

## ***Interactive comment on “Freshwater discharge controlled deposition of Cenomanian-Turonian black shales on the NW European epicontinental shelf (Wunstorf, North Germany)” by N. A. G. M. van Helmond et al.***

**N. A. G. M. van Helmond et al.**

n.vanhelmond@uu.nl

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We thank Dr. Naafs for his positive evaluation of our manuscript and the constructive comments and suggestions. We will reply to his comments below and aim to revise the manuscript accordingly.

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

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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: We agree with Dr. Naafs's comment that the preservation of palynomorphs, where an important conclusion of the paper is relying on, should be discussed in more detail in the revised manuscript. First of all it is unclear whether there are (large) differences in preservation between biomarkers and palynomorphs. Based on our record for the Wunstorf section we suggest that oxidation had a larger effect on the GDGTs compared to the palynomorphs. This is also shown by data from other paleosettings, where palynomorphs are present while GDGTs (and some other biomarkers) are already degraded (e.g., Ruhl et al., 2011). Studies on the F-turbidite 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 F-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, on the other hand, 100% of the oxygen sensitive dinocysts were degraded (Zonneveld et al., 2008). This implies that the types of palynomorphs (oxygen sensitive or not) are essential in determining the effect of oxidation.

We are familiar with the work by Dr. G. Versteegh. This work 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

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by differential preservation is based on some of the studies he co-authored. In these studies (e.g., Zonneveld et al., 1997, 2001), focusing on Quaternary sediments, it is shown that a group of dinoflagellates "(Proto)peridinioids" are most sensitive to oxygen, and thus affected by differential preservation. No consensus exists in the field if this differential preservation is imprinted in the sedimentary record. 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 would be one dinocyst taxon potentially prone to be selectively degraded in the assemblages we record, it would be the thin-walled dinocyst *Paleohystrichophora infusorioides*, which also belongs to the peridinioids. The presence of *Paleohystrichophora infusorioides*, throughout the record, supports our reasoning that the palynological assemblage is less (or not) influenced by preferential preservation of palynomorphs. We will include these discussions in the revised manuscript.

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: As stated in the current manuscript, saccate gymnosperm pollen are initially dispersed by wind but transport to the marine realm also takes place by river systems (e.g., Mudie and McCarthy, 1994). The pollen encountered in Wunstorf are a mixture of non-saccate pollen and saccate pollen, which dominantly rely on fluvial transport. So the pollen assemblage at Wunstorf is indeed a mixture of both transport mechanisms. We will clarify this in the revised manuscript.

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

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ning of the abstract.

Author's Reply: We agree, and will rephrase this part of the abstract

Reviewer's Comment: Page 3578 Line 25: rephrase sentence.

Author's Reply: Sentence will be rephrased.

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 will adjust the sentence as suggested by the reviewer.

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

Author's Reply: We will adjust 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: will be rephrased and m/z's will be provided.

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

Author's Reply: Crenarchaeol is indeed also produced by thaumarchaeota in soil. Many studies have indicated, however, that BIT is still a useful tracer for continental

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organic matter (e.g., Schouten et al., 2013; review). We will briefly elaborate on the limitations of the BIT-index in the revised manuscript.

Reviewer's Comment: Page 3764: Line 5: Again, how was this selection made and how many samples did you look at? Why weren't all samples used for TEX86 measured on the GC-MS to infer the thermal maturity for each TEX86 data point? Some sections are characterized by large variations in hopane distributions across OAEs. You have the fractions, so I don't understand why not all samples were run on the GC-MS to assess the maturity. Did I miss something? I urge the authors to measure all samples on the GC-MS. Or at least plot the C31 hopane  $\beta\beta/(\alpha\beta+\beta\alpha+\alpha\alpha)$  of all the measured samples in figure 2 and 6. Also show the S/R ratio. Are the samples all immature enough to be confident in your TEX86 estimates? Line 5: C31  $17\beta(H)$ ,  $21\beta(H)$  hopane. Line 7: Even if you don't have detectable amounts of  $\alpha\beta$ -hopanes (but see next comment), the  $\beta\beta/(\alpha\beta+\beta\alpha+\alpha\alpha)$  ratio can still be  $\hat{=}$  1 if you have  $\beta\alpha$ -hopanes. Line 8: Blumenberg and Wiese (2012) do report (C31)  $\alpha\beta$  (and  $\beta\alpha$ )-hopanes in their samples (Fig. 6 of their manuscript). So do you really only have  $\beta\beta$ -hopanes in your samples and if so, why are the results different from the previous study?

Author's Reply: We measured the degree of isomerization of the C31 hopanes to check if the degree of thermal maturity was not too high for TEX86 palaeothermometry (cf. Schouten et al., 2004) in two samples. We only could identify C31  $\beta\beta$ -hopanes and consequently the isomerization ratio is 1. We only checked two samples because typically the degree of thermal maturation in a section like this will be similar. Distribution of hopane biomarkers was not the target of the study; therefore, we only analyzed two samples. We don't really see why we would need to analyze the hopanes in all of the samples analyzed as requested by the referee.

Reviewer's Comment: Page 3767 Line 20: In my opinion, there is no significant cooling if you take out the one data point at  $\sim$ 47 m from figure 6c. So the whole story of a  $\sim$ 5°C cooling during the Plenus cold event is based on one single data point. I suggest deleting the section(s) that deal with cooling during the Plenus cold event or at least

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mention that this is based on very few data points. I concur with the other reviewer that a few more TEX86 datapoints during the event would be ideal to confidently identify a cooling, although I'm not sure whether the high BIT values prevents the authors from doing this.

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

Reviewer's Comment: Page 3768 Line 19: Can you elaborate a bit on the possible TEX86 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 TEX86H-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.

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: There might be a preferential degradation effect. The high P/G ratio's for samples with low TOC content around 49,5 and between 35 and 30 meters, how-

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ever, suggest that this effect is relatively minor because P cysts are considered more prone to oxidation than G cysts (e.g., Zonneveld et al., 2008). Additionally the preferential degradation effect seems to be larger for GDGTs, compared with palynomorphs, see Author's reply on the first comment.

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.

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: Indeed 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 530A (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).

Sincerely,

Also on behalf of all authors,

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Niels van Helmond

#### References

Blumenberg, M., and Wiese, F.: Imbalanced nutrients as triggers for black shale formation in a shallow shelf setting during the OAE 2 (Wunstorf, Germany), *Biogeosciences*, 9, 4139–4153, doi:10.5194/bg-9-4139-2012, 2012.

Forster, A., Schouten, S., Moriya, K., Wilson, P.A., and Sinninghe Damsté, J.S.: Tropical warming and intermittent cooling during the Cenomanian/Turonian Oceanic Anoxic Event (OAE 2): Sea surface temperature records from the equatorial Atlantic, *Paleoceanography*, 22, PA1219. doi:10.1029/2006PA001349, 2007.

Forster, A., Kuypers, M.M.M., Turgeon, S.C., Brumsack, H.-J., Petrizzo, M.R., Sinninghe Damsté, J.S.: The Cenomanian/Turonian oceanic anoxic event in the South Atlantic: new insights from a geochemical study of DSDP Site 530A, *Palaeogeogr. Palaeoclimatol.*, 267, 256–283, doi:10.1016/j.palaeo.2008.07.006, 2008.

Huguet, C., de Lange, G.J., Gustafsson, Ö., Middelburg, J.J., Sinninghe Damsté, J.S., and Schouten, S.: Selective preservation of soil organic matter in oxidized marine sediments (Madeira Abyssal Plain). *Geochimica et Cosmochimica Acta*, 72, 6061–6068, 2008.

Kuypers, M.M., Pancost, R.D., Nijenhuis, I.A., and Sinninghe Damsté, J.S.: Enhanced productivity led to increased organic carbon burial in the euxinic North Atlantic basin during the late Cenomanian oceanic anoxic event. *Paleoceanography*, 17, 3-1, 2002.

Kuypers, M.M., Lourens, L.J., Rijpstra, W.I.C., Pancost, R.D., Nijenhuis, I.A., and Sinninghe Damsté, J.S.: Orbital forcing of organic carbon burial in the proto-North Atlantic during oceanic anoxic event 2. *Earth and Planetary Science Letters*, 228, 465–482, 2004.

Mudie, P.J., and McCarthy, F.M.: Late Quaternary pollen transport processes, western North Atlantic: Data from box models, cross-margin and NS transects. *Marine Geology*

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118, 79-105, 1994.

Ruhl, M., Bonis, N.R., Reichart, G.J., Sinninghe Damsté, J.S., and Kürschner, W.M.: Atmospheric carbon injection linked to end-Triassic mass extinction. *Science*, 333 (6041), 430-434, 2011.

Schouten, S., Hopmans, E. C., and Sinninghe Damsté, J.S.: The effect of maturity and depositional redox conditions on archaeal tetraether lipid palaeothermometry, *Organic Geochemistry*, 35, 30 567–571, doi:10.1016/j.orggeochem.2004.01.012, 2004.

Schouten, S., Forster, A., Panoto, F.E., and Sinninghe Damsté, J.S.: Towards calibration of the TEX86 palaeothermometer for tropical sea surface temperatures in ancient greenhouse worlds. *Organic Geochemistry*, 38, 1537-1546, 2007.

Schouten, S., Hopmans, E.C., and Sinninghe Damsté, J.S.: The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: a review. *Organic geochemistry*, 54, 19-61, 2013.

Sinninghe Damsté, J.S., van Bentum, E.C., Reichart, G.-J., Pross, J., and Schouten, S.: A CO<sub>2</sub> decrease-driven cooling and increased latitudinal temperature gradient during the mid-Cretaceous Oceanic Anoxic Event 2, *Earth Planet. Sc. Lett.*, 293, 97–103, doi:10.1016/j.epsl.2010.02.027, 2010.

Van Helmond, N.A.G.M., Sluijs, A., Reichart, G.J., Sinninghe Damsté, J.S., Slomp, C.P., and Brinkhuis, H.: A perturbed hydrological cycle during Oceanic Anoxic Event 2, *Geology*, 42, 123-126, doi:10.1130/G34929.1, 2014.

Zonneveld, K.A.F., Versteegh, G.J.M., and De Lange, G.J.: Preservation of organic walled dinoflagellate cysts in different oxygen regimes: A 10 000 years natural experiment; *Marine Micropaleontology*, 29, 393–405, 1997.

Zonneveld, K.A.F., Versteegh, G.J.M., and De Lange, G.J.: Palaeoproductivity and post-depositional aerobic organic matter decay reflected by dinoflagellate cyst assemblages of the Eastern Mediterranean S1 sapropel: *Marine Geology*, 172, 181–195, C2070

2001.

Zonneveld, K.A., Versteegh, G., and Kodrans-Nsiah, M.: Preservation and organic chemistry of Late Cenozoic organic-walled dinoflagellate cysts: a review. *Marine Micropaleontology*, 68, 179-197, 2008.

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Interactive comment on *Clim. Past Discuss.*, 10, 3755, 2014.