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Discussions

Interactive comment on "Cretaceous Oceanic Anoxic Events prolonged by phosphorus cycle feedbacks" *by* Sebastian Beil et al.

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Reply to Interactive comment on "Cretaceous Oceanic Anoxic Events prolonged by phosphorus cycle feedbacks" by Sebastian Beil et al.

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Dear Babette, dear Sebastian and co-authors,

let me first say that I don't tend to write reviews that I haven't been invited to. I do not mean to make the authors' lives harder than they already are. However, the topic your

nice manuscript is about is quite close to my heart, and I have therefore decided to add a few comments that might help to widen the perspective of the manuscript and put into context of a few publications that the authors might have missed. As it happens, some of these publications are (co-) authored by me and my review could be understood as shameless self-promotion. This is not my intention, but the editor might have a different view on this and may therefore decide to ignore my comment.

The manuscript prepared by Beil et al. is an impressive data set on an impressive number samples from two locations that resolve two OAEs (1a and 2) in very high temporal resolution. I have read the comment by Hugh Jenkyns, which focuses on the definition/duration/isotopic expression of the OAEs, and I will not go into any detail on those. Instead, my comment refers to the phosphorus side of the story. I applaude the authors for having generated a very nice P speciation data set, for re- porting the recovery of their extractions relative to total P, and for a very detailed method description in the appendix. In the broadest sense, I also agree with the interpretation of the authors that P recycling from the seafloor during much of OAE2 has potentially led to higher primary productivity, fueling an anoxia-productivity feedback loop that has been previously suggested to extend the "lifetime" of OAEs. My comments, which are all included in the attached PDF as annotations, relate to the (a) a more precise distinction between different redox conditions (namely ferrugi- nous versus euxinic) and (b) the weathering regime. The main reason for raising these issues is that Poulton et al. (2015) conducted a study on the onset of OAE2 from a different Tarfaya core, with a focus on the potential effects of weathering conditions on land on ocean redox, and the related response of the P cycle to these redox changes. Since this manuscript is using very similar methods and proxies on samples from effectively the same location, I think it would be an omission and a missed opportunity to not refer to the published manuscript, and put the new data into context. My comments in the PDF are hopefully self-explanatory, but please feel free to ask for clarificaton.

We would first of all like to thank Christian März for helpful, detailed comments that helped us to clarify and improve our manuscript.

We will include a short discussion on the problematic definition of ferruginous in the context of the Cretaceous in section 4.4 (see below). This point was fully discussed by Scholz et al. (2019), who compared iron-speciation proxies in Cretaceous and modern OMZ sediments (Peruvian margin).
An earlier study by Poulton et al. (2015), focusing on Fe speciation proxies during the onset, peak and early plateau phase of OAE2 in nearby drill core S57, found cyclic variations between euxinic and ferruginous conditions. The stratigraphically extended interval (from MCE to early Turonian) investigated at lower resolution by Scholz et al. (2019) is characterized by a high proportion of unpyritized reactive Fe in the total Fe pool. The results of this study are consistent with a proxy signature that is indicative of anoxic and non-sulfidic, so-called ferruginous, water column conditions throughout the studied interval (Poulton and Canfield, 2011). However, by taking into account the low terrigenous sedimentation rates and tropical weathering on the adjacent continent, Scholz et al. (2019) argued that dissolved Fe (and hydrogen sulphide) concentrations in the water column of the Tarfaya system were unlikely higher than those observed in modern upwelling zones (e.g., Peru margin).
Previous studies proposed that phosphorus burial might be enhanced under ferruginous conditions, implying a negative feedback for the oceanic phosphorus pool and primary production (e.g., März et al., 2008). However, Scholz et al. (2019) did not observe a close relationship between Fe and P burial, despite a ferruginous signature in the sediments, which supports the notion that dissolved Fe concentrations and rates of Fe oxide precipitation in the Tarfaya Basin were moderate and overall similar to modern upwelling systems (Wallmann et al., 2019).

I hope the authors will take my relatively minor comments in the good spirit of scientific exchange, and I am looking forward to seeing the final version of the manuscript published in Climate of the Past.

Please also note the supplement to this comment: https://www.clim-past-

discuss.net/cp-2019-118/cp-2019-118-SC1-supplement.pdf

lines 77-78: Which environments does this refer to? Typically, in sediments underlying most of the oxygenated parts of the world ocean see a "sink switching" not only from organic matter, but also from oxide-bound P to authigenic apatite (see Ruttenberg and Berner, 1993).
As suggested, we revised the text and now include authigenic apatite (Ca-P). We also refer to supplementary material S1 for further information.
Phosphorus remains mainly bound to manganese- and iron-oxides and -hydroxides and occurs as authigenic calcium-bound phosphorus (Supplementary Material S1) in deep-sea sediments underlying well-oxygenated bottom water masses, which typically exhibit C:P below the Redfield ratio.

line 81: I am not sure I would quote this reference as an estimate that is still being used - Ruttenberg's work and especially the discovery of pervasive authigenic apatite formation has superseded this earlier estimate, and I don't think this is being argued with by anyone in the current community.
We acknowledge that the more recent data of Ruttenberg (2003) are now widely accepted. We included the older publication of Broecker and Peng (1982) to underline the point that until recently estimates of the residence time of phosphorus were highly variable. These estimates may still change, as there appear to be imbalances in the phosphorus budget.

lines 93-94: I do not disagree with this statement, but I think the authors should be a bit more cautious regarding the term "anoxic". The increased recycling of P relative to OC from sediments under oxygen-depleted waters is well-documented in many parts of the ocean (nice review paper by Algeo and Ingall, 2001). The formation of phosphorites in the upwelling areas off Peru and Namibia, on the other hand, occurs under quite specific conditions and with the support of specific microbial communities -

and most importantly, under dominantly sulfidic conditions (although the fast changes in bottom water/seafloor redox might also play an important role in enriching P in these shallow environments). In addition, a third line of thought exists regarding the behaviour of P under anoxic, non-sulfidic conditions, which suggests that P can be sequestered into the seafloor under these ferruginous conditions (co-precipitated with Fe minerals or as Fe(II) phosphates). This has been hypothesized for Cretaceous black shales, but also for modern lake sediments, and for subsurface sediments where no sulfide but some dissolved Fe is available. The author won't be surprised that I am raising this point, but I think it is an important one that is well documented in the literature and should be mentioned (even if the authors may come to the conclusion that it is irrelevant in their study).
We agree that complexities of the phosphorus cycle are commonly underestimated. We do not want to discuss in detail the reasons for phosphorus depletion during Cretaceous OAEs, as this would require more extensive data sets. The main aim of this manuscript is to document the availability of the essential nutrient phosphorus and to underline its role in maintaining increased productivity over extended periods of time. A detailed discussion of the mechanisms for increased phosphorus remobilization or non-deposition is beyond the scope of this publication and will be addressed in a future study focused on redox-trends in the Tarfaya Basin (Scholz et al., in prep.).

lines 194-200: Could the authors provide some quality control data for the elements determined (accuracy based on reference materials, precision based on repeat analyses)? I am sure the data are fine, but just to stick to good practice.
The missing values for accuracy and precision based on standards and repeated measurements will be provided in the revised version of the manuscript.

lines 363-366: Are any of these fish remains, nodule, or crusts visible in the core, or do they crop up in the XRF scanning data? If they are, they should be highlighted clearly

as diagenetic features in the data plots - otherwise, it should be mentioned that they were not observed.
We added a sentence clarifying that no fish remains or nodules were visible on the core surfaces nor obvious in the XRF data (see below):
Earlier studies found finely distributed fish debris and fecal pellets in Cenomanian sediments of the Tarfaya Basin (e.g., El Albani et al., 1999) partially reprecipitated as phosphate nodules during early diagenesis (e.g., Leine, 1986; Kuhnt et al., 1997). Phosphatic particles were not observed on the core surfaces and were not apparent in the XRF data of Core SN°4. They were only encountered as minor components in the residues of micropaleontological samples.

lines 370-374: 89 percent is what I would expect as recovery from the chosen extraction technique. But could the authors provide a downcore plot of recovery rates in the Supplement? I am just curious whether this might reveal something about organic P that, even in these old sediments, can still reside in organic matter (after all, the organic matter is still there, in some intervals quite a lot, so it should contain some P as well).
We added a reference to Supplementary Material Figure S16 with the Preact/Ptotal ratio. The overall high ratio of Preact/Ptotal and the increased maturity of sediments from the Tarfaya Basin imply diagenetical sink-switching from organic matter into the more stable phosphorus pools of Ca- and Al/Fe-bound phosphorus.

lines 382-385: Here I would be a little careful regarding anoxic and euxinic conditions. It has been shown by Poulton et al. (2015) that OAE2 at Tarfaya experienced periodic ferruginous conditions; and also Wallmann et al. recently showed independently that ferruginous conditions could be generated in the Cretaeous North Atlantic. In their study, they did not see an increased sequestration of P by Fe-P minerals (different to what Maerz et al., 2008, observed for OAE3 on Demerara Rise). The reasoning

behind this might be quite complex but is related to continental weathering as well as redox conditions and the Fe-C-S cycling on the Tarfaya shelf. I would encourage the author to engage more with that manuscript, especially since it is on material from Tarfaya as well.
See previous reply above concerning the problematic definition of ferruginous in the context of the Cretaceous in section 4.4.

line 425: Shouldn't Corg/Preact be used here?
Corg/Ptotal was intentionally included in Supplementary Figure S16 to show the similar pattern to Corg/Preact, when using total phosphorus concentrations.

lines 471-472: This is at odds with the arrow in Figure 2, which points into the wrong direction for intensified weathering (it's correct in Figure 3).
We corrected the arrow in Figure 2.

lines 475-476: How do you infer that the response to orbital forcing is reduced? There is still a lot of variability in the K/Al record (which is in agreement with the K/Al record in Poulton et al., 2015, who state that orbital pacing is not recorded as clearly in Tarfaya due to the potential for discontinuous sedimentation in shallow waters). It would further be interesting, especially given the very high resolution XRF scanning record, to check if changes in K/Al are correlative with subtle changes in redox conditions, as indicated, for example, by P speciation of the TOC/Rreact ratio.
Figure 2 shows low amplitude variability of the weathering proxy Log(K/Al) during the main phase of OAE2, especially in comparison to the preceding interval, implying low hydrological variability. This dampening suggests a weak response of the hydrological cycle to orbital forcing. Enhanced variability during the plateau phase possibly suggests enhanced response during recovery of the climate-carbon cycle system. We agree that discontinuous sedimentation could erase cyclic pattern in marine

sediments, but no obvious hiatuses are evident in Core SN°4, which would account for the loss of cycles with wavelengths of multiple meters.

lines 587-590: Similar to comment before, this should be visible in the core or other XRF scanning parameters, shouldn't it?
We deleted this sentence, as a discussion on the influence of major sea level variations would be beyond the scope of this manuscript.

lines 607-609: This statement was also made by Poulton et al. (2015), notably during both euxinic and ferruginous intervals that occurred in the early phases of OAE2 at Tarfaya. So apparently no formation of Fe-P minerals that sequestered P during ferruginous intervals on the deeper Demerara Rise.
The high resolution study of Poulton et al. (2015) focused on the onset, peak and early plateau phase of OAE2. By contrast, our lower resolution data set over the mid Cenomanian to early Turonian interval in Core SN°4 allows comparison of background variability with changes occurring during the MCE and OAE2. Our extended data set shows that phosphorus depletion in the Tarfaya Basin exclusively occurred during carbon isotope excursions, which correspond to periods of drastically enhanced organic carbon burial on a global scale. This long-term perspective allows fresh insights into the role of the essential nutrient phosphorus for maintaining increased organic carbon burial over extended periods of time.

Kind regards, Christian Maerz

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