

Biogeosciences Discuss., author comment AC2
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Reply on RC2

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-AC2>, 2021

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

RC2: 'Comment on bg-2021-124', David Archer, 25 Jun 2021 reply

This is a valuable and well-written paper clearly worthy of publication. The new idea is to combine changes in methane hydrate stability driven by sea level change to diagenesis chemistry that would release phosphorus to the ocean, stimulating biological production and ultimately possibly the enigmatic decrease in the CO₂ concentration of the atmosphere. Any new mechanism for volatility of the ocean phosphate reservoir is interesting, because of the profound biological impact of the P in the ocean.

We wish to thank Dr. Archer for his positive and incisive comments

I think it would be illuminating to put characteristic depth and concentration scales into Figure 2, to try to constrain how much phosphorus could be mobilized on which time scales. On the shallow end of the depth range, the hydrate stability zone is thin, so the released P would be near the sea floor, where it could diffuse to the ocean relatively quickly. On 100,000 years, the mean free path for molecular diffusion is about 50 meters. But if the stability zone is 500 meters thick, a change at the bottom of the stability zone would be pretty isolated from the ocean. In this way perhaps one could estimate the amount of methane that is properly poised to release phosphorus on a glacial time scale, which would tell you also the magnitude of the potential P dose. Putting characteristic depth and concentration units onto the profiles in Figure 2 would allow you to calculate a diffusive gradient and flux for P, another way to address the same issue, I guess. My hunch is that this depth-restriction of where this process could be relevant on 100,000-year time scales might diminish the potential scope for driving ocean P cycles, but that would not diminish for me at all the value of this paper or its worthiness of publication.

A very good point. We will add characteristic depth and concentrations scales to Figure 2 or its caption. We only hinted at these in section 3.7 of the original manuscript and they were implicit but unspecified in Figure 2. They are, indeed, critical factors in determining the responsiveness of the sediment to sea-level change.

Dr. Archer indicates that if the stability zone is 500 meters thick, a change at the

bottom of the stability zone would be pretty isolated from the ocean. We agree with him: little of SRP released 500 m below the seafloor would reach the SWI. But as mentioned in our manuscript (section 3.4, line 220-225) Borowski et al. (1999) and Gorman et al. (2002) show that methane gas, produced by hydrate dissociation at the lower stability boundary, can be injected well into the overlying hydrate stability zone. The data indicate that methane, in the form of free gas, can migrate hundreds of meters through the hydrate stability zone before re-forming as solid phase hydrate.

We propose the following addition in section 3.7. after line 312 of the original manuscript:

“The potential flux of phosphate fed by the ascent of the SMT is actually significant if the diffusional transport of P is sufficient for this phosphate to reach the sediment surface. The flux equation for transport via molecular diffusion is:

$$J = -\phi D_s (\Delta(\text{PO}_4)/\Delta z)$$

where J is the phosphate flux across the sediment-water interface; ϕ is the mean porosity of the sediment; z is the depth coordinate; $(\Delta(\text{PO}_4)/\Delta z)$ is the phosphate concentration gradient. D_s is the bulk sediment molecular diffusion coefficient, assumed to be equal to $D_s = D_o/(1 - \ln \phi^2)$ (Boudreau, 1996), where D_o is the diffusion coefficient in water at in situ temperature. Considering a porosity of 0.7 and D_o of $0.0124 \text{ m}^2 \text{ yr}^{-1}$ for HPO_4^{2-} at 5°C (Schulz and Zabel, 2006), a mean flux of $1 \times 10^{10} \text{ mol yr}^{-1}$ from a sediment surface of $23 \times 10^6 \text{ km}^2$ ($= 4.35 \times 10^{-4} \text{ mol m}^{-2} \text{ yr}^{-1}$) requires a concentration gradient $(\Delta(\text{PO}_4)/\Delta z) = J/(-\phi D_s)$ of $0.086 \text{ mol m}^{-3} \text{ m}^{-1}$ or $86 \mu\text{mol L}^{-1} \text{ m}^{-1}$. Such a gradient is only 2 to 4 times higher than the highest gradient observed on continental slope sediments by Niewohner et al. (1998) or Charbonnier et al. (2019), suggesting that molecular diffusion is not an obstacle to the transfer the inventory of mobilizable phosphate toward the sediment-water interface, as long as the concentration gradient becomes high, as our scenario predicts.”

I think it would be worth mentioning, in the background to the ocean nutrient inventory as a driver of atmospheric CO_2 , that the extent of this effect should be reflected in the plankton – benthic $\delta^{13}\text{C}$ difference, a measure of the strength of the biological pump. I think this “ $\Delta\delta^{13}\text{C}$ ” says that the biological pump is not the entire answer to the glacial CO_2 drawdown. That also does not diminish the value of this paper at all; the proposed coupling between methane and phosphorus cycles should clearly be elucidated, as this paper nicely does.

Cartapanis et al. (2016) provide evidence of greater OM burial during the glacial period, but does not include isotopic data to confirm the role of the biological pump. This reference appears in the Table 2 in the original manuscript. We propose to add a sentence line 57 “This is supported by observations: global rate of organic matter burial is maximal during the glaciation (Cartapanis et al., 2016; Boyle, 1986; Wallmann, 2010) ”

Line 105: A citation for the “until recently” would be useful. I note that there is further discussion of this topic later in the paper.

We propose to add Egger et al. (2015) to support this statement.

Line 127 My distant recollection is that there is a lot of particulate phosphorus in rivers,

stuff that gets scavenged in the estuary double-layer-collapse sedimentation zone. It might be helpful to clarify how this flux fits into the P budget. Could it be that it is this phosphorus flux that gets periodically mobilized, maybe along with biologically-deposited phosphorus? Thinking about this might be complicated by estuaries that exist or not through glacial cycles, possibly changing where the P deposits. Perhaps that would increase the potential P mobilization, if you're not limited by P that was deposited by primary productivity during the past glacial cycle (which is a very clever idea).

Many estuaries serve as nutrient traps and these P-rich estuarine sediments are likely to be remobilized (or colonized by plants (Filippelli et al., 2007) when sea level decreases and exposes shelves, but, like with the shelf-nutrient hypothesis, a mechanism to release SRP from these sediments would be required.

Line 277 I'm not sure I agree that a linear P gradient implies that there is no impediment of diffusion by adsorption onto solid phases. There is clearly a diffusive flux, but it could be linear in a long-term steady state, with a higher concentration of adsorption P going with higher porewater concentrations at depth; the pore waters could still be buffered by the sediment. That might be important for thinking about the time dependence of the phosphate concentration and hence cycles in the diffusive flux. In a more buffered case, I guess the relevant depth range for driving P cycles would get shallower.

There might be some authigenic precipitation, but we believe (Sundby et al., 1992) that, given that P adsorption is an equilibrium process and, barring significant co-precipitation (or solid-state diffusion) with iron oxides, iron oxide surfaces should be mostly saturated.

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

As explained in the comment about diffusive flux calculation (see above), molecular diffusion is not an obstacle to the transfer the inventory of mobilizable phosphate toward the sediment-water interface , as long as the concentration gradient becomes high enough.