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Comment on bg-2021-124

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Referee 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-RC1, 2021

In this thought-piece, Sundby et al. consider the impact that diagenesis of methane might play in amplifying glacial-interglacial changes via a phosphorus mechanism. Broecker pioneered the concept of climate transition amplification to explain the rapid ~10 ky transition from glacial to interglacial that is reflected in the geologic record. The climate forcing would indicate a sine curve transition, but the record shows that there are significant internal earth mechanisms that alter this external driver to result in a slow freeze-down followed by a rapid melting. Sundby et al. turn to a recent study of theirs dealing with Mn diagenesis to posit that perhaps a similar process occurs with methane, in such a way that it interacts with sedimentary phosphorus diagenesis and then triggers a nutrient-productivity feedback impacting atmospheric carbon dioxide.

First, kudos to the authors for refreshing the shelf-nutrient hypothesis and considering other processes to explain the “still not explained” paleo-productivity records and rapid glacial-interglacial transition. Though conjectural at this point, the basic premise of methane destabilization and changing the diagenetic front in sediments to release phosphate into the overlying water column is tenable at face value at least.

I have some overall “thought responses” to various aspects of this paper, to be taken as reflections rather than as criticisms of this excellent work.

The authors state beginning on line 62 “The amount of sediment that has to be deposited and eroded on the relevant time scale appears to be far greater than can be supported by observations (Peacock et al., 2006). Another weakness of the hypothesis is the absence of an explicit mechanism that would release

phosphate into the aqueous phase once the sediments are eroded."

This is indeed a challenge to the shelf-nutrient hypothesis, particularly if one considers this an on-off switch of glacial-not glacial. But it is not a binary system—as the Earth creeps its way into a glacial period, sea levels successively falls, exposing more and more of the shelf to subaerial exposure and yielding less and less burial space for phosphorus on the shelf. One would expect to see a steady increase in phosphorus delivery to the deep sea sink, which has a much longer internal residence time wrt to phosphorus given great recycling extent of falling organic matter through a longer water column. Furthermore, once exposed to subaerial weathering by acidic rainfall and by plant colonization, the shelf sediments can be a critical additional source of phosphorus into the deep sea sink, further increasing phosphorus loading. We interrogated this phenomenon in "Filippelli, G.M., Latimer, J.C., Murray, R.W., and Flores, J.A., 2007. Productivity records from the Southern Ocean and the equatorial Pacific Ocean: Testing the Glacial Shelf-Nutrient Hypothesis. *Deep Sea Research II*, 54/21-22: 2443-2452," and found that, with a proper lag, one could see the shelf transfer of phosphorus in deep sea sedimentary records.

At face value this finding supports the classic shelf-nutrient model and I think more faithfully documents the real, gradual progression into a glacial interval. It could thus be argued that we need no additional source of phosphorus beyond what is present on the shelfs plus the phosphorus that avoid shelf deposition in the first place in lower sea levels. But as the author of this, there are several weaknesses, or at least unconstrained components, that provide ample room for an additional phosphorus source argument, like the methane one in this Sundby et al. contribution. First is the issue of scale of input. As Sundby et al. point out, there simply doesn't seem to be enough phosphorus transferred from the shelfs to produce the productivity and CO2 response observed in the record. Second is one of timing—how quickly might exposed shelf sediments be colonized by land plants and weathered through acidic processes? Probably not fast enough to get the rapid response seen in the CO2 record.

Sedimentary methane oxidation and phosphorus diagenesis

Sundby et al. advance a really novel hypothesis that is nevertheless rooted in the stabilization history of methane clathrates. Namely, could the oxidation of hydrates from lowered hydrostatic pressure (lowered sea level) drive a diagenetic front through iron oxyhydroxides, releasing the ample phosphorus stored in this mineral phase? We know that methane hydrates are ample in marine sediments, and that their stability is dictated by pressure and temperature (in marine sediments, it is likely the pressure component that is most at play here). And the oxidate of these hydrates would then release chain of chemical processes that might reduce the overlying iron oxydroxide layer.

Given how much phosphorus is typically trapped in this phase (based on our work and others it is typically 20-30% of the total soluble phosphorus in marine sediments), this seems to be a plausible, and quite significant, additional source of phosphorus to the deep ocean reservoir, and perhaps one that is previously missing in the shelf-nutrient

hypothesis model. What I really like about this mechanism proposed by Sundby et al. is its speed—an advancing front of iron oxide reduction would yield "near instantaneous" (on geologic timescales) release of phosphorus into the overlying water column. Plus, this front can progress in stages, as supported by intervals of sea level stabilization observed as glacial intervals progress. This speed and dynamic response is an interesting and welcome addition to the overall concept of phosphorus playing a key role in ocean productivity and biogeochemical cycling in glacial intervals. Of course, as Sundby et al. point out, let's not get too carried away by the power of phosphorus—certainly, you could hit a point where the limiting scale leans toward nitrogen, and it is important to keep the N/P ratio in mind when reconstructing nutrient limitation for various ecosystems.