

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

Nikki Dijkstra et al.

n.dijkstra@uu.nl

Received and published: 2 December 2017

Anonymous Referee #1 Received and published: 29 October 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 is a well-written paper presenting a large data set from cores taken in the Baltic Sea. The take home message that post-depositional vivianite formation can confound sediment P records is reasonable. The good news in terms of sedimentary P records is that vivianite forms and is mobilized under fairly unique conditions. Thus, especially in records where one sees fresh water to marine transitions, one should be mindful of potential alterations involving iron phosphates. I am not sure how com-

C1

mon such transitions are in the geologic record. Nevertheless, it is good to be aware of this potential complication. Perhaps I sense some frustration of the authors in this manuscript in that their studies yielded no direct evidence of the mineral vivianite in their system. Essentially the presence is inferred from extractions, modeling, blue particles and its presence in other similar marine systems. The XANES measurements were not consistent with the presence of vivianite and the molar ratios of iron to phosphorus in SEM-EDS analyses do not seem to be that close to the values expected for vivianite. I have no doubt that there is some form of iron phosphate in these sediments but it may not be vivianite. There are many different iron phosphate minerals. My guess is that the iron phosphates are mixture of a number of poorly crystalline iron phosphate minerals. Given the absence of clear and direct evidence for vivianite, I believe it is a bit bold to state that its presence is “demonstrated” (line 7, page 2). Rather, it would be more accurate to say vivianite presence is inferred. Although using the term vivianite is a nice shorthand, it would be more representative of the findings to say something like “iron phosphates” in the title and throughout the text. Discussion of the blue aggregates could be expanded. Mole percent analyses are presented in Figure 8 but they are not deeply discussed. How do these mole percent values compare with vivianite? How do they compare with other possible iron phosphate containing minerals? Overall this is a very nicely presented study, other than the overly bold assertion for the specific presence of vivianite.

Reply: We agree that no direct evidence of vivianite has been presented in this study. However, we note that all the evidence points towards the presence of vivianite and not to other P minerals. The blue colour of the crystals is very typical for vivianite minerals. In addition, the Fe-P aggregates were almost identical in shape, color and size as vivianite minerals synthesized by Zelibor et al. (1988). It is also not unusual for the Fe:P molar ratio of vivianite, as determined with EDS, to deviate from 1.5 as discussed in our earlier work (Dijkstra et al., 2016). A previous study in the Bothnian Sea (Egger et al., 2015), to which we also refer in the main text, has shown that P-XANES is not always a conclusive method to provide evidence for (or against) the presence of

C2

vivianite in bulk sediments. Even in sediments in which the presence of vivianite was proven by XRD, bulk P-XANES spectra did not always show features characteristic for vivianite possibly due to interference with the sediment matrix.

To address the reviewer's comment, we now refer to these minerals as vivianite-type minerals and iron(II)-phosphates in the text.

We also added the following sentences to page 20 line 12: "(as proven by XRD) in the Bothnian Sea. Due to this lack of direct evidence for the presence of vivianite, we refer to the blue Fe-P aggregates as vivianite-type minerals."

We now expanded the discussion part on the EDS results of Fig. 8 (page 19 line 20-25): "The P content of the aggregates was low compared to the Fe content of the aggregates, resulting in Fe:P-ratios that are higher than the expected stoichiometric Fe:P-ratio of vivianite (> 1.9 versus 1.5 mol mol⁻¹). A similar discrepancy was observed in vivianite aggregates (as proven by XRD) in Dijkstra et al. (2016) and might reflect a surface coating of Fe, Mn and/or Mg of the aggregates, as has been observed in cold-seep sediments (Hsu et al., 2014)."

We removed "clearly" from page 20 line 2.

Comment: Figure 11 is hard to understand. The graphs are tiny and it is unclear what all the lines and shadings represent. Either the figure should be redesigned or a more extensive caption is needed to help the reader.

Reply: We redesigned figure 11 and extended the caption as suggested (see supplement to this comment).

The added text reads: "The increase in salinity at 7500 BP marks the onset of the lake-marine transition. The subsequent deposition of sediment in a brackish-marine environment and the related changes in the porewater chemistry led to major changes in solid phase chemistry as a function of sediment depth and time. The distinct bands of Fe-carbonate and vivianite (Fe₃(PO₄)₂) minerals formed in the sediments are par-

C3

ticularly striking."

In section 3.6, we also added a reference to the online supplementary information with an overview of the present-day process rates as a function of sediment depth: "Present-day rates of processes as calculated in the model are given in the online supplementary information"

Comment: Line 9 page 13 change "is" to "are"

Reply: Change made.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-295/bg-2017-295-AC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-295>, 2017.

C4