

Review of Sundby et al. , Biogeosciences

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.

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. 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.

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. 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.

The scenario presented also does not consider the processes that occur in exposed shelf sediments during glacial sealevel 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?

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.

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 ?

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?

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.

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.

L. 46: methane hydrates

Ls. 46 ff: I do not agree with the scenario that sealevel 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 sealevel 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?!

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

L. 119: drive instead of imply

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.

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)

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.

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).

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“.

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*).

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.

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.

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.

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).

L. 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).

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.

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.

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.

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.

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.

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.

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.).

L. 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.

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.

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.

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

I hope that my comments and considerations help focussing the manuscript. It was fun reading and considering your hypothesis/scenario (this is also why my comments are so lengthy ;-)).

All the best,

Sabine Kasten