

## ***Interactive comment on “Vivianite formation in ferruginous sediments from Lake Towuti, Indonesia” by Aurèle Vuillemin et al.***

### **Anonymous Referee #1**

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**General comments** The manuscript describes geochemical feature from a long sediment core collected in a deep lake of Indonesia. This lake and a neighbouring lake, Lake Matano, are known for their unique current processes related to iron geochemistry. These lakes have been studied as a proxy for conditions that prevailed in the Archean Ocean. The authors provide new information on iron-phosphorus relationships in this particular context through their study. A good knowledge of phosphorus dynamics in a context of anoxic and non-sulfidic ferruginous water mass can provide interesting knowledge to better understand the phenomena that determined the bioavailability of this nutrient salt during the first episodes of the history of life on Earth. The work presented here focuses mainly on a core more than 100 m long, and more particularly on an interval between 20 and 50 m deep, which contains diatomaceous oozes

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and levels rich in vivianite, a ferrous iron phosphate. The authors try to understand how vivianite was formed and under what conditions this mineral traps phosphorus. To do this, they used mineralogical techniques to study the succession of authigenic phases during diagenesis. They also measured dissolved parameters in pore waters and the isotopic signature of iron in vivianite. The issue is of interest to the scientific community, which is seeking to better understand the phosphorus cycle. The discovery and description of the large vivianite crystals is original. While the introduction is well written, some issues related to the results raise questions and the discussion/interpretation of the results is often based on questionable assumptions. This is why I exercise some restraint in validating the publication of the article.

specific comments

Section 2.4 line 27: phosphate was measured by ion chromatography. This method has the disadvantage of having a rather poor detection limit. The authors announce a limit of quantification of  $14.3 \mu\text{M}$ , which is insufficient here. Commonly used colorimetric methods give at least 20x better detection. The main problem here is that all the concentrations presented in pore water are between 0 and  $1 \mu\text{M}$ , well below the limit of quantification. Figure 2 shows a  $\text{PO}_4$  profile with variations between 0 and  $1 \mu\text{M}$ . There is therefore a problem with these  $\text{PO}_4$  data, either in the description of the method or in the results; this must be seriously corrected.

line 29 : pH is measured in the supernatant after homogenization of 2 mL sediment in 2 mL deionized water. I have never seen that the pH of pore water can be measured in this way. Is there a reference? The pH is measured here in pore water diluted with deionized water. This cannot give the in-situ pH value. In addition, the authors solve the carbonate system with this questionable pH measurement. Why did the authors not measure the pH in the water used to measure alkalinity?

Section 3.4 line 25: "Given that vivianite is a  $\text{Fe}^{2+}$ -bearing mineral phase, the isotopically light  $\delta^{56}\text{Fe}$  values we measured in vivianites from Lake Towuti are consistent

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with the direction of fractionation occurring during Fe<sup>3+</sup> reduction.” This interpretation is based on the principle that Fe(II) is the result of the reduction of Fe(III). But there is no evidence of that. The interpretation given here is indeed the one that would be given for "classical" sediments. But here, the context is very particular and it cannot be excluded that the Fe<sup>2+</sup> that produced the vivianite does not come from the dissolution of an initial Fe(II) phase. This point should be discussed.

Discussion section p.11, first paragraph: the first paragraph is not precise enough and is based on too many insinuations. “The ferrous Fe and P released from these reactions may produce vivianite, and/or be consumed through reactions with other dissolved elements such as S.” Be more specific. HS<sup>-</sup> in line8 and H<sub>2</sub>S in line 13. “Because rates of sulfide production are so low compared to the Fe delivery flux ” and “in sediments such as Lake Towuti’s, siderite is an expected mineral phase” what are the quantitative elements to assert this?

line 27 “Because of the high concentrations of Fe oxides in Lake Towuti’s sediment (~ 20 wt %), it is very unlikely that much P could escape to the bottom water.” This is another unjustified statement. If the ferric phases have their PO<sub>4</sub> adsorption sites saturated, PO<sub>4</sub> can migrate line 30 “In the deep sediments, pore water PO<sub>4</sub><sup>3-</sup> concentrations are constantly low in the interval where vivianite crystals are observed (Fig. 2a), suggesting that vivianites acted as a main P sink during diagenesis”. PO<sub>4</sub> concentrations are not quantified, given the method used. Are there not the elements to calculate the theoretical concentration of PO<sub>4</sub> that would be at thermodynamic equilibrium with vivianite? Such a calculation could strengthen the assertions. p. 12 line 8 “they are (...) rather subject to variety of processes that are variable down core.” the conclusion of this paragraph reflects its vague and speculative nature. The processes mentioned should be better described. Methane production suddenly appears without any other explanation. It would be better to specify the presentation.

line 29: “The presence of diatomaceous oozes, with vivianites below and above these sediments, indicates that P concentrations in the water column were much higher dur-

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ing this time interval compared to present-day levels” The authors suggest here that the fossilization of more diatoms suggests that primary production was higher at the time of these deposits and that the increase in primary production was due to an increase in phosphate inputs. If this is the case, it should be detailed as such. But I am not sure that this is necessarily the case, because the exact opposite can be interpreted. Indeed, one could also imagine that an increase in eutrophication due to PO<sub>4</sub> input would favour cyanobacteria rather than diatoms, as observed in many lakes. Thus, more diatoms could indicate less PO<sub>4</sub>. This should be discussed. In addition, the preservation of diatoms may also come from conditions more favourable to their fossilization than other periods.

section 4.3 line 12: “Dissimilatory microbial reduction of iron releases Fe<sup>2+</sup> in pore water that is up to 2 ‰ lighter than the original substrates ” the fractioning will depend on the rate of reduction. line 21: δ<sup>56</sup>Fe values measured on vivianite are compared to “expected” values for iron oxides. From this point on, all the following in this paragraph is speculative and not supported by data.

Last sentence of the conclusion: “Although crystallization time was not constrained, supply of pore water PO<sub>4</sub><sup>3-</sup> and Fe<sup>2+</sup> during diagenesis maintained saturation with respect to vivianite and supported the continuous growth of crystals with depth.” Here again, this statement is not validated by calculations. The degree of water saturation with respect to vivianite has not been calculated.

Figure and supplementary material are of good quality.

technical corrections

section 2.1, line 10: Describe in more detail the chronology of the operations: date of drilling, extraction of pore water.... the minerals were extracted after more than 6 months of storage. Please specify it.

section 2.2 line 24: the carbonate removal technique to measure the total organic

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carbon goes through a washing and centrifugation phase. Doesn't this step cause the loss of organic matter less dense than water?

section 2.4 line17: Dissolved Fe is measured using Ferrozine. Authors have used the method described by Viollier et al., 2000. This study recommends using ascorbic acid to transform all dissolved iron ( $Fe^{II} + Fe^{III}$ ) into  $Fe^{II}$ . Was ascorbic acid used here?

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