

## Reply to referee#1

We are grateful to referee#1 for his/her comments. Below you find the detailed answers (normal font) to the issues raised by the reviewer (typewriter). Added text blocks for the revised version of the manuscript are written in *italics*, citations of the original manuscript are enclosed in brackets [].

### Summary

The paper presents results from a characterization of the vivianite content in a lake sediment using a new analytical procedure. It assesses the accumulation of vivianite in the sediment layer that corresponds to the period after the lake was treated with iron versus the vivianite content in the layer below. A significant result is that the vivianite content was found not to correlate with the degree of porewater supersaturation, which suggests that the mineral precipitation is controlled by mechanisms other than thermodynamic driving forces. Vivianite is an important mineral for the long-term retention of P in lake sediments, and the dynamics of its formation is still poorly understood. This manuscript presents important information that should help our understanding of P retention as well as can influence management practices. The study and the interpretation of results appear carefully conducted. I believe the specific criticisms listed below can be addressed upon a minor revision.

### Major comments

Both porewaters and solid sediment were handled aerobically. I would like to see a brief mentioning of how this might have affected the results. My feeling is that the porewater results should stand, as they were already filtered through the dialysis membrane and quickly fixed in acid, whereas the vivianite content in the solid fraction might have been modified slightly. A potential effect of freeze-drying is also worth discussing.

The porewater samples were handled according to the normal sampling procedure which keeps oxygen contamination to a minimum. As we described in the Materials and Methods section, the sampling of the membrane covered chambers was done immediately after the recovery of the dialysis samplers. Sampling was done with syringes which were plunged through the dialysis membrane to avoid oxygenation of the chambers. Samples were then fixed with hypochloric acid. The use of in-situ dialysis samplers and the sampling procedure described, guarantees a minimum of oxygen contamination. Prior to deployment of the dialysis samplers in the lake, the samplers were purged with nitrogen for 24 h to remove any oxygen from the chamber water.

The aerobic handling and the freeze drying of the sediment do modify the vivianite as the nodules will be slightly (surface-) oxidised and change their colour from translucent-white to blue. Nriagu (1972) pointed out that this slightly oxidised form of preserved vivianite is stable in the laboratory almost indefinitely. From our results the contact with air does not significantly change the XRD pattern of the mineral. We have added the reference line patterns of vivianite and metavivianite from the Crystallography Open Database (COD) to Fig. 4a and have included the XRD-pattern of a heated synthetic vivianite sample (60 °C for 24 h) in the revised version of the manuscript. From these diffraction patterns it becomes clear that the blue vivianite nodules in the high-density samples and the synthetic vivianite powder (blue appearance) still feature the same lattice parameters as unoxidised

vivianite. Upon heating at 60 °C for 24 h the synthetic vivianite powder changed its colour to orange-brown and became XRD-amorphous (most likely Fe(III)–PO<sub>4</sub>). Based upon these results, aerobic handling of sediment neither alters vivianite significantly (except for the colour change and the correspondent surface oxidation of Fe<sup>2+</sup>) nor does it prevent detection of the mineral by XRD. Freeze-drying also has an impact on the speciation of sulphur (Hjorth, 2004). Oxygen exposure might therefore alter crystalline FeS<sub>2</sub> and FeS phases.

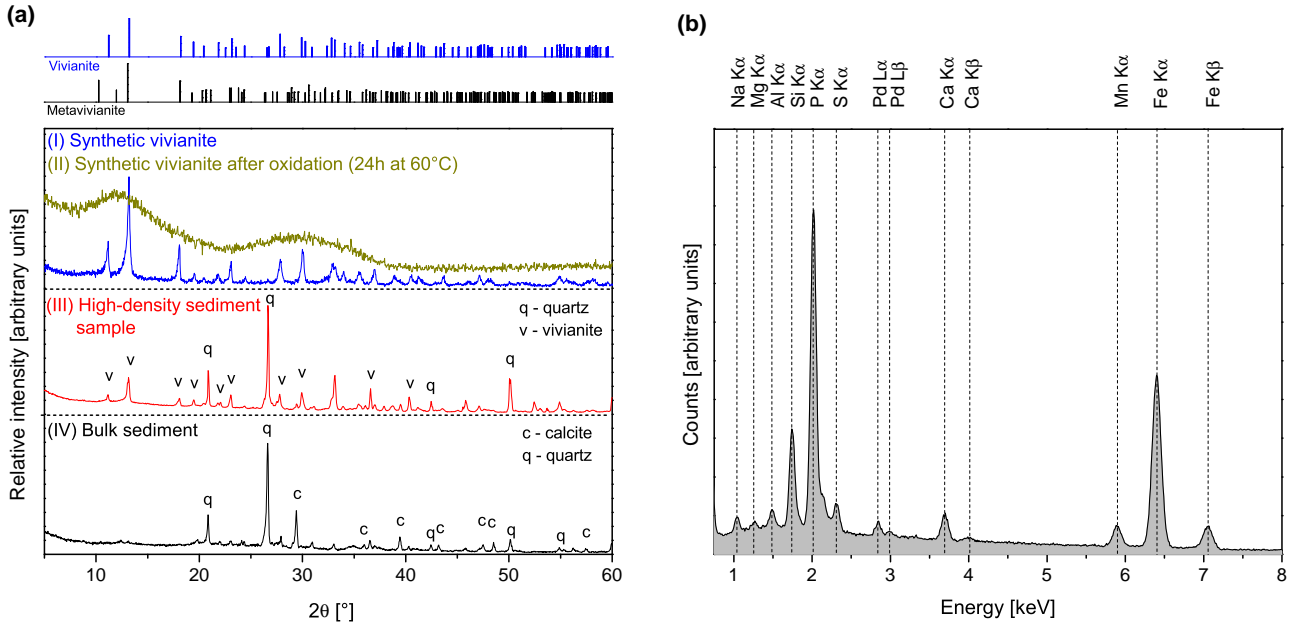


Fig. 4. (a) XRD patterns of (I) synthetic vivianite, (II) synthetic vivianite after oxidation at 60°C for 24 h, (III) high-density sample, and (IV) bulk sediment. Characteristic reflexes of vivianite could only be observed after heavy-liquid separation in the high density sample (II). The line patterns of vivianite (blue, file number 96-901-2899) and metavivianite (black, file number 96-100-1784) use data from the Crystallography Open Database (COD) REV 64680 (2012 edition). (b) SEM-EDX elemental spectrum obtained from a dark blue sediment concretion from Lake Groß-Glienicke. The correspondent atomic Fe:P ratio is 1.49. Note that elemental peaks of carbon and oxygen were omitted.

We have discussed this issue in the discussion part of the revised version of the manuscript.

[In our study, X-ray diffraction was successful, even though the vivianite nodules were partially oxidised due to contact with air (Figs. 3a and 4a) and already are an alteration product of unoxidised, *pristine* vivianite.] *The diffraction pattern of synthetic vivianite powder, both in its slightly oxidised form (blue appearance) and after heating at 60 °C for 24 h supported that the vivianite nodules detected in the sediment were slightly surface-oxidised only and did not loose their characteristic diffraction pattern upon exposure to air. Comparing the diffraction pattern of the high-density sample with the reference diffraction pattern of vivianite and metavivianite (which accounts for a partial oxidation of Fe(II)) there was even a higher conformity with the vivianite reference pattern than with the metavivianite reference pattern (Fig. 4a). This finding confirms that the aerobic handling of sediment does not lead to a significant oxidation of vivianite and the mineral can be detected*

by X-ray diffraction even after contact with air; this is contrary to what has been reported by Olsson et al. (1997) and März et al. (2008). [According to these studies, vivianite is not expected to be detectable by X-ray diffraction after contact with air due to its high sensitivity towards oxidation.] *Aerobic handling of sediment and freeze-drying, however, might have impacted the speciation of sulphur i.e. crystalline FeS<sub>2</sub> and FeS might have been oxidised and altered to amorphous phases (Hjorth, 2004).*

#### Minor comments

p.7361, lines 5-7: I suggest adding a reference to support the statement about the importance of long-term burial vs short-term immobilization, as this subject has been a source of confusion in the past (e.g., Katsev et al. 2006, Hupfer and Lewandowski 2008).

We have added a reference here.

p. 7364, line 6: I suggest specifying the pore size for the dialysis samplers.

In the Materials and Methods section the following information has been added:

[To document the geochemical conditions within the upper 30 cm of the sediment, we used two in-situ dialysis samplers (Hesslein, 1976) each with 14 chambers and a vertical resolution of 4 cm.] *The samplers were filled with deionised water and covered by a 0.2 µm membrane filter (Gelman<sup>®</sup> HT 200 tuffryn). To remove oxygen from the chamber water the samplers were degassed with nitrogen for 24 h and subsequently [deployed at the deepest site in the lake for 20 d in September 2013 during thermal stratification.]*

p. 7365, line 16: Would any of the dissolved Fe in the porewater samples be associated with organically-complexed Fe?

We cannot exclude that to some extent dissolved Fe is organically-complexed. However, the measured DOC concentrations in the water column of the lake (5-7 mgL<sup>-1</sup>) in combination with the complexation constants we used for the thermodynamic calculations (see Steinmann and Shotyk (1997)) showed the association of Fe<sup>2+</sup> with organic compounds to be insignificant. Even if DOC concentrations in the pore water of the sediment were by a factor of 5 higher than in the water column this would not have a significant effect on the activity of Fe<sup>2+</sup>.

p. 7376, line 27: Attributing the spherical shape of the vivianite crystals to pore voids is strange, or perhaps worded confusingly. Would pore voids be expected to be spherical? Wouldn't the shape of the crystal be more strongly affected by the regime of precipitation, e.g. slow near-equilibrium growth vs. fast disequilibrium precipitation, perhaps catalyzed by some surface?

Maybe this sentence is worded confusingly and the content is not clear. We want to point out, that the structure of the sediment matrix and the correspondent properties might have a significant influence on crystal growth. Pore voids could act as reaction chambers and hydrophobic, carbon-rich fibres, which form a network of walls could catalyse the growth of

seed crystals within these voids. We rephrased this sentence as follows:

[Through the activity of bacteria, cell-mediated microenvironments within the sediment matrix may evolve, sustaining vivianite-supersaturation during crystal growth, even on a small scale (Cosmidis et al., 2014).] *Hydrophobic, negatively charged, carbon-rich fibres which build up a structure of walls within the sediment may thereby serve as crystallisation sites for seed crystals (Zelibor et al., 1988).*

## References

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