

## ***Interactive comment on “Post-depositional vivianite formation alters sediment phosphorus records” by Nikki Dijkstra et al.***

**Nikki Dijkstra et al.**

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Anonymous Referee #2 Received and published: 8 November 2017

First of all, we would like to thank the reviewer for his/her comments and suggestions. Our response can be found below.

Comment: This work investigates the potential role of vivianite (an iron II- phosphate mineral) precipitation in altering the trends of sedimentary P, a commonly used paleo-productivity proxy. The samples were collected in the Bornholm Basin (Baltic Sea) in 2013. A combination of modeling, biogeochemical and electron microscopy analyses and experiments shows that manganese and molybdenum rich vivianite precipitation under sulfidic conditions can strongly alter P sedimentary records after their deposition,

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especially when environmental perturbations such as primary productivity changes associated to marine-lake transitions occur. The authors nicely summarized an intensive laboratory work and they present a coherent manuscript. The results are relevant because they provide new insights to the use of sedimentary solid phase phosphorus analysis to reconstruct paleo environments. Vivianite in particular, seems a potentially useful proxy for the occurrence of freshwater – marine transitions in systems like fjords in other parts of the world during, for instance, the last glacial maximum. However, the authors showed that vivianite peaks in the sediment could be strongly affected by sulfidic conditions and the presence of  $\text{Fe}^{2+}$ , resulting in concentration peaks not directly related to water column productivity but to diagenetic reactions. I only have a few comments after reading the manuscript. My concerns are mostly related to format and some passages that I found a little bit “obscure”.

In methods I think the redaction of the paragraph referred to P XANES analysis could be improved (page 16, lines 10-14). I found hard to follow the procedure, probably because I am not familiar with this particular technique. In the text the authors mention a “white line” that I cannot see in Fig. 7.

Reply: We have now added the main features (post-edge oscillations, white line, and shoulder feature) of the XANES spectra of the bulk sediment to the caption of Fig. 7 (see supplement). We now refer to the features in Fig. 7 in the main text (page 16, line 11): “See Fig. 7 for positions of XANES features.”

Text added to caption: “The positions of main features of the bulk sediment spectrum (the white line, post-edge shoulder and the post-edge oscillations) are indicated in the figure. The white line (main absorption step) is observed in all P spectra, whereas the shoulder features are only visible in the bulk sediment spectrum and the fluorapatite spectrum.”

Comment: There is a problem citing first Fig. 11 (page 17, line 15) and then figure 10 (page 21, line 14).

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Reply: We now discuss the results of Fig. 10 in section 3.5 (page 17, line 9-14): “Precipitate 1 and 4 were also examined by SEM-EDS before the start of the experiment (Fig, 10). Precipitate 1 generally consisted of  $\sim 5 \mu\text{m}$  crystals that contain phosphorus (P), iron (Fe) and magnesium (Mg). Precipitate 4 consisted of a mixture of crystals rich in P, Fe, manganese (Mn) and Mg, and irregular shaped precipitates that contain both Mg and P.”

Fig. 11 is cited on page 17, line 19. To avoid duplication, we now removed the following sentences from the subtext of Fig. 10: “Precipitate 1 generally consisted of  $\sim 5 \mu\text{m}$  crystals that contain phosphorus (P), iron (Fe) and magnesium (Mg). Precipitate 4 consists of a mixture of crystals rich in P, Fe, manganese (Mn) and Mg, and irregular shaped precipitates that contain both Mg and P.”

Comment: In addition, I think that Fig. 11 is complex compared to the rather brief references to it within the text.

Reply: We have now redesigned Fig. 11 to make it easier to see the main trends (see supplement to this comment). The caption is now also more extensive. We note that most of section 3.6 discusses the trends in Fig. 11.

Comment: Moreover, where did ages the authors mention came up? (e.g. Page 18, lines 3-6). It is not clear if the authors used an age model and how they derived it. I guess they probably used ages estimated in the IODP report by Andr n et al. (2015) or maybe, they used a constant sedimentation rate to estimate a composite core depth – age relationship. I think the authors should clarify this!

Reply: Unfortunately, no age model for this site was available at the time of writing of this manuscript. This is why we relied on previous dating of the lake-marine transition and used a constant sedimentation rate in our model. This is also explained in the text (page 14, lines 4-9): “The sedimentation rate for the marine phase was estimated at 1.6 mm/y and kept constant for the entire simulation period, as we have no information on the sedimentation rate in the lake phase. This rate

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corresponds to a lake-marine transition at  $\sim 7.5$  kyr as estimated by Zillen et al. (2008).”

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-295/bg-2017-295-AC2-supplement.pdf>

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