

## ***Interactive comment on “Imbalanced nutrients as triggers for black shale formation in a shallow shelf setting during the OAE 2 (Wunstorf, Germany)” by M. Blumenberg and F. Wiese***

**M. Blumenberg and F. Wiese**

[martin.blumenberg@geo.uni-goettingen.de](mailto:martin.blumenberg@geo.uni-goettingen.de)

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The manuscript by Blumenberg and Wiese reports new organic geochemical and bulk d15N data across the Cenomanian-Turonian Anoxic Event (OAE-2), and uses them to infer the trajectory and causes of change in marine ecosystem in this crucial interval of Earth history. Cause of anoxic events and formation of black shales are an old and new problem – the conventional views have regarded black shales and intercalating organic poor sediments as representing ‘eutrophic’ and ‘oligotrophic’ conditions, respectively. However, much new organic geochemical data generated in the past decade have revised the conventional debates. This study also investigates changes in marine

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ecosystem based on new organic geochemical data which would extend our knowledge about what happened during the OAE-2. The conclusions in this manuscript, linking the environmental changes, particularly the changes in marine ecosystem association with climatic condition and associated change in seawater nutrient condition, would add new details and a welcome increase of geographic coverage by reporting from shallow shelf area. The topic is interdisciplinary and the paper would appeal to different segments of the journal's readership, geochemists, paleontologists, and people interested in Earth systems science of environmental changes in deep time at critical episodes. Although I find the topic well-suited for this journal, I have some comments and raise some issues that should be addressed for revising the manuscript.

*Referee comment:* I am confused how the authors interpret the controversy of 2-methyl hopane indices between anhydro-BHTs (Figure 8a) and those calculated from hydrocarbons (Figure 9) which show opposite trends against  $\delta^{15}\text{N}$ . Although the authors mentioned briefly that, using anhydro-BHTs, lower 2-methyl hopanoid indices of 5 and 15

***Reply:*** We agree that the opposing trends for functionalised versus defunctionalised (hopanoid hydrocarbons) 2-methyl hopanoid might be confusing. The general problem of different sources for different pools in the organic matter, however, has been recognized in many different studies (e.g. Kim *et al.*, 2009). We think that similar processes can explain this also for our samples. (2-methyl) anhydroBHT represent the least degraded structures in the samples, which makes it the most genuine and therefore best record of processes in the former overlying water column. (2-methyl) hopanoid hydrocarbons, in contrast, may have been – due to their stability – transported over wide distances. Consequently, hopanoid hydrocarbons are not suitable as biomarker of water column processes, particularly in a shelf environment, which is potentially strongly influenced by lateral transport. Our explanation for the negative correlation of 2-methyl hopane ratios with TOC is that the defunctionalized 2-methyl hopanes

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from the water column are obscured by desmethylated hopanes, which were laterally transported into the basin. These processes were particularly high in times when continental run-off was also high, namely time when black shales were deposited. To overcome the problem of potentially wrong interpretation based on hydrocarbons, we focused our work on functionalized structures and explained this in our MS (p. 5376; line 16 ff.). We disagree with the reviewer that we did not explain the problem of different sources of functionalized hopanoids and hopanoid hydrocarbons as well as the conflicting 2-methyl hopanoid ratios. At page 5388 (line 16 ff.), the scenario described above is interpreted, and we feel that the problem has been sufficiently considered. Based on the reviewer's comment, we therefore also do not see a need to further justify the discussion about the relationship between N<sub>2</sub>-fixation and cyanobacteria, which is in line with numerous publications on the OAE-2 (e.g., Kuypers *et al.*, 2004; Ohkouchi *et al.*, 2006). However, due to the careful consideration of the referees comments, we noticed that we have to correct an imprecise identification of ring A methylated functionalized hopanoids in the MS (the identification of ring A methylated hopanoid hydrocarbons was correct). We used a novel HT-GC column (VF-5 HT; erroneously described as DB-5 HT), and two standard components (C-2 $\beta$  methyl and C-3 $\beta$  methyl bacteriohopanetetrol standards from *Beijerinckia indica* and *Gluconacetobacter xylinum*) were used to test the elution order again. We can show that the originally assigned C-2 methyl anhydroBHT (as well as the C-2 methylated trishomohopanol) was actually the C-3 methyl homologue. Due to this misidentification, we decided to re-analyse the samples and to do co-elution experiments to check for the presence of C-2 methyl anhydroBHTs. We found the concentrations much lower than those of the previously assigned structures. However, the negative correlation with  $\delta^{15}\text{N}$  was still observed, which is in line with our previous interpretation, and we will therefore exchange the data with the new results for C-2 methylated anhydroBHT (Figure 8a). All these points will be discussed in a revised version of the MS. Relevant figures will be changed cor-

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respondingly. Due to the already lengthy discussion, the high co-occurrence of C-3 with C-2 methylated AnhydroBHT is not further discussed in the paper. However, C-3 methyl bacteriohopanepolyols are often reported from methanotrophic, methylotrophic and/or acetic acid bacteria (see for an overview, Talbot Farri-  
mond, 2007), which are all plausible candidates thriving at pelagic redoxclines. This is in accordance with our interpretation of a stratified water body during periods of BS deposition. We will add a respective comment in the revised version of the MS.

*Referee comment:* I think that the manuscript needs careful correlation of their data with the lithological, bio/chemostratigraphical, and organic geochemical data from deep-sea sites (e.g., North Atlantic) to clarify and strengthen the model shown in Figure 11. How the organic geochemical data from the Wunstorf core are correlated to the data such as TOC, 2- methyl hopanoids and isorenieratane provided by previous studies (e.g., Kuypers *et al.*, 2002 Paleooceanography, Kuypers *et al.*, 2004 Geology). Are they well supportive to Figure 11?

**Reply:** Our Figure 11 is valid for the duration of well-established, world-wide OAE 2 positive  $\delta^{13}\text{C}$  carbon isotope excursion (CIE). This CIE provides an excellent isochronous marker, which enables an extremely precise correlation of the data from the Atlantic deep-sea sites with our data from the shelf deposits. In fact, the Atlantic part in our synthesizing Figure 11 is particularly based on those studies, which focused on the deep water facies (e.g. findings of isorenieratane, high occurrences of sulfur-bond 2-methyl hopanoids; Kuypers *et al.* 2004; Pancost *et al.* 2004, Sinninghe Damsté and Köster, 1998). However, the reviewer is correct that we did not consider Kuypers *et al.* (2002) in our discussion. In the revised version, we add the reference as a study, supporting productivity induced BS formation not only in Wunstorf, but also in the Proto-Northatlantic. In addition, we will provide a detailed list of references, on which our Central Atlantic scheme is based in the caption of our Figure 11.

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*Referee comment:* The manuscript needs more careful explanation to convince readers that the negative bulk- $\delta^{15}\text{N}$  records suggest  $^{15}\text{N}$ -depleted biomass associated with the  $\text{N}_2$ -fixation. I think that the authors need to justify that the bulk- $\delta^{15}\text{N}$  represents that of the source organisms.

**Reply:** We agree with the reviewer that this can be potentially a problem. In a recent study of Higgins *et al.* (2012), it was nicely shown that bulk  $\delta^{15}\text{N}$  and that of the source organism must not necessarily be similar. Higgins *et al.* presented in fact evidence that cyanobacterially fixed nitrogen is recycled and subsequently used by algae, a scenario which is explained in the MS. Moreover, different ways of microbial overprint may also affect  $\delta^{15}\text{N}$  values (Lehmann *et al.*, 2002). This relates to oxic versus anoxic turnover, and oxic conditions in surface sediments during non-black shale formation (which is indicated by the occurrence of trace fossils), could indeed explain the observed  $\delta^{15}\text{N}$  values. However, as also shown by Lehmann *et al.*, diagenetic alteration of organic matter should have also affected C/N values in the opposite way as observed at Wunstorf. Thus, we think that a diagenetic explanation is rather unlikely, but we will add a paragraph in chapter 5.1, explaining why we surmise  $\delta^{15}\text{N}$  to record varying nitrogen fixation activity and not diagenetic overprint. Moreover, in almost all previous biomarker studies on the OAE 2 (e.g., Jenkyns *et al.*, 2007; Kuypers *et al.*, 2002, 2004; Ohkouchi *et al.*, 2006), bulk  $\delta^{15}\text{N}$  values were used and interpreted in terms of biomass input from the water column. We followed this line of evidence.

*Referee comment:* Is there any difference in biomarker or N-isotopic compositions between black shales deposited during and after the OAE-2? Explain whether the post-OAE2 black shales are distinctive or identical to the OAE-2 black shales. In Figure 11, what do APB, MCB, and LSB stand for?

**Reply:** As written on p. 5384, line 7 in our MS, no differences between OAE and post-OAE BS are seen. Differences between the samples were rather related to black shale and non-black shale facies. We will add a sentence mentioning this

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observation in chapter 5.3 in a revised version of the MS. Currently, we lack an explanation for the post OAE 2 BS in Wunstorf. However, we could speculate that – even though the volcanogenic-driven input of P ceased after the CIE – P could have been remobilized from already deposited BS, fueling further organic deposition and maintaining a stratified water body still some time, until a critical threshold was reached and the BS system finally collapsed. This, however, remains speculation and is beyond the scope of the MS. The lacking abbreviations (APB: Anglo-Paris Basin; MCB: Münsterland Cretaceous Basin; LSB: Lower Saxony Basin) will be provided in the revised version.

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