

RESPONSE TO THE REVIEWER'S COMMENTS

(Note that our responses to the comments are in boldface.)

We thank the associate editor and reviewer for their incisive comments as well as for the opportunity to address these. There is no doubt that the revised manuscript has benefitted from their comments.

Reviewer #3 expressed dissatisfaction with your revision of the manuscript, because despite providing sufficient responses in the discussion, insufficient implementation into the manuscript was provided.

All of the reviewer's comments were addressed in detail in our responses and appropriate modifications to the manuscript were implemented. The implementations alerted the reader to the concerns raised by this reviewer, but we did not expand extensively on these within the revised manuscript as we did not want to unduly lengthen the manuscript.

Aside from revisiting the original suggestions made by Reviewer #3 (and implementing them as applicable), Reviewer #3 suggests a stronger and more accurate literature discussion to compare methane seep sites featuring different methane fluxes/SMTs with the respective phosphate profiles/fluxes.

We are afraid that the reviewer is missing the point and has not read our reply carefully. The methane flux and the position of the SMT do not alter the phosphate profiles or its flux at the sediment-water interface. Only an upward, vertical migration of the SMT, induced by a destabilization of methane hydrates or an increased flux, will trigger the dissolution of phosphate-laden iron oxides that accumulated above the SMT prior to its vertical migration. Only then will the pore-water phosphate concentration gradient above the SMT increase and potentially increase the flux of phosphate across the sediment-water interface. With time, as the phosphate-laden iron oxides are exhausted, the phosphate gradient will decrease and, thus, its upward flux will subside.

The reviewer is making the important point (based on field measurements and published literature) that high methane fluxes do not necessarily have to be correlated with high phosphate fluxes. Some examples show the opposite trend caused by geochemical features currently not considered in your manuscript. It therefore seems oversimplified that sea-level fall (and associated increase in methane fluxes) would automatically lead to an increase in phosphate fluxes.

We absolutely agree with this point. In fact, if the methane flux has been persistent and/or methane seeps out of the sediment (or if the SMT is close to the sediment-water interface), we would not expect a significant phosphate flux out of the sediment, because the phosphate-bearing oxides would either not accumulate in these sediments or have long been dissolved by the sulfidic pore waters. Also see our response to the previous comment above. Furthermore, as indicated in the original and revised manuscript, the phosphate flux will be episodic. In other words, an increase in the pore-water phosphate gradient and a phosphate flux across the sediment-water interface should follow an upward, vertical migration of the SMT in response to a lowering of the sea level, but both the gradient and the flux will wane with time as the phosphate-laden iron oxides are reduced by sulfide produced by AMO within the vertical interval of the SMT

migration and are ultimately exhausted. There will be no increase in phosphate gradient and, consequently, no increase in phosphate flux across the sediment-water interface if the amount of phosphate-bearing iron oxides within this interval is negligible, as they may not have accumulated within this interval or been reduced in a previous episode of SMT migration. This scenario was not described explicitly in the previous versions of our manuscript but is now presented on lines 270-282 of the annotated, revised manuscript.

I agree that the mechanism you are proposing is very interesting; but before I can accept your manuscript for publication I like to see a stronger discussion about potential alternative scenarios under certain geochemical settings that can be reasonable assumed based on published data sets.

We hope that additional precisions about the proposed scenario, as presented above and the revised manuscript (lines 270-282 of the annotated, revised manuscript), will satisfy the editor and Reviewer#3, as these additions provide ample justification for current observations.

Please follow the (former and current) suggestions by Reviewer #3 and submit a revised version together with:

- track-changes manuscript
- point-by-point response including line numbers in the revised manuscript, in which the reviewer's comments have been addressed.

Please let me know in case you have any questions.

Tina Treude

Dear Dr. Sundby, dear co-authors,

first of all, I would like to apologize for my delayed response. I thank you very much for addressing the points and questions raised in my review of the initial submission in your cover letter. I now also had a detailed look at the revised version. I have to admit that I was a bit disappointed to see that many of the issues that I have brought forward have not been mentioned or clarified in this new version. So, as a consequence many of my initial points/comments still hold and I will not repeated them in detail here.

As noted above, all comments were addressed in detail in our previous responses and appropriate modifications to the manuscript were implemented. The implementations alerted the reader to the concerns raised by this reviewer, but we did not expand extensively on these within the revised manuscript as we did not want to unduly lengthen the manuscript.

I would only like to point out again that I think it is very important to more specifically and critically outline in your manuscript that 1) the flux of phosphate across the SWI is ultimately controlled by the concentration gradient across the SWI (and not necessarily by that in the deeper subsurface sediments and/or the depth location of the SMT/steepness of P gradient around the SMT), and that 2) there are almost no data available for pore-water phosphate concentrations in cold-seep surface sediments. This is why it may be very promising to refer to sites from more or less the same study area that display different depths of the SMT and

the corresponding phosphate profiles in the surface sediments proper as also suggested by the editor Dr. Treude. My feeling is that this would significantly strengthen your manuscript.

We agree with the reviewer, there cannot be a flux of phosphate out of the sediment without a concentration gradient across the sediment-water interface (SWI). In our proposed scenario, a sea-level drop will induce a destabilization of methane hydrates, increase the flux of methane towards the SWI and displace the SMT upwards. The sulfide produced by AMO will reduce, if present, the phosphate-bearing iron oxides within the displacement interval, releasing phosphate and increasing the phosphate concentration gradient between the SMT and SWI, thus supporting an increasing flux of phosphate across the SWI. As indicated above, if phosphate-bearing iron oxides are absent within the displacement interval (either they never accumulated or were reduced by a previous migration of the SMT) then the phosphate concentration gradient would not be altered significantly, as would the flux of phosphate across the SWI. Even if phosphate-bearing iron oxides are present within the displacement interval, the phosphate gradient and flux across the SWI will wane with time as the phosphate-bearing iron oxides are deactivated (by FeS coating or Fe(II) adsorption) or exhausted (reduced). Hence, to re-iterate what is said above, if the methane flux has been persistent and/or methane seeps out of the sediment (or if the SMT is close to the sediment-water interface), we would not expect a significant phosphate flux out of the sediment, because the phosphate-bearing oxides would either not accumulate in these sediments or have long been dissolved by the sulfidic pore waters, as observed by Niewöhner et al. (1998) in sediments of the upwelling area off Namibia. In fact, the pore-water profiles reported by Wunder et al. (2021) in the Church Trough sediments of South Georgia are exactly what we would expect. Hence, one would not expect to find current examples of phosphate fluxes associated with cold methane seeps. A phosphate flux might have accompanied the methane flux when the latter was first initiated, but would have waned with time. These arguments are now presented on lines 270-282 of the annotated, revised manuscript.

With respect to comment 1): there is generally considerable difference between the shapes of pore-water profiles and thus gradients/fluxes of PO₄ between deeper sediments (retrieved by gravity corers) and those of the surface sediments proper. In this context I would like to bring to your attention a recent paper on biogeochemical processes in sediments of South Georgia. In the study by Wunder et al. (2021, *The ISME Journal*) we have examined surface sediments from 4 sites in the coastal/shelf environment of this archipelago, which are all located close to methane seep sites and thus are affected by active methane seepage. I.e. they exactly represent the kind of nonsteady-state/transient depositional/geochemical environments that you hypothesize to evolve during glacial sealevel-lowstands. As shown in Fig. 2 of this paper there is no correlation at all between the depth of the SMT/the intensity of upward methane flux and the pore-water profile shapes and gradients of phosphate. In contrast, the site with the highest methane flux and shallowest depth location of the SMT (Church Trough) is the site with the lowest flux of phosphate into the overlying bottom water. What we also see in the solid-phase data of sites in the area is that even in sulfidic sediments the amount of reactive Fe minerals is similar to that at Fe-rich sites – mostly due to the fact that the inner/bulk Fe oxide mineral is shielded from further reduction by the formation of Fe-sulfide coatings around the mineral particles. The study thus also highlights the importance to differentiate between Fe-rich and sulfide-rich sediments continental margin sediments (see below).

We thank the reviewer for bringing this publication to our attention. As detailed above, the pore-water profiles reported by Wunder et al. (2021) in the Church Trough sediments of South Georgia are exactly what we would expect after the SMT has settled for some time close to the SWI and no phosphate flux across the SWI would be observed. We also agree that the reactive iron minerals can be shielded from further reaction by Fe-sulfide precipitation or even Fe(II) adsorption. The latter deactivation mechanism has been called upon before as a means to inhibit reactive iron mineral reduction, including in the sapropelic sediments of ferruginous Lake Matano (Crowe et al., 2008). See additions at lines 270-281 of the revised, annotated manuscript.

Crowe, S.A., Jones C., Katsev S., Magen C., O'Neill A.H., Sturm A., Canfield D., Haffner G.D., Mucci A., Sundby B. and Fowle D.A. (2008) Anoxygenic phototrophs thrive in an Archean Ocean analogue. *Proc. National Academy of Sciences* 105(41): 15938-15943.

Without any doubt there is release of phosphate into the overlying water column across the SWI (e.g. see global map of benthic phosphate fluxes by Hensen et al.) due to diffusion and additionally by activity of benthic fauna. Nowhere in my comments did I put this in question. I also fully agree – and there is in fact quite some evidence – that phosphate can diffuse upward and downward over considerable distances in the seabed. The depth or source/process from/by which phosphate is liberated into the pore water can, however, be quite different/differ considerably. There is considerable difference between organic-rich/sulfidic sedimentary environments and those rich in iron.

I also fully agree that a decrease in hydrostatic pressure during glacial sealevel lowstands (among other processes) can increase the upward flux of methane and shift the SMT to a shallower sediment depth – thus (of course) also increasing the steepness of the upward directed sulfate gradient and hence the upward diffusive flux of sulfate.

However, based on this you then hypothesize that also the upward flux of phosphate increases from sources deeper in the sediment (namely the SMT) resulting in an increased flux of phosphate across the sediment/water interface. I find it hard to agree with this hypothesis for at least two reasons.

First, in organic-rich sediments (as underlying high-productivity upwelling areas; e.g. Niewöhner et al., 1998) phosphate is not liberated into the pore water at the SMT but diffuses up from much greater sediment depth most likely as a consequence of organic carbon mineralization in deeper sediments (please check again the figures in Niewöhner et al., 1998). As a consequence there is no reason why the upward directed phosphate concentration gradient should change if the SMT moves upward during glacial times.

We agree with this observation, but as highlighted above, an upward displacement of the SMT, such as would be induced by a sea-level low stand, would burn through a layer (within the displacement interval of the SMT) of phosphate-bearing iron oxides and release phosphate to the pore waters. If the position of the SMT is invariant, one would not expect to see much phosphate released at the SMT, as reported in Niewöhner et al. (1998). See additions at lines 270-282 of the annotated, revised manuscript.

Second, it could be that the upward directed phosphate flux from the SMT would increase as a consequence of an upward shift of the SMT as is the case in high-accumulation settings where large amounts of reactive Fe minerals are rapidly buried and where phosphate is primarily released at the SMT by reductive dissolution of Fe (III) minerals with hydrogen sulfide (e.g. Riedinger et al., 2005, 2014; März et al., 2008, 2018). This does, however, not

mean that this elevated phosphate flux also „makes it“ across the SWI. Please, also compare the paper by Wunder et al. (2021, The ISME Journal).

It may well be if metal oxide surfaces within the oxic layer of the sediment are not saturated with phosphate, but we found that detrital and diagenetic iron oxides in organic-rich sediments have very high but sliding buffering adsorption capacities. Hence, if the pore-water phosphate flux to the SWI is increased, much of the phosphate will be intercepted by these oxides, but the concentration of maximum buffering capacity of the sediment (or zero equilibrium phosphate concentration (EPC₀)) will increase and the concentration gradient and flux of phosphate across the SWI will also increase. Accordingly, we have modified the text and it now reads (lines 291-298 of the annotated, revised manuscript): “ Irrespective, detrital and diagenetic iron oxides in organic-rich sediments have very high but sliding buffering adsorption capacities (Sundby et al., 1992). Hence, if the pore-water phosphate flux to the SWI is increased, much of the phosphate will be intercepted by these oxides, but the concentration of maximum buffering capacity of the sediment (or zero equilibrium phosphate concentration (EPC₀)) will increase and the concentration gradient and flux of phosphate across the SWI will also increase (Froelich et al., 1988; Sundby et al., 1992). Sorption should therefore not fully restrict the transport of phosphate diffusing up from the SMT towards and across the sediment-water interface.”.

Specific comments

L. 46: methane is also released into the surrounding pore water and diffuses upward if gas hydrates are well within the hydrate stability field (cf. Egorov et al., 1999, Geo-Marine Letters; Lapham et al., 2010, Earth Planet. Sci. Lett.). It is a matter of saturation state of the surrounding pore water with respect to methane and the rate of upward diffusion of methane from the hydrates/hydrate-bearing sediments into the overlying sediments.

Whereas this information may be factual, it should not be added here since we are, for the sake of setting up the context of our work, paraphrasing a scenario previously proposed by Paull et al. (1991).

Ls. 87 ff.: phosphate release by sulfide generated by AOM

The text in parentheses was replaced by “phosphate released to the pore waters upon the reductive dissolution of iron oxides by sulfide produced during anaerobic methane oxidation”.

L 121/122: This statement only holds for high accumulation continental margin settings rich in terrigenous material (like off larger river mouths/fans like the Amazon, Congo, La Plata, Zambesi, etc.). In these sediments relatively large amounts of reactive Fe(III) are rapidly buried and associated phosphate is primarily released into the pore water by reductive dissolution of Fe (III) minerals with hydrogen sulfide at the SMT (e.g. Riedinger et al., 2005, 2014; März et al. 2008, 2018). These sites often only show a thin sulfidic zone around the SMT.

However, in organic-rich sediments – like those underlying upwelling areas like off Namibia - phosphate is not liberated at the SMT but diffuses up from significantly greater sediment

depth where it is most likely released by deep subsurface organic carbon degradation (cf. Niewöhner et al., 1998).

Agreed, the text was modified and now reads “According to the depositional setting, pore-water phosphate profiles in marine sediments tend to display a concentration maximum below the dissimilatory iron and sulfate reduction zone (e.g., Krom and Berner, 1981), within or near the sulfate-methane transition zone (e.g., März et al., 2008) as well as at greater depths where it is most likely released by deep subsurface organic carbon degradation (e.g., Niewöhner et al., 1998).”

L. 140: the total sum

The “sum total” is the proper English expression and, thus, it was not modified.

L. 149: bioirrigation „and bioturbation“

Bioturbation was added to the text of the revised manuscript.

Ls. 168 ff.: In this paragraph you have not addressed two further fundamental controls on the preservation/burial of both „primary“ and authigenic Fe (III) minerals - namely sedimentation/accumulation rate and sulfide exposure time. I would suggest to add these as well.

The text was modified accordingly.

L. 178: This statement is still too general. Several more recent studies have shown that this is not necessarily the case Please check the papers by Riedinger et al. (2005, 2014, 2017), Egger et al. (2015, 2017) and März et al. (2008, 2018).

This is what we have observed in estuarine and coastal sediments on both sides of the North Atlantic but, according to the papers the reviewer directs us to, this may not always be the case. Hence, we have tempered the statement. It now reads: “ ... the bulk reactivity of the sedimentary iron oxides typically decreases with time ...”.

L. 250 ff.: This is not necessarily what we see when the SMT moves upward. If the SMT migrates upward (i.e. into sediments which have not yet been exposed to high sulfide concentrations) most of the sulfide produced in the first stage of this transient situation is immediately trapped in the solid phase (cf e.g. Riedinger et al., 2005).

We agree that much of the sulfide originating from AMO will likely be trapped by precipitation of a solid sulfide and little will diffuse beyond the SMT. This does not invalidate our proposed scenario of phosphate release to the pore waters as the sulfide will reduce iron oxides before solid sulfides are precipitated, it only restricts the locus of phosphate remobilization to the vicinity of the SMT. In response, we have slightly modified the statement, it now reads: “The upward displacement and ultimate location of the SMT in the sediment column is critical since the reduction of iron oxides by sulfide occurs at this location and within the displacement interval and releases phosphate to the pore water. The closer the SMT migrates to the sediment surface, the greater is the instantaneous flux of sulfate ...”.

L. 255 ff.: As outlined in my review of the initial submission it is in no way clear that during periods of a shallower depth SMT (and a steeper gradient and higher upward flux of P from the SMT) also the flux of phosphate across the sediment/water interface is increased. Cf. Wunder et al. (2021).

Again, as emphasized above, an increased phosphate flux is only expected soon after an upward vertical migration of the SMT if phosphate-bearing iron oxides are present within the displacement interval. Once these oxides are deactivated or exhausted, both the concentration gradient and flux of phosphate will wane. This detail did not appear in the original and first revision, but was added to the latest revision (Lines 270-282 of the annotated, revised manuscript).

L. 269: ... can form carbonate fluorapatite and vivianite

Agreed, vivianite was added to the text of the revised manuscript.

Ls. 277 and 326: has to be Niewöhner

Corrected as requested.

L. 319: But this needs to be shown.

As it cannot readily be demonstrated, we mitigated the statement by adding “potentially” to the sentence.

L. 331: yes, I agree It could increase the flux But not necessarily ...

We have added several caveats to our proposed scenario throughout the revised manuscript and Table 1, these will hopefully satisfy the editor and this reviewer.

It is interesting to note that, according to ResearchGate, the preprint of this paper (Biogeosciences Discussions) has already been read more than 106 times and recommended by two readers. After all, the original manuscript received two very laudable reviews from two reputable experts in the field. Hence, we are grateful for the opportunity to share the results of our deliberations.