

Biogeosciences Discuss., author comment AC3
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Reply on RC3

Bjorn Sundby et al.

Author comment on "Ideas and perspectives: Sea-level change, anaerobic methane oxidation, and the glacial–interglacial phosphorus cycle" by Bjorn Sundby et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-124-AC3>, 2021

Reviewer comments are repeated below and are followed by our responses **in bold**

RC3: 'Comment on bg-2021-124', Sabine Kasten, 21 Jul 2021

Review of Sundby et al. , Biogeosciences, by Dr. S. Kasten

The „Ideas and Perspectives“ manuscript by Sundby et al. presents a new potential scenario that adds to the suite of processes that may have contributed to the rapid climate changes observed along glacial/interglacial transitions - namely the documented rapid increase in atmospheric CO₂ concentrations during deglacials or more precisely prior to glacial terminations. The authors suggest a mechanism that links sealevel, rates of anaerobic oxidation of methane and benthic fluxes of phosphate in this way contributing a new mechanism to the so-called „shelf nutrient hypothesis“ initially developed by Broecker (1982).

I find it very interesting and scientifically fruitful to put forward this scenario and in particular in this way stimulate discussion over a broad spectrum of disciplines.

Being a „sediment diagenesis“ person myself, I hope you understand that I will mostly focus on related issues.

We thank Dr. Kasten for her constructive comments. The four co-authors, being seasoned sediment diageneticists, can provide informed responses to the various comments.

The authors propose the following suite of conditions and processes: 1) during glacial sea level lowstands hydrostatic pressure is lowered, 2) this enhances the upward flux of methane from underlying gas hydrates and shifts the sulfate/methane transition (SMT) to a shallower depth in the sediment, 3) as a consequence rates of anaerobic oxidation of methane (AOM), hydrogen sulfide formation, reductive dissolution of reactive Fe oxide minerals by sulfide and associated release of adsorbed phosphate into the pore water all increase, 4) this induces higher upward (and downward) fluxes of phosphate, and 5) also increases the flux of phosphate across the sediment/water interface into the bottom water.

While I fully agree with the conditions and processes in points 1 to 4, I am not convinced with the statement given as point 5 above – namely elevated benthic fluxes of phosphate into the water column during a shallower position of the SMT during glacials. Unfortunately the authors have neither presented nor discussed data that demonstrate that phosphate fluxes into the bottom water are indeed higher when the SMT is positioned at shallow sediment depth.

We propose to clarify this point in the revised version of the manuscript. First, we point out that it is not the difference in the vertical location of the SMT in the sediment column at two different sites that determines the phosphate flux, it is rather the fact that the SMT migrates closer to the sediment-water interface during the glacial cycle that increases the concentration gradient and the flux.

Our manuscript is listed under "ideas and perspectives" precisely because there are no new data available to present or to discuss. We therefore propose a scenario for the diagenetic remobilization of inorganic phosphate that is based on reasonable assumptions relative to what is understood about sediment diagenesis. We exploit the idea that diagenetic processes in the sediment column can be driven by an electron flux from below (in this case, a methane flux) and that this flux can vary with changing physical conditions (sea level/hydrostatic pressure, temperature) during the glacial cycle. Here, we explore the impact this may have on the flux of inorganic phosphate from the sediment to the ocean; we are testing a hypothesis, not discussing data.

Dr. Kasten: They exclusively discuss gravity core data, however, completely neglect the part of a sediment that is key in determining the flux of phosphate across the sediment/water interface – namely the sediment surface. Benthic fluxes can only be assessed if the pore-water gradients of phosphate in the uppermost few decimeters of the sediments are determined. In order to quantify the diffusive flux of phosphate from the sediment back to the bottom/deep water – and thus into the oceanic reservoir - pore-water data of multiple cores or push cores (or benthic chambers) are required, which allow a proper disturbance-free sampling of the sediment surface. Hence, also the schematic representation given in Fig. 2 is not correct, at least as given. With the constant concentrations of phosphate displayed in the uppermost part of the graphs, there is/can be no phosphate flux across the sediment-water interface (SWI) – neither during interglacials nor glacials.

Froelich, P. N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnology and Oceanography*, 33: 649-668.

Sundby B., Gobeil C., Silverberg N. & Mucci A. (1992). The phosphorus cycle in coastal marine sediments. *Limnology and Oceanography*, 37, 1129-1145.

There is also some contradiction and imprecise discussion with respect to the assumed phosphate concentrations in the oceanic reservoir/deep waters and the major particulate carrier phases that transport phosphorus into the sediment (organic matter, Fe-bound phosphate) throughout the manuscript, which needs to be sharpened and better structured. Moreover, parts of the manuscript contain several incorrect statements and assumptions. concerning the stability of methane gas hydrates and the characteristics of methane transport both in dissolved and gaseous form in marine sedimentary environments.

We respond to these comments below, in the section on specific comments.

I was also wondering whether considering issues related to the (potential) release of methane during glacial/interglacial sea level changes really falls into the scope of this manuscript.

We mention this in the beginning of the text, which seems pertinent, since in our scenario, the diagenetic processes that generate the enhanced inorganic phosphate flux are fueled by this methane.

The scenario presented also does not consider the processes that occur in exposed shelf sediments during glacial sea level low-stands. As presented and suggested by Kölling et al. (2019) aeration/oxidation of shelf sediments during sea-level low stands will oxidize reduced iron sulfide minerals resulting in the formation of abundant reactive Fe(III) that will certainly serve as an efficient trap for phosphate either by co-precipitation or adsorption of phosphate on Fe(III) mineral surfaces. I would therefore assume, that these (bio)geochemical processes acting in exposed shelf surface sediments are a significant sink for phosphate during glacial periods. How important is this potential sink compared to the (potential) release of phosphate from continental margin sediments into the oceanic reservoir?

We thank Dr. Kasten for bringing this article to our attention. The article by Kölling et al. (2019) proposes a mechanism of CO₂ release in response to the oxidation of pyrite to iron oxides during the emersion of continental shelf sediments when the sea level drops during the glacial period. This article does not refer to the impact of this mechanism on the phosphate pool. Since this scenario refers to the formation of iron oxides in areas that are above sea level during glacial periods, these oxides cannot trap marine phosphate unless eroded and resuspended in the open ocean. It is therefore impossible to compare the phosphate fluxes resulting from such a scenario with our own. The proposed mechanism could contribute to the rise in atmospheric CO₂ during the glacial period and, as such, deserves to be highlighted in the revised manuscript when we discuss oceanic processes leading to an increase in atmospheric CO₂.

So, to conclude, the major issue I have is that the authors have not convincingly shown and discussed that benthic PO₄ fluxes from continental margin sediments were/are indeed higher during glacial times or in general during times of a shallower position of the SMT – mainly because they have not at all considered and discussed pore-water data for the sediment surface proper. I think that such a scenario could be easily and convincingly tested by comparing sites – i.e. data of MUC or push cores that allow to sample the sediment surface proper – where the SMT is located at different sediments depths. Perhaps also pore-water phosphate data for active seep sites are available/published. In this way the authors could test their hypothesis that during periods of a shallower position of the SMT (and/or periods of active methane seepage) phosphate fluxes across the SWI are/were indeed higher than with a deeper SMT.

To help validate our hypothesis, Dr. Kasten suggests that we compare dissolved phosphate profiles in pore waters near the SWI of sediments from different sites where SMT is currently at different depths. The suggested exercise would be useless since these are steady-state conditions, unlike our proposed transient-state scenario in which the SMT migrates vertically in response to a change in sea level, destabilization of methane hydrates, and a consequent upward flux of dissolved methane, so that the resulting sulfide front will reductively dissolve iron oxides that accumulated above it and release the inorganic phosphate associated with them. In summary, it is not the depth of the SMT that defines the phosphate fluxes in our scenario, it is the change in the depth of the SMT that generates an increase in the SRP flux.

I also think that the argumentation can be significantly strengthened by better structuring the manuscript with respect to 1) precisely stating the postulated changes in phosphate concentrations in the oceanic reservoir during glacial and interglacial times, 2) precisely and consistently discussing the main carrier phases of P into marine sediments – namely organic matter and Fe-bound P, and 3) also carefully checking the parts of the manuscript where you discuss (changes in) hydrate stability and the processes transporting methane through sediments and across the SWI.

Specific comments and corrections

Line 13: „additional“ to what precisely?

The use of “additional” is justified as the potential flux of SRP generated by the destabilization of methane hydrate and consequent vertical migration of the SMT is above and beyond the steady-state flux of SRP sustained by organic-P remineralization during early diagenesis.

Ls. 15/15: Here you only mention biomass as a carrier phase to return/carry P back to the sediment. What about Fe-bound P, which – as you state on page 3 – is the key issue of your study/scenario?

In this statement, we wish to note that increasing the phosphate flux to the oceanic reservoir should stimulate the biological pump.

Ls. 20/21: This somehow contradicts your statement in lines 13-15 that phosphate fluxes were/are higher during glacial. Why does the deep water then has lower P concentrations during/at the beginning of a deglaciation? I find this very confusing.

The sentence on lines 20/21 refers to the beginning of the deglaciation when the phosphate released previously during the glacial period has been consumed, whereas the sentence on lines 13/15 refers to the period of sea-level fall.

Page 2: In this context, I would like to draw your attention to the recent paper by Kölling et al. (2019) who have presented a scenario explaining the rapid increase in atmospheric CO₂ concentrations prior to glacial terminations – also linking sealevel changes to atmospheric CO₂ concentrations, more precisely considering high rates of pyrite oxidation on continental shelves exposed during glacial sealevel low-stands.

Kölling, M, Bouimetarhan, I, Bowles, MW, Felis, T, Goldhammer, T, Hinrichs, K-U, Schulz, M, Zabel, M (2019): Consistent CO₂ release by pyrite oxidation on continental shelves prior to glacial terminations.- nature geoscience **12**, 929-934. doi 10.1038/s41561-019-0465-9.

We thank Dr. Kasten for bringing this article to our attention. We will add this reference to line 42.

- 46: methane hydrates

The correction will be applied, as proposed.

Ls. 46 ff: I do not agree with the scenario that sea level fall-induced lowering of the hydrostatic pressure necessarily leads to a transport of significant amounts of methane into the water column and subsequently into the atmosphere. Of course a lower sea level will induce a thinning of the gas hydrate stability zone (GHSZ). If methane is transported by diffusion, the methane transported upward from gas hydrates will be more or less completely oxidized/consumed before it can reach the water column. If methane is

transported in the form of free gas, these bubbles can reach the lower water column. However, numerous studies have shown that they do not significantly contribute to transport of methane into the atmosphere because methane is rather oxidized aerobically in the water column and/or dispersed by horizontal advection and dilution. Moreover, rising bubbles constantly change their internal gas composition due to counterdirected diffusion of gases (methane out, N and CO₂ in) across the bubble/water interface (cf. studies by Mc Ginnis or Leifer). As a consequence even in shelf settings with shallow water depth, methane does not reach the atmosphere in considerable amounts (e.g. Mau et al., 2015; Biogeosciences; Geprägs et al., 2016; G3).

Ls. 82 ff.: I also do not fully understand why you discuss the (very controversial) role of methane in the atmospheric carbon cycle over glacial/interglacial changes – please see comments above. Is this really in the scope of your manuscript?!

The sentences on Lines 46-50 simply reiterate what previous authors have proposed and end with a statement, based on conclusions from more current literature, that the scenario is questionable because the methane would likely be oxidized before reaching the overlying water column. Hence, the text is appropriate as it provides a chronological, literature review of the potential link between methane, sea-level fall and global warming. We fully agree with Dr. Kasten as the sentence on line 82-84 (“We will also re-examine the idea proposed by Paull et al. (1991, 2002) that sedimentary methane may be directly involved in the atmospheric carbon cycle by escaping to the atmosphere during periods of sea-level fall.”) was inadvertently left in the manuscript from a previous version and this may have lead to some confusion. It was not our intention to describe all the processes that prevent methane accumulating in marine sediments from reaching the atmosphere. We simply wanted to point out that the scientific community has long been interested in the link between methane hydrate stability and glacial/interglacial fluctuations. We will remove this sentence from the revised manuscript. Dr. Kasten rightly writes that most of the methane is oxidized in the pore waters before reaching the ocean water column. In fact, in the original manuscript, we wrote: “...but it is doubtful that the vast quantities of methane that would be required to trigger substantial warming could reach the atmosphere before being oxidized in the sediments and the overlying water (Archer et al., 2000; Archer, 2007).”. We will add some of the references recommended by the reviewer to the revised manuscript. It is precisely the process of anaerobic CH₄ oxidation that is the basis of our scenario, where the oxidation of methane results in an electron transfer that allows the reduction of iron oxides and the release of large quantities of inorganic phosphate to the pore waters. This scenario is laid out in detail in section 3.3 of the original manuscript.

- 116: ... downward (and upward) diffusion ...; into sulfate- and sulfide-depleted pore water below the SMT

This is an interesting observation: the data show both upward and downward transport of phosphate within the same core (Marz et al., 2008). The suggested explanation for this is that vivianite forms (authigenesis) deep in the sediment.

- 119: drive instead of imply:

To be replaced by “drive’

Ls. 124 ff.: Please, also check the earlier papers by Hensen et al. in this context:

C Hensen, H Landenberger, M Zabel, HD Schulz (1998) Quantification of diffusive benthic fluxes of nitrate, phosphate, and silicate in the southern Atlantic Ocean. *Global Biogeochemical Cycles* 12 (1), 193-210.

C Hensen, M Zabel, HN Schulz (2006) Benthic cycling of oxygen, nitrogen and phosphorus. *Marine Geochemistry*, 207-240.

The article by Hensen et al (1998) presents an analysis of an impressive data set. The global benthic flux estimate of Hensen et al. (1998) (3.2×10^{11} mol/yr) is lower than that proposed by Colman and Holland (2000) (12.5×10^{11} mol/yr). The flux measurements of Hensen et al. (1998) are mainly concerned with deep marine environments (>1000 m) while those of Colman and Holland (2000) focus more on continental margins. Qualitatively, the conclusions of Hensen et al. (1998) agree with those of Colman and Holland (2000): benthic fluxes greatly exceed river fluxes. We will add the reference proposed by the reviewer in the revised manuscript.

Ls. 130 ff.: Can you specify? In which kind of environment? Oxygen minimum zones? In this context please also consider the release of Fe-bound P in sediments underlying continental margin oxygen minimum zones – as also typically observed in anoxic lakes (sometimes referred to as internal fertilization)

Phosphate is released from continental margin sediment to the overlying seawater. One example is described in Sundby et al. (1992) where SRP fluxes to the overlying water were estimated on 27 undisturbed box cores collected in the Laurentian Trough in Canada. Other examples are given by Colman and Holland (2000). They examined pore-water profiles of soluble reactive phosphorus on nearly 200 sediment cores (some of which were collected by divers). They concluded that the return flux of phosphate from continental margin sediments to the overlying water was more than one order of magnitude larger than the riverine flux of total dissolved phosphorus to the ocean.

Ls. 144 ff.: As already stated above, the sediment surface (upper sediment column) is not only important with respect to bioirrigation and bioturbation, but the key locus that determines the diffusive flux of phosphate across the sediment surface into the bottom water.

We agree that the sediment surface (upper sediment column) is important with

respect to bioturbation and bioirrigation and as the locus that determines the diffusive flux across the sediment surface into the bottom water. We will modify the penultimate sentence of this paragraph of the revised text to further emphasize this point: "Soluble forms of phosphorus are transported by diffusion along concentration gradients that often develop in sediment pore waters and across the sediment-water interface. Transport via bioirrigation can also be important in the upper sediment column."

Ls. 166 ff.: No, Fe²⁺ generally does not diffuse across the Fe(II)/ Fe(III) redox boundary but is mostly oxidized at this redox boundary by nitrate and generally does not make it further up to the lower boundary of the oxic zone (cf., Froelich et al., 1979; Berner 1981; Kasten et al., 2003).

If there is a concentration gradient of Fe(II) across the Fe(II)/Fe(III) boundary, then this gradient can drive a flux. The magnitude of the flux will depend on the strength of the gradient, which depends on the rate of reoxidation. The use of "transport across the Fe(II)/Fe(III) boundary ..." is perhaps what triggered this comment. It is understood that there must be a concentration gradient across the Fe(II)/Fe(III) boundary to drive a flux, but we agree that much of the Fe(II) will be oxidize just above this boundary and, thus, we will substitute "across" by "to". Keep in mind that a similar process takes place with Mn(II) but, because of its slow oxidation kinetics, Mn(II) can diffuse well above the Mn(II)/Mn(IV) boundary before being oxidized and precipitated as authigenic manganic oxides.

Ls. 174 ff.: No, the reactivity of sedimentary Fe oxides does not necessarily decrease with time or depth of burial. As numerous studies have shown for shelf and continental margin sediments (Riedinger et al., 2005, GCA; Riedinger et al., 2017, Frontiers in Earth Sciences; März et al., 2008; Oni et al., 2015, Frontiers in Microbiology; Köster et al., 2021, G3) high amounts of reactive Fe (III) minerals can be buried to substantial sediment depth if sedimentation rates are high (as typical for continental margin settings) - thus limiting „sulfide exposure time“.

We agree that the reactivity of sedimentary iron oxides does not necessarily decrease with time. Accordingly, we will modify the sentence on Line 171 to: "Once buried, authigenic iron oxides may go through an aging process ... ".

Ls.: 200 ff.: The depth of the SMT may not only fluctuate over glacial/interglacial timescales (e.g. Henkel et al., 2012, GCA) but also be affected by increases/changes in the upward flux of methane induced by overpressuring of the underlying gas reservoir and/or triggered by earth quakes or sediment mass movements (e.g., Fischer et al., 2013, Nat. Geoscience; Henkel et al., 2011, G3; Henkel et al., 2012, Springer book on Submarine Mass Movements).

We agree that the depth of the SMT may also fluctuate and the upward methane flux may increase in response to overpressuring of the underlying gas reservoir, earthquakes and sediment mass movements. The following sentence will be added on Line 200: "The depth of the SMT may also fluctuate and the upward flux of methane increase in response to overpressuring of the underlying gas reservoir, earthquakes or sediment mass movements (Henkel et al., 2011; Fischer et al., 2013)".

Ls. 206 ff.: I do not agree with this statement. A shallow SMT does not necessarily mean that the flux of phosphate across the SWI is increased. Please, give examples/data of MUC or push cores that demonstrate this.

What do you mean with „instantaneous“ flux? This is not clear to me at all.

We agree. The flux of phosphate across the sediment-water interface is determined by the strength of the concentration gradient, but the gradient will increase if the SMT suddenly migrates upwards and Fe oxides that accumulated in the sediment above it are reductively dissolved by sulfides (a by-product of AMO), releasing the associated phosphate to the pore water. Accordingly, the sentence on Lines 207-208 will be modified to: “The closer the SMT migrates to the sediment surface, the greater is the flux of sulfate into the sediment and the shorter is the path that phosphate travels before it escapes the sediment.”.

By ‘instantaneous flux’, we mean the flux at any given moment.

Ls. 119 ff.: This paragraph on gas hydrate stability and transport of gas contains several flaws and imprecise statements. L. 119: methane is not „produced“ by hydrate dissociation but released from the hydrate phase.

The upper boundary of the gas hydrate stability zone (GHSZ) is determined by temperature and water depth/pressure and not by sediment accumulation.

What do you mean with „instantaneous“ methane flux? Bubble ebullition, migration of free gas? Please, specify.

The reviewer likely meant Ls. 220. We agree that methane is not produced by hydrate but released upon the destabilization/dissociation of the hydrate phase. Hence, “produced” will be replaced by ‘released’. We agree that the gas hydrate stability zone (GHSZ) is determined by temperature and water depth/pressure, but as sediments accumulate the overburden increases and the GHSZ migrates with it.

Again, by ‘instantaneous flux’, we mean the flux at any given moment.

Ls. 238-240: Again, what do you mean with „instantaneous“ methane flux? I do not at all agree with the statement in this sentence. At least you should give examples and also precisely state which part/interval of the sediment you refer to. The fluxes of both constituents can indeed be higher in the deeper sediments around the SMT but not necessarily at/across the SWI.

By ‘instantaneous flux’, we mean the flux at any given moment.

Ls. 244-245: No, this is not exactly what we see. There is both a downward flux and an upward flux of Fe²⁺ towards the SMT (cf., Riedinger et al., 2005, GCA, 2017, Frontiers; März et al., 2008).

There is no contradiction with having both upward and downward fluxes within a sediment layer. Riedinger et al. (2014) observed both an upward and a downward directed flux of Fe(II). The direction of the flux and the magnitude of the flux depend on the concentration gradient of the species that are diffusing.

- 249: No, as already stated above, I do not agree that during a shallow location of the SMT the flux of phosphate across the SWI is increased (at least I have seen no data).

Please see our response to the comment on Ls. 206 : The location of the SMT in the sediment column is critical since this is where reduction of iron oxides releases phosphate to the pore water. The closer the SMT shifts to the sediment surface, the greater is the flux of sulfate into the sediment and the shorter is the path that phosphate travels before it escapes the sediment.

Ls. 254 ff.: The benthic phosphate flux is also significantly dependent on the redox/oxygen conditions of the overlying bottom water. Cf. comment for l. 130.

We agree.

Ls. 265 ff.: I do not fully agree with the discussion in this paragraph. It may be that Fe(III) phases arriving at the seafloor are already close to saturation with respect to potential sorption sites for phosphate. This does, however, not hold true for the freshly formed/ authigenic Fe oxides at the Fe redox boundary. You have also discussed this in previous paragraphs of the manuscript. Numerous data show that most of the upward diffusing phosphate is trapped in the vicinity of the Fe redox boundary, i.e. the pore-water gradient of phosphate changes and only minor amounts of phosphate make it to the overlying bottom water.

We agree that numerous data show that much of the upward diffusing phosphate in sediment pore water is trapped in the vicinity of the Fe redox boundary. On the other hand, the case has been made that large amounts of dissolved inorganic phosphate actually escapes the sediment into the water column (see Colman and Holland (2000)). A similar claim is supported by nearly 30 box core-based phosphate pore-water profiles in the Gulf of St. Lawrence using state-of-the-art sampling and millimeter-scale pore water extraction techniques (Sundby et al., 1992).

Whereas some of the SRP may be sequestered by authigenic iron oxides near the SWI, SRP can nevertheless diffuse out of the sediment. This can be observed under nearly all the sedimentary conditions that result from organic matter remineralization : pore-water SRP immediately below the SWI nearly always exceed the overlying water concentrations and, thus, SRP diffuses out of the sediment. If the flux of SRP from below is very large, the concentration of maximum buffering capacity of the sediment (or zero equilibrium phosphate concentration (EPC_0), see Sundby et al. (1992), a concept first introduced by Froelich (1988)) will be rapidly exceeded and the pore-water SRP concentration as well as its concentration gradient across the SWI will build up. Ultimately, the buffering (or adsorption) capacity of the authigenic iron oxides might be overwhelmed and the linear gradient could extend all the way to the SWI.

Ls. 270 ff.: You are absolutely right that phosphate may diffusively migrate in pore water over relatively large distances of several meters and more – i.e. Niewöhner et al. (1998). This is particularly true for sediments underlying high productivity areas like off Namibia, in which only low amounts of reactive Fe(III) are preserved at depth due to the high rates of sulfate reduction/sulfide production. However, this is certainly not the typical situation in the vast area of continental margin/slope depositional settings. Moreover, please consider that this Niewöhner et al. (1998) paper (and others you have discussed in your manuscript) only shows data for gravity cores. During sediment sampling with gravity cores the uppermost decimeters of the sediments are always lost, so these data do not allow to assess the flux of phosphate across the SWI.

We found several examples in the literature where the SRP shows a regular gradient over several meters in long cores. Charbonnier et al. (2019) reported such profiles from cores taken on the Bay of Biscay continental slope, which is not an area of exceptionally high productivity.

We agree that there are problems with using gravity cores to assess the flux across the SWI. On the other hand, examples exist where other types of cores that preserve the integrity of the SWI have been used. We refer the reviewer to the box core collection from the Gulf of St. Lawrence (Sundby et al., 1992.)

Charbonnier, C., Mouret, A., Howa, H., Schmidt, S., Gillet, H., and Anschutz P.: Quantification of diagenetic transformation of continental margin sediments at the Holocene time scale, *Cont. Shelf Res.*, 180, 63-74, 2019

Chapters 3.7 and 4, pages 9 ff.: I do not agree to several of the assumptions presented and discussed here. First, I find it confusing that in your calculation of the sedimentary inventory of P you do not consider organic matter (OM) – although you highlight the OM burial pathway as a key carrier phase of P to the sediment in the abstract and other parts of the manuscript. How much is it compared to the Fe-bound P and how much P is released to the pore water as a consequence of mineralization of OM (compared to reductive dissolution of Fe(III) minerals by sulfide? Second, I do not agree that the calculated inventory of Fe-bound phosphate has a chance of ultimately ending up in the water column.

Our scenario involves the Fe-bound phosphorus. Dr. Kasten signals her disagreement with our calculated inventory of phosphorus and with our assertion that the calculated inventory ultimately ends up in the water column. Given the absence of a solid-phase phosphorus-inventory in the literature, we had no choice but to make our own estimate of the Fe-bound phosphorus inventory in the sedimentary reservoir. What is of particular interest is that the estimated inventory of solid phase phosphorus in marine sediment is of the same order of magnitude as the oceanic reservoir, i.e. the oceanic inventory. This supports our two-box model scenario until other estimates of the sedimentary inventory become available.

In the revised version of the manuscript, we will write on line 303 : “Therefore, 100,000 years of sediment accumulation corresponds to a sedimentary column that is 15 to 42 m thick, containing between 0.69×10^{15} and 1.93×10^{15} moles of mobilizable Fe-bound phosphorus. ”

You also have not discussed whether you think that methane transport occurs via diffusion

and/or advection – i.e. by methane seepage/bubble ebullition. If methane transport mostly occurs via diffusion then both methane and phosphate – although initially released into pore water - will be mostly trapped in the sediments overlying the gas hydrates (methane at the SMT) and phosphate at the Fe redox boundary close to the sediment surface.

Within a simple scenario such as ours, one has to overlook some of the details such as the mode of transport (for example methane bubbles vs. seepage). The subject is important, as witness the use of acoustics to locate the lower boundary of the SMT. For a brief discussion, see the following two paragraphs.

From recent studies in continental margin oxygen minimum zones we see that phosphate is only transported from the sediments into the overlying bottom water at high rates under conditions of oxygen-depleted/anoxic bottom waters or at times of active methane seepage – i.e. ebullition of gaseous methane. – phosphate may be transported at elevated rates into the overlying water column. – in a process similar to mixing of pore water into the bottom water produced by bioturbating/bioirrigating benthic organisms.

If methane transport occurs in the gaseous form – i.e. as bubble ebullition, this occurs along preferential migration pathways, which are spatially (and temporarily) restricted and thus AOM occurring close to these sites/pathways of gas migration also does not have the capacity to drive reductive Fe(III) reduction over a broad front. Therefore certainly not being able to reductively mobilize the calculated Fe-bound P inventory.

Page 11, upper paragraph: Here, you only speak of OM as a carrier phase to transfer P to the sedimentary reservoir. See also previous comment above.

Biomass is an important carrier phase, as is phosphate adsorbed to inorganic phases.

Chapter 4.3: Here are numerous flaws and imprecise statements with respect to the GHSZ and the transport of methane in marine sediments. A few examples:

Ls. 349/350: No, during sea level drop the upper boundary of the GHSZ moves down (not up). Thus the GHSZ in the sediment gets thinner. There also seems to be some confusion with respect to the upper boundary of the GHSZ and the upper boundary of gas hydrate-bearing sediments. The upper boundary of the GHSZ is (with typical water column temperature and in water depths deeper than about 300 m) found in the water column. However, hydrate formation does not occur in the shallow sediments due to a lack of methane, which is lost to the SMT overlying the gas hydrate-bearing sediments. Methane hydrates also constantly dissolve and release gas from the upper hydrate layers due to the concentration gradient produced by AOM occurring in the overlying SMT. This occurs even if hydrates are well within the hydrate stability zone due to undersaturation of the surrounding pore water with respect to methane (cf. Lapham et al., 2010, EPSL; Kasten et al., 2012, Geo-Marine Lett.).

We agree that the thermodynamic stability domain of gas hydrates is defined by temperature and pressure and is not the same as the zone where gas hydrates are found in the sediment. Methane concentrations must be at saturation for hydrates to form in the thermodynamic stability domain. As Dr. Kasten points out, the upper thermodynamic limit is in the water column in environments where the sediment is several hundred meters below the surface, whereas the actual limit is in the sediment, where methane is present in sufficient quantities. As sea level drops, the upper limit of thermodynamic stability becomes deeper in the water column, but does not change the actual upper limit in the sediment. Our scenario involves the change in depth of the lower limit of stability as sea level drops and the GHSZ thins (or the lower thermodynamic limit moves up, as Dr. Kasten points out), which generates an upward flow of methane and raises the actual upper limit of methane hydrate stability. We will correct the revised manuscript accordingly, which should make it clearer.

- 355: No, as stated above I am not convinced that this necessarily increases the P flux into the oceanic reservoir.

Figure 1: What precisely do you mean with „pulsed“ release of phosphate? This is not clear at all and has also not been discussed in the text. Please indicate where and how the two most important particulate carrier phases of P – i.e. OM and Fe-bound P – are transported into the reservoirs.

We use pulsed as opposed to steady or invariable.

Figure 2 needs a complete overhaul. The caption of the figure does not correspond to what is shown in the figure (e.g., the profiles of methane and Fe²⁺ are not shown) and for part of the profiles it is not clear what is shown (what are Fe oxides and what are Fe sulfide minerals?).

Also the schematic representation in this figure does not correspond or represent what the authors discuss. The phosphate profiles shown (seems that they have been adopted from gravity core data of Niewöhner et al. (1998)) have uniform concentrations in the uppermost part of the sedimentary column. This means that there is definitely no diffusive flux of P across the sediment/water interface – neither during interglacials nor glacials.

As stated above, Figure 2 will be revised.

Table 1: Point 6, column on the right: no, as already outlined above it is definitely not true for continental slope/margin sediments that the most reactive forms of Fe occur in the upper part of the sediment. Please revise and specify.

The kinetics of iron oxide reduction by H₂S depends on the reactivity of the oxides, itself a function of the mineralogy, time since deposition. etc...

Point 10, left column: it has to be „increases“ instead of „lowers“

We agree, we will make the substitution in the revised manuscript.