

Reviewer 3

We thank the reviewer for his/her positive and careful review of our manuscript, which highly helped us improving the new version of the manuscript to be submitted. We have addressed all of the Reviewer's concerns with additional data, namely:

- Downcore profiles for both highly reactive and total iron in bulk sediment.
- Pore water SO_4^{2-} , Ca^{2+} , Mg^{2+} and Mn^{2+} concentrations were added to Figure 2a and are discussed in the revised manuscript.
- Based on geochemical modeling of pore water major ions, we calculated saturation indices for specific minerals (e.g. vivianite, siderite). These indices are listed in a new table (Table 1) now included in the revised manuscript.

We did our best to fulfill all the remarks and suggestions brought by the Reviewer. Each comment has been addressed in separate answers, and all the corresponding changes are highlighted in red in the text. Please, find here after our point by point answers to Reviewer 3.

Yours sincerely,
Aurèle Vuillemin

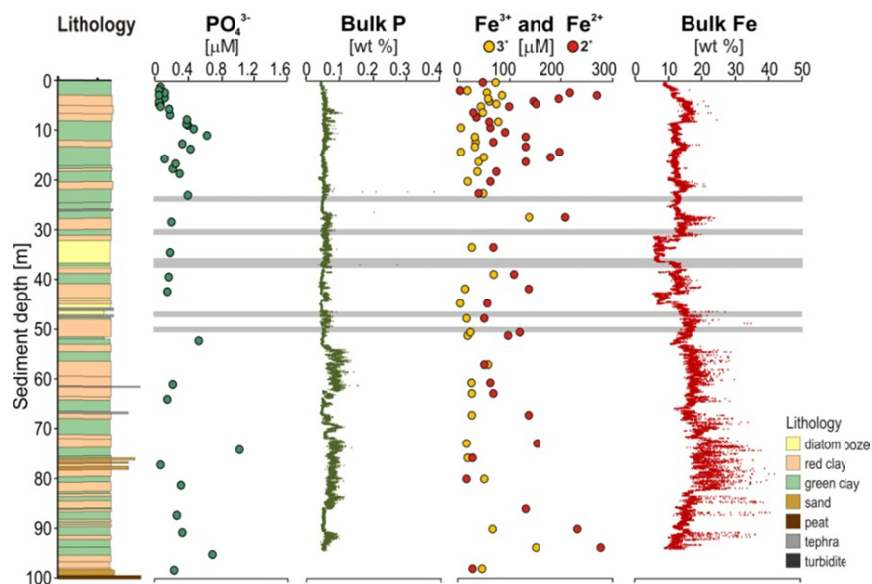
General comments

- **Comment 1:** In my opinion, the impact of the paper could increase by adding an implications section at the end of the discussion. Here the authors could present a mass balance for P and discuss the importance of vivianite in the burial of P in this and other lake sediments. Now it is only briefly mentioned that vivianite might act as the main sink for P (page 11, line 31).

Answer 1: We do not have sufficient quantitative measurements of P concentrations and vivianite crystals in bulk sediment to accurately model the P mass balance. To satisfy the Reviewer's interest, we provide at his/her discretion preliminary XRF profiles (here under) and compare them with those of pore water. We are reluctant to provide XRF data for publication or discuss them any further since they are not calibrated and are part of another manuscript in preparation.

To address the relevance of vivianite in P burial, we oriented the discussion around saturation indices modeled for vivianite and siderite (Table 1), and show how pore water saturation with respect to vivianite increases with depth and leads to the gradual depletion of dissolved phosphate with burial.

We further discuss P cycling in the present ferruginous analogue and compare pore water concentrations to those interpreted from the Archean rock record. We added a short paragraph at the end of the discussion summing up the implications of P cycling processes in modern ferruginous sediment and use those interpretations from the rock record of Archean marine sediments (see answer no. 2).



Preliminary XRF profiles

5 m depth	Saturation	10 m depth	Saturation
talc	1.43	siderite	1.00
siderite	1.29	quartz	0.71
quartz	0.71	vivianite	-0.04
vivianite	-0.45	talc	-0.31
calcite	-0.68	calcite	-0.83
dolomite	-0.77	aragonite	-0.97
aragonite	-0.82	dolomite	-1.27

Table 1

- **Comment 2:** The authors mention in the abstract and introduction that Lake Towuti can be used as an analogue for the Archean ocean. However in the discussion, I miss the implications that this study has for the Archean ocean.

Answer 2: We added a paragraph at the end of the discussion summing up the implications of the diagenetic processes observed in modern ferruginous sediment for the Archean oceans as interpreted from the ancient rock record. This paragraph reads as follows:

“Whether they relate to microbial reduction in soft ferruginous sediment or past conditions in bottom waters, biotic and abiotic diagenetic processes remain challenging to constrain in terms of ancient rock record (Johnson et al., 2013). Concentrations estimates for deep anoxic waters interpreted from the Archean rock record typically range from 40 to 120 µM for Fe and 0.1 to 0.3 µM for P (Holland, 2006; Konhauser et al., 2007; Jones et al., 2015), which are similar to those presently observed in the pore water of ferruginous analogue Lake Towuti (Fig. 2a). Concerning P diagenesis, it is hypothesized that P availability in the Archean ocean was limited by the lack of terminal electron acceptors and oxidative power used to recycle most of the OM-bound P rather than by scavenging by Fe minerals (Kipp and Stüeken, 2017; Michiels et al., 2017; Herschy et al., 2018). The present Ca²⁺ and Mg²⁺ concentrations in pore water exert apparent control

on the precipitation of siderite and/or vivianite during early diagenesis (Vuillemin et al., 2019a), which is comparable to interpretations of ancient P availability in regards to hydrothermal and continental weathering of mafic rocks (Jones et al., 2015). In this context because secondary P-bearing minerals cannot form if P remains bound to OM, we suggest that the precipitation of millerite, siderite, and vivianite in the sediment constitute a likely diagenetic sequence stemming from the depletion of pore water electron acceptors and related loss of oxidative power during OM remineralization, with consequent long-term P sequestration.”

Additional references:

- Herschy, B., Chang, S. J., Blake, R., Lepland, A., Abbott-Lyon, H., Sampson, J., Atlas, Z., Kee, T. P., and Pasek, M. A.: Archean phosphorus liberation induced by iron redox geochemistry, *Nat. Commun.*, 9, 1346, <https://doi.org/10.1038/s41467-018-03835-3>, 2018.
- Kipp, M. A., and Stüeken, E. E.: Biomass recycling and Earth’s early phosphorus cycle, *Sci. Adv.*, 3, eaao4795, <https://doi.org/10.1126/sciadv.aao4795>, 2017.
- Konhauser, K. O., LaLonde, S. V., Amskold, L., and Holland, H. D.: Was there really an Archean phosphate crisis?, *Science*, 315, 1234, <https://doi.org/10.1126/science.1136328>, 2007.
- Michiels C.C., Darchambeau, F., Roland, F. A., Morana, C., Llirós, M., Garcia-Armisen, T., Thamdrup, B., Borges, A. V., Canfield, D. E., Servais, P., Descy, J.-P., and Crowe, S. A.: Iron-dependent nitrogen cycling in a ferruginous lake and the nutrient status of Proterozoic oceans, *Nat. Geosci.*, 10, 217-221, <https://doi.org/10.1038/NGO2886>, 2017.

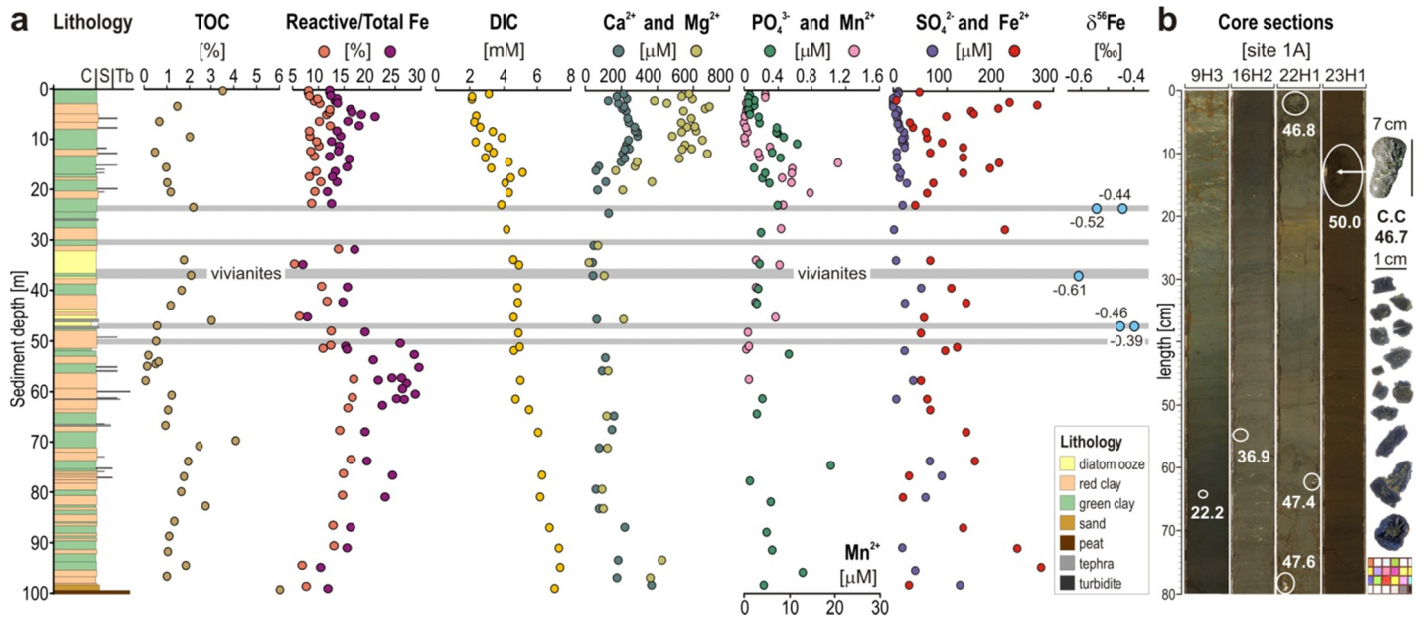
- **Comment 3:** I would like to also see the Fe extraction data for this core. It is mentioned in the method section that Fe extractions were carried out, however they are now only used to calculate the total Fe present.

Answer 3: Because sequential Fe extractions constitute the main part of a manuscript presently in preparation, we refrain from providing the complete dataset. To satisfy the reviewer’s legitimate comment, we provide downcore profiles for the highly reactive Fe (i.e. the sum of four successive Fe pools) and total Fe (i.e. reactive + non-reactive) pools in the revised Figure 2a.

We clarified the extraction procedure in the method section, part 2.2, and cite the corresponding manuscript available as preprint at <https://www.EarthArXiv.org>. We also updated Figure 2a (here under) and complemented the results, part 3.2, accordingly.

Additional reference:

- Bauer, K. W., Byrne, J., Kenward, P., Simister, R., Michiels, C., Friese, A., Vuillemin, A., Henny, C., Nomosatryo, S., Kallmeyer, J., Kappler, A., Smit, M., Francois, R., Crowe, S. A.: Magnetite biomineralization in ferruginous waters and early Earth evolution, *EarthArXiv Preprint*, <https://doi.org/10.31223/osf.io/prhuz>, 2020.



Revised Figure 2

Specific comments

Introduction

- **page 2, line 8:** “under anoxia”. Here reducing conditions are also important, not only anoxic conditions.

Answer 4: Rephrased to “...reducing conditions and long-term anoxia...”

- **line 8:** “..phosphate..”. Phosphate should be phosphorus (or P) in this case.

Answer 5: Modified accordingly.

- **line 10:** This is only the case when there is sufficient organic matter, otherwise there is no formation of sulfide and eventually Fe sulfides.

Answer 6: Modified accordingly to “...high sulfate (SO₄²⁻) concentrations and sufficient labile OM,...leads to the formation of sulfides and eventually iron sulfides that decrease...”

- **line 12:** “Formation of iron phosphate minerals..”. Mention that these are reduced iron phosphate minerals.

Answer 7: Mentioned accordingly.

- **line 22:** “In such systems..” Besides the presence of P also the rate/amount of Fe reduction is important in oligotrophic environments. When the organic matter content is low this can lead to limited Fe reduction, low concentrations of pore water Fe and limited formation of vivianite. This has recently been shown in a modeling study for an oligotrophic estuary in the Bothnian Sea (Lenstra et al., 2018)

Answer 8: We added the following sentence to the text:

“Besides P concentrations, low content and reactivity of OM may also narrow rates of Fe reduction and thereby preclude vivianite formation due to limited release of Fe^{2+} to pore water (Lenstra et al., 2018).”

We added (Lenstra et al., 2018) to the list of references and cite it where appropriate in the manuscript.

- **line 27:** (Egger et al., 2015; Dijkstra et al., 2016) show vivianite formation in brackish (not marine) environments. The formation of vivianite, when there is sufficient organic matter, is sensitive to the production of sulfide in the sediment. So at a higher salinity (enhanced sulfide production) the formation of vivianite is expected to be lower. The dependence of vivianite formation on salinity is also discussed in the modeling study by (Lenstra et al., 2018).

Answer 9: Thank you for this correction. We replaced “marine” by “brackish” in the corresponding sentence. We also added one sentence to clarify the influence of salinity and OM content on sulfide production in the sediment:

“However, high salinities and substantial burial of OM can promote microbial reduction of SO_4^{2-} and sulfide production, which tend to restrict the formation of vivianite in the sediment (Lenstra et al., 2018).”

- **page 3, line 22:** “...is stable under anoxic conditions..” Add that it is also important to have non-sulfidic conditions. (anoxic/non sulfidic).

Answer 10: Modified accordingly.

Section 2.3

- **page 5, line 2:** In these steps, you do not extract Fe present in pyrite. I guess this is a very small pool in these environments but to correctly determine the HR Fe pool this should be included or mentioned that this is not included.

Answer 11: We added the following information in the methods, part 2.2.:

“For reactive and total Fe sequential extraction, we processed 200 mg of sediment according to Poulton and Canfield (2005). The highly reactive Fe pool is defined as the sum of carbonate-associated Fe (acetate extractable Fe), hydrous Fe (oxyhydr)oxides including ferrihydrite and lepidocrocite (0.5 N HCl extractable Fe), ferric (oxyhydr)oxides including hematite and goethite (dithionite extractable Fe), and magnetite (oxalate extractable Fe). These reagents do not extract the Fe present in pyrite (Henkel et al., 2016). The non-reactive Fe pool is defined as Fe contained in silicate minerals after removal of reactive phases (near boiling 6N HCl extractable Fe). Total Fe was obtained by summing up the highly reactive Fe pools and the non-reactive Fe contained in silicate minerals (Bauer et al., 2020).”

- **line 2:** How is the non-reactive Fe fraction determined?

Answer 12: The non-reactive Fe pool is defined as the Fe contained in silicate minerals after removal of reactive phases (near boiling 6N HCl extractable Fe). See answer 11.

Section 2.4

- **line 13:** Was this carried out under anoxic conditions?

Answer 13: Yes, all pore water extractions were carried out in an anaerobic chamber. This was already mentioned in part 2.1:

“Pore water was extracted on site from 5-cm-long whole round cores (6.6 cm diameter) that were cut from the core sections, immediately capped and transferred to an anaerobic chamber flushed with nitrogen to avoid oxidation during sample handling (Friese et al., 2017).”

We now mention this once more in part 2.3: “After transfer of the whole round cores to the anaerobic chamber, pore water within the upper ten meters was extracted using Rhizon...”

Section 2.5

- **page 6, line 6:** “Below and above this interval, vivianites are rarely present in the sediment, which was confirmed by smear slide analysis (Russell et al., 2016) and X-ray diffraction (Supplementary Fig. S2).” This should be moved to the discussion section.

Answer 14: Moved accordingly to the discussion, part 4.2 (page 14, line 10).

Section 3.2

It would be interesting if you can also show your Fe extraction results in this section. Maybe in the appendix, if you don't want to add an additional figure to the manuscript.

Answer 15: Please refer to answers no. 3, 11 and 12.

Section 4.1

- **page 11, line 24:** Is it possible that the orientation of the mineral in the sediment changed during coring? I wonder because the mineral is located very close to the core liner.

Answer 16: Although sediment disturbance cannot be fully excluded, we observed multiple vivianites in different core sections, with crystal orientation reflecting an upward growth (Supplementary Fig. S5) so that polarity and growth direction can be inferred without difficulty.

- **line 27:** Would it be possible to include the solid phase Fe speciation in the paper?

Answer 17: See answers no. 3, 11, 12 and 15

- **line 30:** But concentrations of phosphate are generally low not only at places where vivianite is found. I would therefore, based on only the phosphate data, not suggest that vivianite is the main sink of P.

Answer 18: Rephrased from "...acted as a main P sink..." to "...could act as a P sink from the pore water to the sediment during diagenesis".

- **page 12, line 10:** Here and elsewhere Potsma should be Postma

Answer 19: Corrected accordingly.

- **line 11:** "...depending on the local pH, CO₂, PO₄³⁻, and the amount of reactive ferric oxides buried..". Here, also the amount and reactivity of organic matter is important.

Answer 20: This was added to the sentence accordingly.

Conclusions

- **page 13, line 5:** I do not understand what partially dissolved iron oxides are.

Answer 21: Rephrased to "...partially dissolved goethite..."