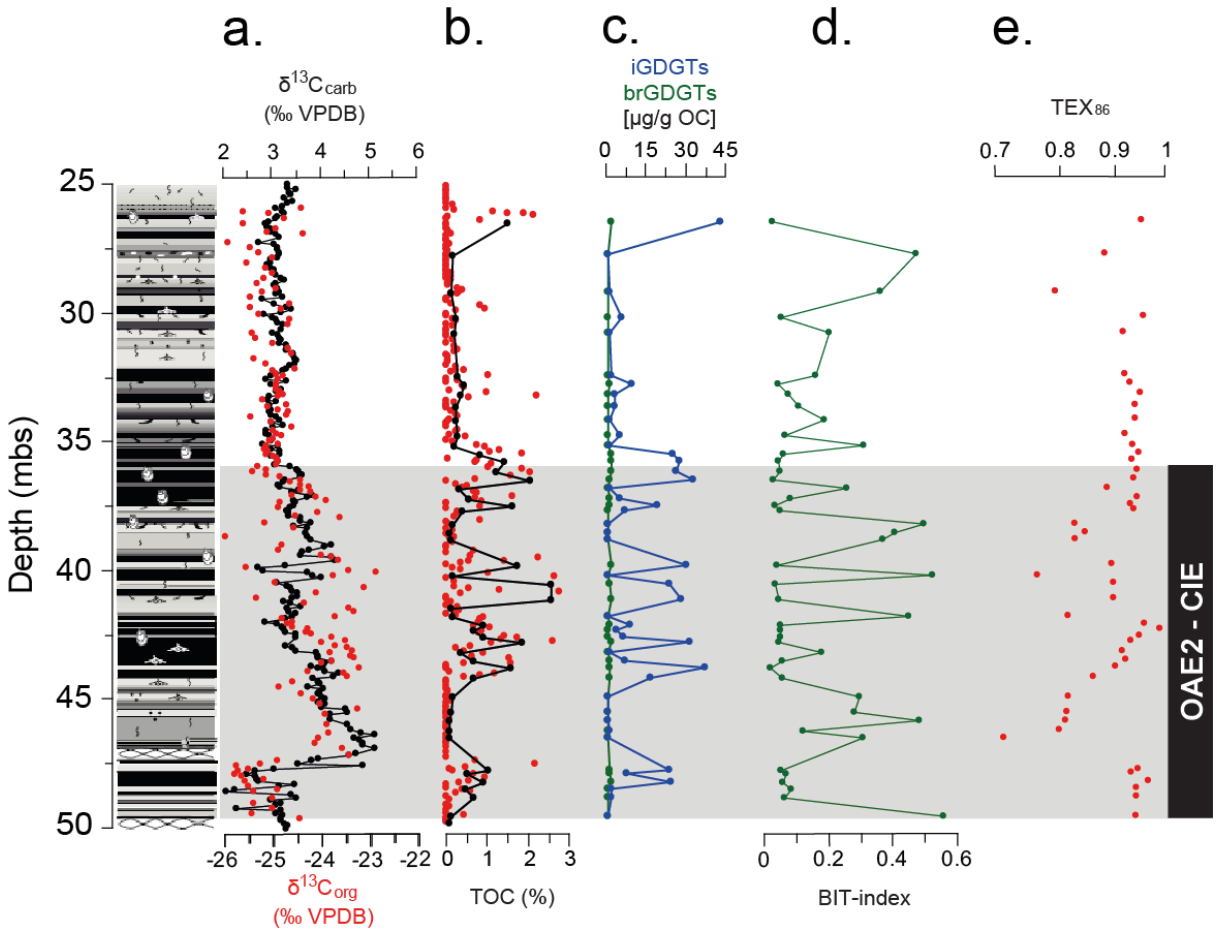

Figure 2. Geochemical results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al.(2008). (a) $\delta^{13}C_{carb}$ (Voigt et al., 2008) and $\delta^{13}C_{org}$ (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, Hetzel et al.,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

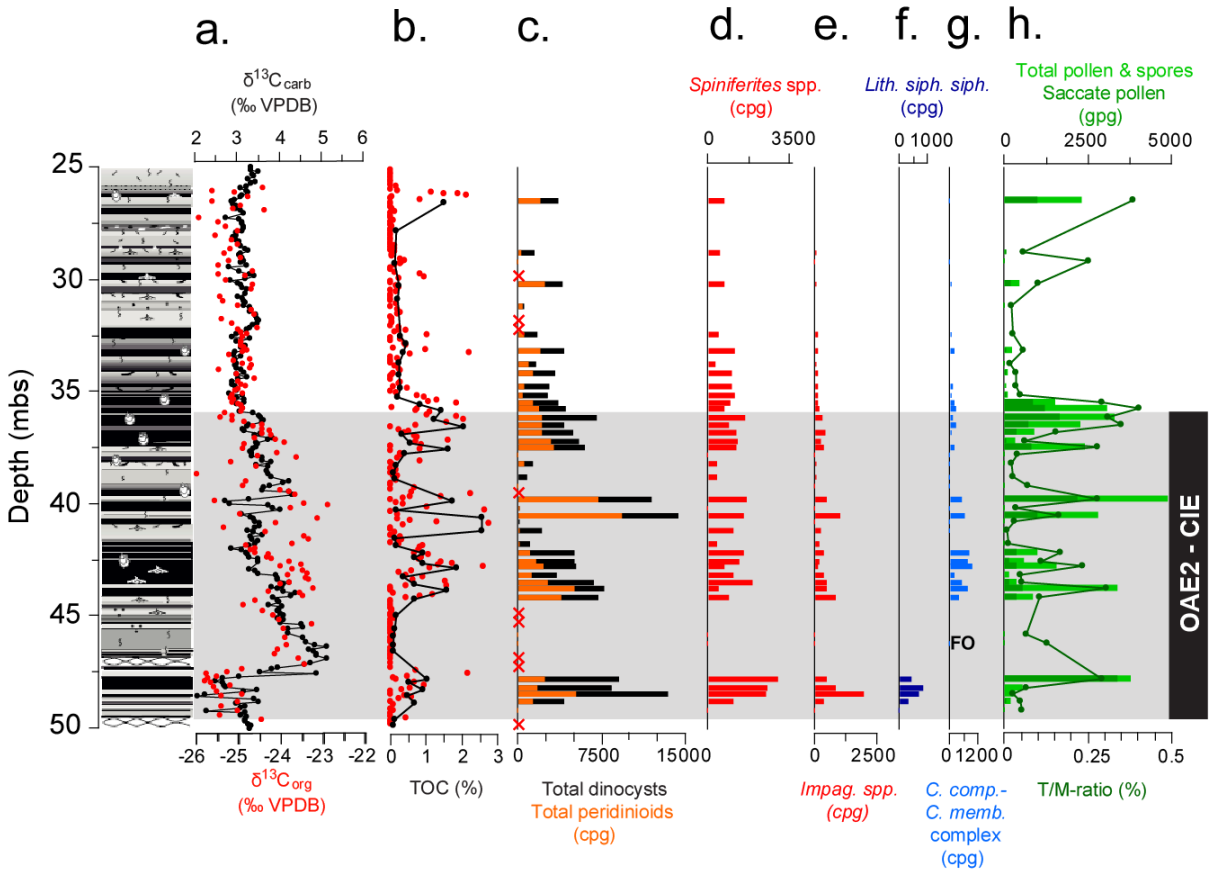

Figure 3.Geochemical and palynological results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al.(2008). (a) $\delta^{13}C_{carb}$ (Voigt et al., 2008) and $\delta^{13}C_{org}$ (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, Hetzel et al., 2011). (c) Total dinocyst concentrations (black) and total peridinioidal cysts (orange) per gram sediment dry weight (cpg). (d) Dinocyst species *Spiniferites* spp. (cpg). (e) Dinocyst species *Impagidinium* spp. (cpg). (f) Dinocyst species *Lithosphaeridium siphoniphorum siphoniphorum* (cpg). (g) Dinocyst species *Cyclonephelium compactum – C. membraniphorum* complex (cpg). (h).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. The grey zone indicates the OAE2 interval after Voigt et al.(2008). mbs = meters below surface.

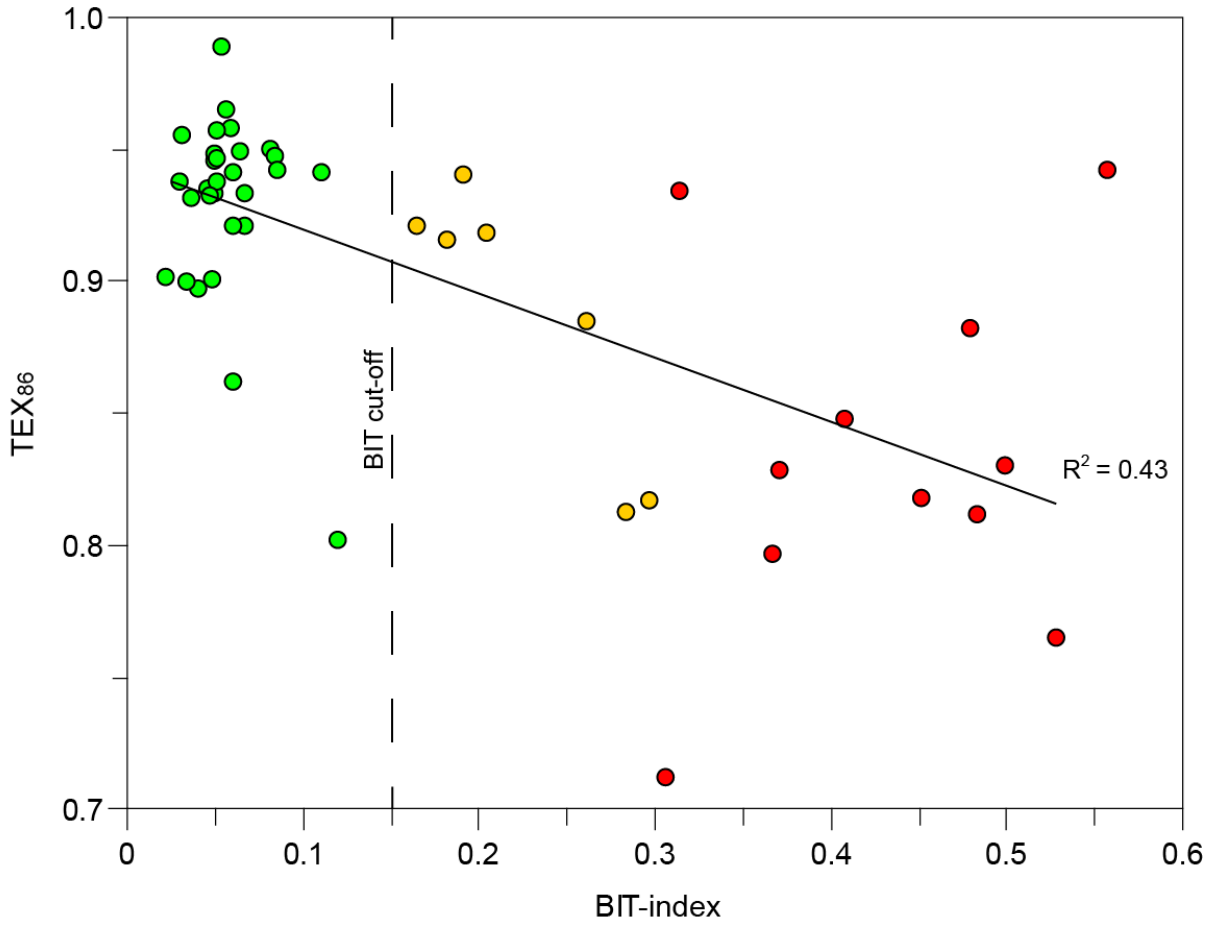

Figure 4. Cross plot of TEX_{86} versus BIT-index values.

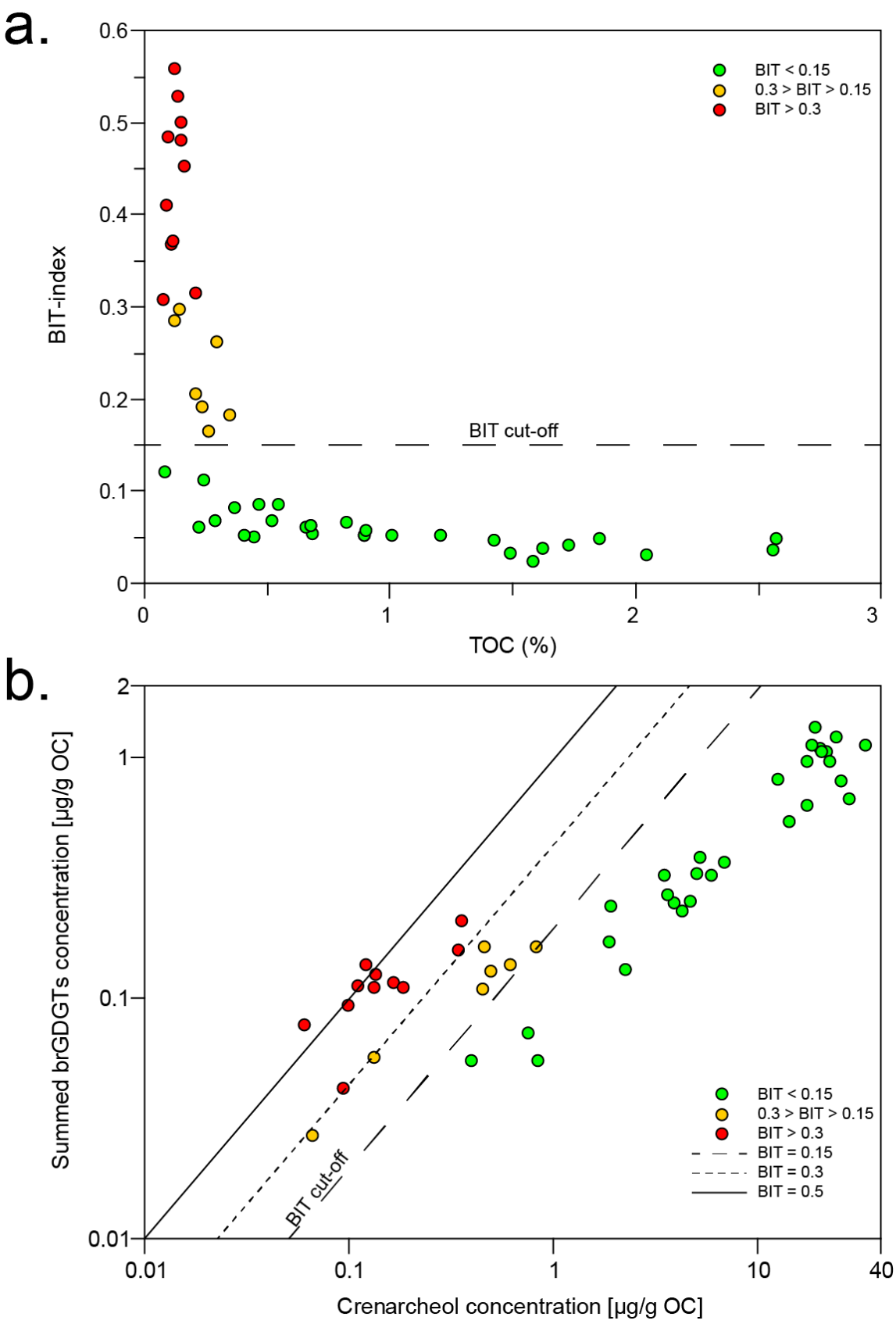

Figure 5. (a) Cross plot of summed brGDGTs (µg/g OC) versus crenarcheol (µg/g OC) on a logarithmic axis. (b) Cross plot of BIT-index values versus total organic carbon (TOC).

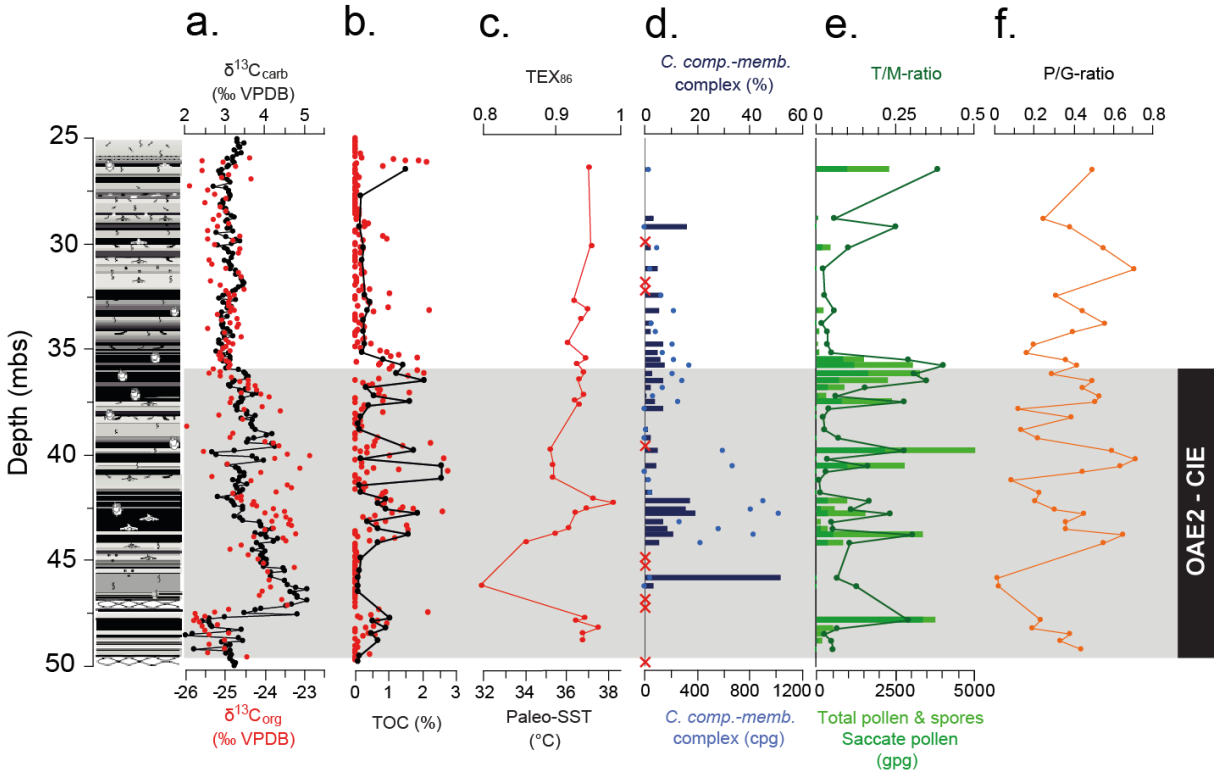

Figure 6. Geochemical and palynological results for the Cenomanian-Turonian transition of the Wunstorf core. Stratigraphy from Voigt et al. (2008). (a) $\delta^{13}C_{carb}$ (Voigt et al., 2008) and $\delta^{13}C_{org}$ (du Vivier et al., 2014; red). (b) Total organic carbon (TOC; black, this study; red, Hetzel et al., 2011). (c) TEX_{86}-values and TEX_{86}^{H}-based SST reconstruction (Kim et al., 2010) (d) Relative abundance (%) and absolute abundancein 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) Peridiniod vs. gonyaulacoid dinocysts (P/G-ratio).The grey zone indicates the OAE2 interval after Voigt et al. (2008). mbs = meters below surface.