

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)-PO₄). Based upon these results, aerobic handling of sediment neither alters vivianite significantly (except for the colour change and the correspondent surface oxidation of Fe²⁺) 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_2 and FeS phases.

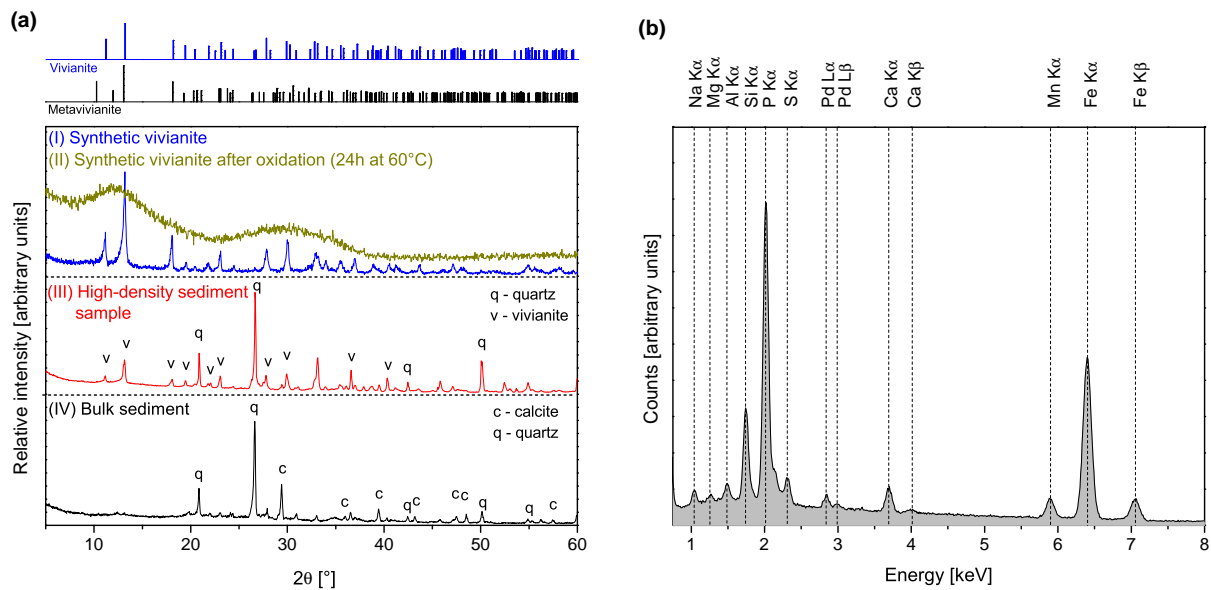


Fig. 4. (a) XRD patterns of (I) synthetic vivianite, (II) synthetic vivianite after oxidation at 60°C for 24 h, (III) high-density sample, and (IV) bulk sediment. Characteristic reflexes of vivianite could only be observed after heavy-liquid separation in the high density sample (II). The line patterns 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 lose 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_2 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® 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⁻¹) in combination with the complexation constants we used for the thermodynamic calculations (see Steinmann and Shotyk (1997)) showed the association of Fe²⁺ 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 Fe²⁺.

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 (Zeliber et al., 1988).*

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Reply to T. Jilbert

We like to thank T. Jilbert for his valuable 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 [].

By presenting an innovative new method for isolating and identifying vivianite nodules in sediments, the study of Rothe et al. may become a significant contribution in this field. There has been a flurry of recent papers investigating Fe (II) phosphate precipitation in shallow-sediment settings (e.g. Jilbert and Slomp, GCA 107, 2013; Cosmidis et al., GCA 126, 2014; Hsu et al., JAES 29, 2014), each of which has come up against the same challenges with respect to direct identification and quantification of P-bearing minerals in sediments.

The method is simple and effective at isolating nodules in the studied sediments, and potentially of wider applicability in the future, so I commend the authors for these advances. However I believe that the approach as outlined here contains some weaknesses, particularly with regards to quantification of vivianite concentrations. Also, despite its obvious success in the present study, I am unsure about the suitability of the method in all vivianite-bearing sediments. I would like to see the authors address these issues in their discussion, if possible with some extra supporting data.

Major comments

The density separation method used to pre-enrich the samples for vivianite identification may also pre-enrich other P-bearing minerals, as acknowledged by the authors on page 7372. Furthermore, the paramagnetic susceptibility of the high-density samples may be partly attributed to FeS_x, as acknowledged on page 7373. Hence, both the chemical and paramagnetic susceptibility analyses on the high-density samples may potentially overestimate the vivianite concentration, yet no quantification of these errors is attempted. I think this issue is crucial for the study, and needs to be improved.

We agree that a quantification of potential overestimation of vivianite content in high-density samples is missing. We accounted for the FeS_x attribution to paramagnetic susceptibility in the revised version of the manuscript (see details below).

If I understand correctly, bulk sediment chemical analysis was performed on the high-density samples, meaning that it should be possible to estimate the FeS_x concentration in order to calculate its effect on the paramagnetism.

We have included this correction and show that the estimated vivianite contents from FeS-corrected paramagnetic susceptibility still match decently with the vivianite contents estimated from chemical digestion. In the results section we have added and rephrased the following paragraph:

[Magnetic hysteresis measurements showed that in comparison to bulk sediment, the high-density samples were enriched with paramagnetica such as vivianite and iron sulfides (FeS_x) (Fig. 5a). Both bulk sediment and high-density samples contained ferrimagnetic material, most probably magnetite, recognized by the opening of the hysteresis loops.]
The vivianite content ($c_{\text{vivianite}}$ [weight as % of total]) in high-density samples was estimated by comparing the measured paramagnetic mass specific susceptibility of a high-density sample (MS_{sample} [m³ kg⁻¹]) with the value given for vivianite, of $MS_{\text{vivianite}} = 1.05 \times 10^{-6}$ m³ kg⁻¹ (Minyuk et al., 2013). The MS_{sample} values were calculated from the slope of the linear

increasing part of the hysteresis loops after magnetic saturation of ferrimagnetic minerals. The relative vivianite content in a high-density sample is then given as follows:

$$c_{\text{vivianite}} = \frac{MS_{\text{sample}}}{MS_{\text{vivianite}}} \times 100. \quad (1)$$

This calculation is valid assuming that: (1) the contribution of diamagnetica, such as calcium carbonate and quartz, to the overall measured magnetic susceptibility is small, and (2) vivianite is the only paramagnetic material present in the high-density samples. Our MS_{sample} values ranged from 1.7×10^{-7} to $3.6 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$, which is equivalent to a relative vivianite content of 22 to 48 weight as % of total. These values exceeded the maximum vivianite content based upon the amount of P present in the high-density samples (Fig. 5b). To correct MS_{sample} for the contribution of paramagnetic FeS_x , we assumed all sulphur (see Table 1) to be present as FeS in the high-density samples. Accordingly, high-density samples contained between 4 and 21 weight as % of total FeS. Assuming a paramagnetic mass specific susceptibility of FeS, of $MS_{\text{FeS}} = 1.54 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$ (Lide, 2004), equation (1) can be re-written as follows:

$$\begin{aligned} c_{\text{vivianite}} &= \frac{(MS_{\text{sample}} - MS_{\text{sample, FeS}})}{MS_{\text{vivianite}}} \times 100 \\ &= \frac{(MS_{\text{sample}} - (MS_{\text{FeS}} \times c_{\text{FeS}}))}{MS_{\text{vivianite}}} \times 100, \end{aligned} \quad (2)$$

where $MS_{\text{sample, FeS}}$ [$\text{m}^3 \text{ kg}^{-1}$] is the contribution of paramagnetic FeS to the measured mass specific susceptibility and c_{FeS} is the content of FeS [weight as % of total] in a high-density sample.

The FeS-corrected vivianite content in high-density samples ranged between 13 and 33 weight as % of total. These values were, except for sample H5, 1 to 15% lower than the vivianite content derived from chemical digestion (Fig. 5b).

[Relating the vivianite content in the high-density samples, calculated from chemical digestion, to the equivalent amount in bulk sediment, we were able to assess the significance of vivianite formation for the retention of P in the sediment.]

As we were aware of the fact that chemical digestion potentially overestimates the vivianite content in the high-density samples we performed magnetic hysteresis measurements. These measurements are based upon a completely different, independent approach (magnetic characteristics vs. elemental analysis) to estimate the vivianite content. Because of the fact that the relative changes in vivianite content between independent samples are in good agreement between both methods this clearly supports that the majority of phosphorus in the high-density samples is vivianite-bound P. In other words: The phosphorus content (from chemical digestion) and the paramagnetic susceptibility of high-density samples are highly correlated, even after the FeS correction. This is because paramagnetic vivianite accounts for the overall majority of phosphorus present in the high-density samples. When correcting the paramagnetic susceptibility data, it is important to keep in mind that the strength of correction highly depends on the value of paramagnetic susceptibility of FeS to be chosen. Tabled values for FeS and FeS_2 range significantly - more than one order of magnitude. However, this would only change the absolute level of vivianite content in samples but variations between different samples would be still in good agreement with data from chemical digestion. In the disussion part of the manuscript we have added the following paragraph:

[However, our results from magnetic susceptibility measurements support the assumption that the amount of P analysed in the high-density samples could mainly be attributed to

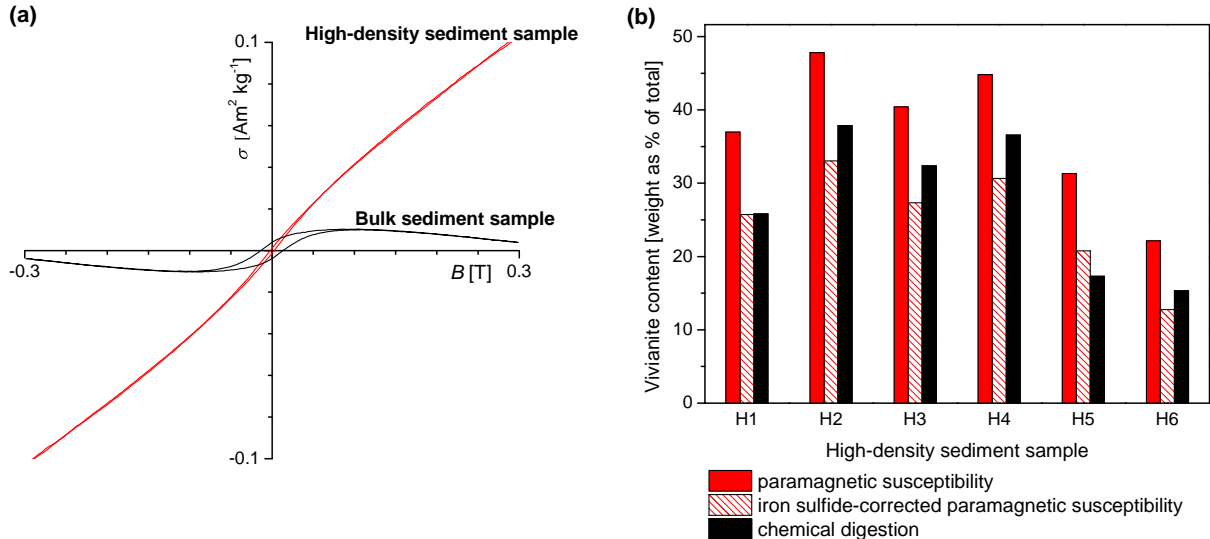


Fig. 5. (a) Magnetization σ [A m² kg⁻¹] versus magnetic field B [T], peak value $B = 0.3$ T of a high-density sample, and a bulk sediment sample from 10 cm sediment depth. The positive slope of the high-density sample at higher magnetic fields indicates enrichment with paramagnetic material after heavy-liquid separation. (b) Variations in vivianite content (expressed as % weight of the sample) in each of six high-density samples, based upon paramagnetic susceptibility, iron sulfide-corrected paramagnetic susceptibility and chemical digestion.

vivianite-bound P.] *Provided that the the weakening of the measured positive magnetisation due to the presence of diamagnetic Si and Ca compounds is small, the vivianite content can be determined from paramagnetic susceptibility. This assumption is valid, since the values of the diamagnetic mass specific susceptibility of SiO₂ and CaCO₃ are more than two orders of magnitude smaller than that of vivianite (Lide, 2004). Even if high-density samples contained 3-5 times more diamagnetic SiO₂ and CaCO₃ than vivianite, the correspondent weakening of the positive magnetisation was negligible. The contribution of paramagnetic FeS_x to the measured positive magnetisation of high-density samples was significant (Fig. 5b) when assuming all sulphur to be present as FeS. For the susceptibility correction we used the MS_{FeS} value given by Lide (2004). The FeS-correction could account for the overestimation of the vivianite content derived from uncorrected magnetic susceptibility data. The FeS-corrected vivianite contents were, except for one sample, lower than values derived from chemical digestion. However, it is important to note, that the relative changes in vivianite content between different high-density samples were determined similarly by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods (Fig. 5b). Considering the range of a factor of two for the mass specific magnetic susceptibility of vivianite (Minyuk et al., 2013), the vivianite contents determined by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods match acceptably.*

[Furthermore, a high-density sample from 35 cm sediment depth (data not shown), containing no vivianite nodules, demonstrated a negative susceptibility at higher magnetic fields, indicative for a majority of diamagnetic material present in the high-density sample.]

A potential overestimation of the vivianite content in the high-density samples may ultimately be compensated by an underestimation through the application of the sieving protocol i.e. small (< 80 μ m) vivianite nodules are missed.

If not attempted already, I would also urge the authors to perform sequential extractions to define the speciation of P, both in the high-density samples

and in the raw sediments (e.g. the SEDEX scheme; Ruttenberg, L&O 37, 1992). Although vivianite can not be isolated from Fe-oxide bound P by this scheme, the combined concentration of CDB-soluble P would give an upper limit to the potential concentration of vivianite.

As suggested, we have performed sequential extractions of the synthetic vivianite powder using the first two steps of the Ruttenberg scheme. However, the results indicate that only about 16 % of the phosphorus bound in vivianite is extracted in the CDB-extraction step (after the first step with $MgCl_2$ -solution less than 0.1 %). The combined concentration of CDB-soluble P would therefore heavily underestimate the potential content of vivianite in the high-density samples even if naturally formed crystals might have a higher solubility than the synthetic vivianite. It seems, that the extraction characteristics of vivianite are not that clear as Nembrini et al. (1983) reported. Interestingly, the blue vivianite powder turned white during the CDB-extraction step and subsequently turned blue again after adding the $MgCl_2$ -solution. To our understanding, the reducing conditions of the CDB-solution reduced the partly oxidised vivianite but did not lead to a significant dissolution of the mineral because vivianite is a Fe(II)-phosphate. The functioning of citrate as a complexing agent for iron however, caused a partial extraction of phosphorus from the mineral. After the addition of the washing solution $MgCl_2$ oxidised conditions are introduced and the remaining vivianite turned blue again.

Moreover, we performed sequential extractions according to the scheme by Psenner et al. (1984) for bulk sediment, high-density samples (sediment depths 0-10 cm, 11-20 cm, 21-30 cm) and the synthetic vivianite powder. Phosphorus from synthetic vivianite was extracted during step II and step III of the procedure: 14 % of total P was extracted in the Bicarbonate-Dithionite solution (represents the redox sensitive-bound P) and 86 % in the NaOH-solution (represents metal-bound phosphorus). There was no single extraction step where all vivianite-bound P is extracted at once. In bulk sediments the combined P concentrations of step II and step III made up 80 % of total P. The remainder was represented by loosely sorbed-P (step I: NH_4Cl), organically-bound P (step IV: NaOH-NRP) and carbonate-bound P (step V: HCl). In high-density samples, the combined concentrations of extraction steps II and III made up 90 to 95 % of total P, whereas step III represented 70 % of total P. The P content in extraction steps representing organically-bound P was less than 1 %. The results support the general assumption that the overall majority of P determined in the high-density samples (by chemical digestion) is vivianite-bound. However, vivianite is extracted during two extraction steps. This fact significantly weakens the sequential extraction approach when trying to quantify the vivianite-bound P. There is no improvement regarding the determination of the upper limit of vivianite-bound P in high-density samples when using the sequential extraction compared to chemical digestion.

With regards to the method's applicability to other sediments: In our recent study of Baltic Sea sediments (Jilbert and Slomp, GCA 107, 2013) we found abundant Fe-P enrichments of 10 μm diameter which we interpreted as vivianite. These would be "missed" by the method presented here, due to the sieving protocol collecting only the $> 80 \mu m$ size fraction. Can the authors give any further information on their selection of sieve sizes? Would the method still work if nodules were not limited to a particular size class and the sieving step was removed?

The sieving step was applied in order to maximize the enrichment of vivianite nodules in high-density samples, and at the same time minimize the relative amount of quartz and calcium carbonate phases. Inspection with a reflected light microscope of size classes smaller than 80 μm revealed a majority of quartz and carbonate phases, and to a much lesser extent also small vivianite nodules. We decided to apply this sieving step as the advantage of the higher enrichment (both magnetic hysteresis measurements and chemical digestion data benefit from this) of vivianite nodules compensated for the disadvantage of missing a minor

amount of small-sized vivianite (which have an even smaller volume compared to the larger nodules). Our method is reliable in separating and concentrating vivianite nodules in the high-density fraction even if there is no sieving applied and nodules are significantly smaller than $80\ \mu\text{m}$. As an example, Fig. A shows a reflected-light microscopic image of a high-density sample from another lake - Lake Arendsee, where we did not apply a sieving step. Initial inspection of freeze-dried bulk sediment from this lake revealed the existence of many small-sized vivianite nodules. These small sized nodules are captured by the density separation method as shown in Fig. A.

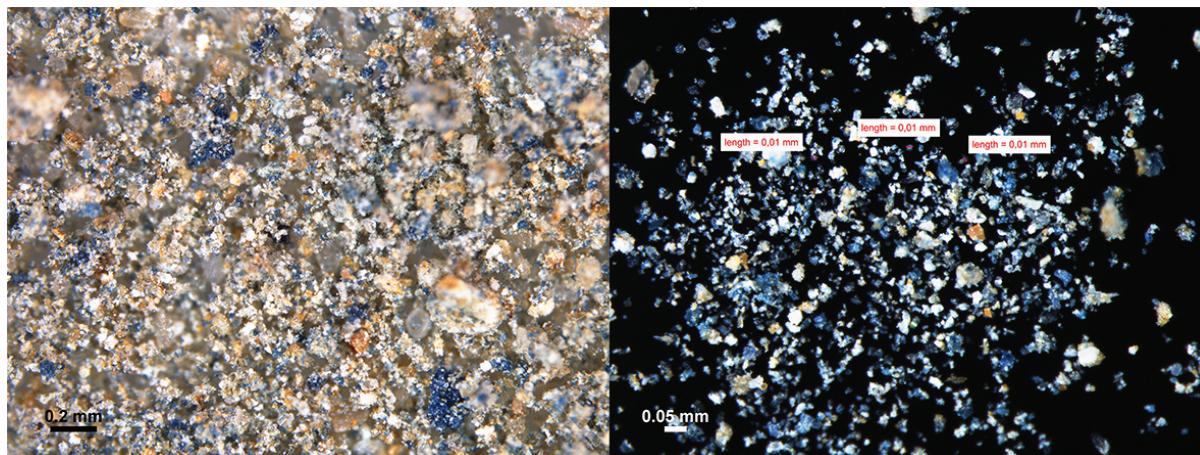


Fig. A. Reflected-light microscopic images of a high-density sample from Lake Arendsee. A sieving step was not applied. Many small-sized ($< 40\ \mu\text{m}$) vivianite nodules (blue appearance) are present.

We have added the following in the discussion part:

[Although the sediment preparation method we used neglected vivianite nodules smaller than $80\ \mu\text{m}$ in diameter, the amount of vivianite present in the high-density samples serve as a reliable proxy for the overall vivianite content in the sediment.] *The sieving step was applied in order to maximize the enrichment of vivianite nodules in high-density samples and minimize the relative amount of small sized ($< 80\ \mu\text{m}$) Si and Ca compounds at the same time.* [Our results suggest a homogeneous vivianite content in the upper 20 cm of the sediment.]

Minor comments

P 7361: Line 20-25: Consider rephrasing: what does ‘‘important’’ mean in this context? (you go on to say that vivianite concentrations are very low and it is hard to measure)

We wanted to point out vivianite as one specific candidate mineral, which is known to be formed in anoxic, iron-rich sediments and is therefore important in binding phosphorus during early diagenesis via secondary mineral formation. ‘‘important’’ has been replaced by ‘‘specific’’.

[One] *specific* [phosphate mineral which forms during sediment diagenesis is ...]

P 7362: Line 9-12: Consider rephrasing: ‘‘Vivianite crystal aggregates found’’ sounds like you are referring to the results of the present study.

The sentence has been rephrased as follows:

Literature reported vivianite crystal aggregates to be needle-shaped or spherical with diameters ranging between a few micrometres to several centimetres.

P 7363: Section 2.1 contains some errors, e.g. the use of ‘und’ instead of ‘and’, a misplaced comma before ‘Chl a’. Also, ‘have been increased’ can be replaced by ‘are higher’.

Thank you. All these errors have been corrected.

P 7368: Line 10: Spelling of ‘indices’.

Has been corrected.

P 7368: Line 15: My reading of Fig. 2 is that Fe²⁺ activity increases with increasing sediment depth, i.e. deeper in the sediments. The phrasing of this sentence suggests the opposite.

Thank you for this hint. “decreased” has been replaced by “increased”.

[At the SWI, the supersaturation of vivianite was about one order of magnitude lower than in subjacent pore fluids (4–30 cm), and 4 cm above the SWI the supersaturation was close to equilibrium.] [There was a sharp] *increase* [in the activity of Fe²⁺ ($a_{\text{Fe}^{2+}}$) with sediment depth, as shown by plotting $a_{\text{Fe}^{2+}}$ against that of $a_{\text{PO}_4^{3-}}$ (Fig. 2).]

P 7368: Line 23–28: Maybe give some background references to explain why you considered the potential effect of DOC.

We have added the following reference here:

[To determine the effect of dissolved organic carbon (DOC) on the output of the equilibrium calculations, and in particular on $a_{\text{Fe}^{2+}}$] (*see e.g., Reuter and Perdue, 1977*), [we performed equilibrium calculations with DOC concentrations ranging from ...]

P 7370: Line 4: Misplaced comma after ‘Both’

Has been corrected.

P 7370: Line 7–15: This calculation may be altered if you include an estimate of the Fe_x contribution. In any case, the calculation needs to be explained more clearly by means of an equation, and explicit statements about assumptions (currently these are only addressed in the discussion).

We addressed this issue in the revised version of the manuscript. Please, see the detailed answer above (major comment).

P 7371: Line 6: Avoid the term ‘burial’. ‘Concentration’ is better because you do not have any information about sedimentation rates.

We have avoided the term “burial” and used the term “content” instead.

P 7371: Line 13–18: This is a very interesting part of the study. It seems that vivianite does not lose its XRD pattern upon oxygen exposure. Is this because the nodules do not oxidize significantly, as the authors suggest, or because the oxidation product has a similar XRD pattern to the pure mineral? This is hard to discern without more information about the standard. How was this synthesized/preserved? What was its appearance? Ideally, we would like

to see oxidized and pristine vivianite XRD patterns for comparison. Are these available?

We agree that information about the synthetic vivianite is missing but is crucial for interpretation of results. In the Material and Methods section the following sentence has been added:

[Mineral composition of sediment was characterized by powder X-ray diffraction (XRD) with a Bruker AXS D8 diffractometer equipped with Cu-K α -radiation and a Sol-X solid state detector.] *Synthetic, slightly oxidised (blue appearance) vivianite powder (Dr. Paul Lohmann GmbH KG) served as an internal XRD-standard.* [The XRD-patterns were measured between 5 and ...]

In order to clarify which effect oxygen exposure has on the XRD-pattern of vivianite, we have added a XRD-pattern of heated (60 °C for 24 h) synthetic vivianite powder to Figure 4a and showed XRD-reference line-pattern from the Crystallography Open Database (COD) of vivianite and the slightly oxidised vivianite “metavivianite”. According to these reference patterns does the crystal structure of vivianite not significantly change upon oxygen exposure but if the mineral is heated at 60°C. It then changes its colour to orange-brown and alters to a XRD-amorphous form (mostly likely Fe(III)–PO $_4$). The comparison between peak intensities and positions of the high-density sample, the bluish synthetic vivianite powder and the reference pattern of vivianite and metavivianite even shows higher coincidence with the vivianite reference pattern than with the metavivianite pattern. We therefore consider the blue vivianite nodules to be surface oxidised only and detectable via XRD upon exposure to air. Nriagu (1972) noted that the ratio of Fe $^{3+}$:Fe $^{2+}$ of blue vivianite is 0.05 and that this preserved form of vivianite is almost indefinitely stable in the laboratory. In the results section we have added the following paragraph:

[However, the XRD-reflexes characteristic for vivianite could not be identified from bulk sediment samples.] *The diffraction pattern of synthetic vivianite powder (blue appearance) was in coincidence with the vivianite reference pattern which use data from the Crystallography Open Database (COD). The synthetic vivianite powder changed its colour from dark blue to orange-brown and lost its characteristic diffraction pattern upon heating at 60 °C for 24 h (Fig. 4a).*

[Examination of sediment with a reflected-light microscope revealed that dark blue nodules were present ...]

We have discussed these results and the aerobic handling of sediment samples in general in the discussion section 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 lose 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

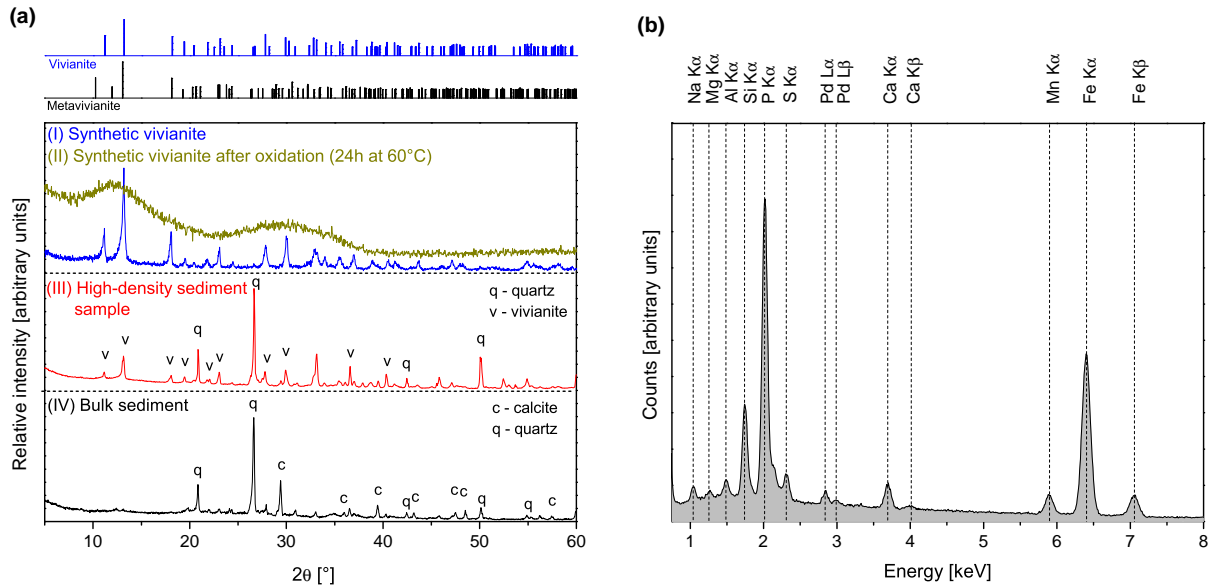


Fig. 4. (a) XRD patterns of (I) synthetic vivianite, (II) synthetic vivianite after oxidation at 60°C for 24 h, (III) high-density sample, and (IV) bulk sediment. Characteristic reflexes of vivianite could only be observed after heavy-liquid separation in the high-density sample (II). The line patterns 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.

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_2 and FeS might have been oxidised and altered to amorphous phases (Hjorth, 2004).*

P 7375: Line 12: Remove comma after ‘‘of’’.

Has been corrected.

P 7376: Line 21: Replace ‘‘these’’ with ‘‘this’’.

Has been corrected.

P 7376: Line 28: Spelling of ‘‘reported’’.

Has been corrected.

P 7376: Line 27-29. I agree with Anonymous Reviewer #1 that it is strange to attribute the spherical shape of the nodules to the shape of the pores. More likely, the crystals make space within the unconsolidated sediments as they grow. Remember that the mean grain size (and hence pore size) is much smaller than the size of these nodules. See for example the very similar nodules in Fig. 4 in Hsu et al. JAES 29, 2014).

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).*

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Reply to referee#3

We like to thank referee#3 for his/her constructive 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 [].

The authors provide convincing evidence of recent and ongoing vivianite formation in Lake Gross-Glienicke (upper sediment layers of the deepest site of 11 m) by a suite of techniques including a novel approach of combining high density centrifugation with XRD and microscopy. Further, they suggest that iron addition (to bind P) some 20 years ago is the trigger for this mineral formation. This argument is also convincing because no (or very little) vivianite is detected below 23 cm depth (the depth where Fe concentration peaks) even if porewater concentrations of SRP, Fe²⁺, and H⁺ suggest supersaturation in all 30 sediment depth. Finally, the authors estimate the contribution of vivianite to the burial flux of P to be 40% and by mentioning that diatom frustules are seen in vivianite crystals they argue convincingly that the vivianite is an authigenic mineral.

To my knowledge this is the first time that such an estimate has been provided for recent lake sediments. In all, this is a very interesting paper that provides important new knowledge on P diagenesis in lake sediments. The paper is definitely qualified for publishing.

I could not figure out how the number of 40% vivianite contribution to total P-burial was reached. Deeming from Fig. 6a I would say that the number was far less because the bars contribute at maximum 1 mg P g⁻¹ dw of 4 mg P g⁻¹ dw. The calculation of 40% needs further explanation.

Vivianite formation accounts for about 20 % of total P in the upper 20 cm of the sediment. However, we consider the iron application to be the trigger for this mineral formation and we therefore state that 40 % of the additional burial of P, which has been accompanied with the iron supplement, can be explained by vivianite formation (prior to the in-lake measure: total P = 1.5 mg g⁻¹; after the in-lake measure: total P = 4 mg g⁻¹). We have rephrased the following sentence in the results section of the revised version of the manuscript:

[Vivianite formation significantly contributed to P retention in Lake Groß-Glienicke, accounting for 20 % of the total sedimentary P in the upper 20 cm of the sediment (Fig. 6).] *Assuming an increase in total sedimentary P due to the artificial application of Fe during lake restoration of 2.5 mg g⁻¹ in the upper 20 cm of the sediment in comparison to sediment layers deposited prior to the in-lake measure, vivianite formation could explain about 40 % of this increase.*[The remaining 60 % of increase in total sedimentary P...]

In the conclusions of the revised version of the manuscript we rephrased the following sentence:

[At our study site at Lake Groß-Glienicke, formation of vivianite was triggered by an artificial Fe supplement, and explains] *20 % of total P in sediment layers deposited* [after the in-lake measure.]

Depth profiles (in bulk sediment as well as in high-density sediment) of several elements are provided and used well in the discussion, however, I missed comments on:

1) Why is Ca concentration decreasing after the iron addition? Less precipitation from surface water? Is the majority of Ca present as CaCO₃?

2) Why is S concentration increased after Fe addition? Was (reduced) S in surplus to Fe in the burial flux before Fe addition?

The course of elemental profiles in the sediment is determined by multiple factors and interpretation is difficult. There is no definite answer here particularly because in course of the lake restoration the inflow regime of the lake was changed, too. Lake Groß-Glienicke was a highly eutrophic lake and massive algal blooms occurred regularly. These algal blooms were accompanied with high pH-values (> 10) (Deneke and Mischke, 1995). After the in-lake measure primary productivity decreased strongly. The decrease in Ca content in the sediment is therefore likely a result of less precipitation from surface water. X-ray diffraction pattern of bulk sediment from various depths showed distinct peaks of calcite suggesting a significant amount of CaCO₃ to be present in the sediment.

The increase in sulphur content after the in-lake measure might be a result of intensified FeS_x formation after the supplement of iron. Sediments of Lake Groß-Glienicke were characterized by a low iron content and the hypolimnion was completely anoxic prior to the in-lake measure. It is likely that free sulfides were present in the hypolimnion prior to the in-lake measure and that the supplement of iron led to intense precipitation of FeS_x. However, the increase of sulphur after the iron supplement might just be a result of the change in elemental ratios and not a change in the absolute burial flux of sulphur.

3) Has the redox state of the sediment changed since the iron addition? To which extent is oxidized Fe being buried before and after the Fe addition? Maybe Mn should also be included in Fig. 6 because a general higher concentration could be an indicator of a more oxidized sediment.

Nowadays there is still intense sulfate reduction taking place close to the sediment-water interface (SWI) and in the upper centimetres of the sediment (see Figure 1 in the manuscript). However, no free sulfides exist due to the surplus of mobile Fe and the relatively low primary production. The surplus of iron may also suppress the production of methane which likely has occurred during hypertrophic conditions prior to the in-lake measure. Due to the iron addition and the corresponding drop in primary productivity redox conditions changed in the hypolimnion of the lake; it has become oxic again. Additionally there has been an artificial hypolimnetic aeration after the iron supplement, however, the aerators have been shut down several years ago. The oxic hypolimnion led to a change in redox conditions at the sediment surface, it has become more oxidised. Now the oxicline is situated directly at or close to the SWI in the hypolimnion (depending on the time of the year). These conditions led to an intensified re-precipitation of iron and manganese. The course of both elements in the sediment is in close correspondence to each other (Figure 6). We suppose that a significant amount of iron is buried in its ferric form now. Sequential P extractions of bulk sediment samples revealed 20 % of "redox-sensitive"-bound P in the upper 20 cm of the sediment. This P can mainly be attributed to ferric iron phases. Both ferric iron and Mn(IV) have resisted reductive dissolution in the sediment because microbial mediated reduction may be carbon limited.

In the revised version of the manuscript we have included Mn in Figure 6.

In the results section of the revised version of the manuscript we added the following sentence:

[Above this, in the upper 23 cm of the sediment, the Fe and P content were on average 2.4 and 3.1 times higher than in the deeper, non-vivianite bearing sediment zone (24–30cm sediment

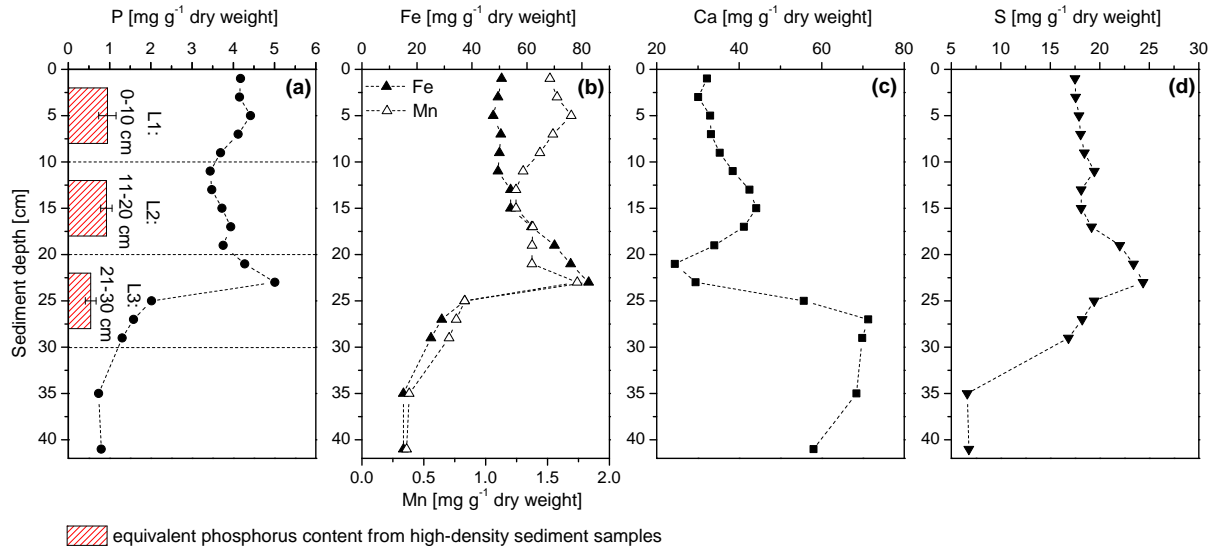


Fig. 6. Sediment stratigraphs of (a) phosphorus (P), (b) iron (Fe) and manganese (Mn), (c) calcium (Ca) and (d) sulphur (S) of Lake Groß-Glienicke from May 2013. Bar charts in graph (a) represent the equivalent P content analysed in the high-density samples from depth layers L1, L2 and L3. Error bars denote \pm SD, $n = 5$.

depth)]. *The course of manganese resembled that of Fe but showed an increasing trend above 12 cm sediment depth (Fig. 6b).* [Calcium concentration showed a reverse trend, ...]

In the discussion section we rephrased the following sentences:

[The Fe] *and Mn* [content is elevated throughout the upper 23 cm of the sediment (Fig. 6b), because there has been a continuous cycling of] *both elements between their dissolved and particulate forms* [at the SWI after the Fe application.] *This feature reflects the change in redox conditions in the hypolimnion and at the SWI after the Fe supplement, i.e. the sediment surface has become more oxidised.* [A high reactive Fe(II) concentration led in turn to the formation of vivianite...]

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List of changes made in the revised version of the manuscript

p. 7361, line 7: we added a reference here

p. 7361, line 17: we added a reference here

p. 7361, line 20: “important” has been replaced by “specific”

p. 7362, line 9-12: this sentence has been rephrased:

Literature reported vivianite crystal aggregates to be needle-shaped or spherical with diameters ranging between a few micrometres to several centimetres.

p. 7364, line 5-8: we added the following information here:

[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[®] 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. 7366, line 6: we added the following sentence here:

Synthetic, slightly oxidised (blue appearance) vivianite powder (Dr. Paul Lohmann GmbH KG) served as an internal XRD-standard.

p. 7369, line 5: we added the following paragraph here:

The diffraction pattern of synthetic vivianite powder (blue appearance) was in coincidence with the vivianite reference pattern which use data from the Crystallography Open Database (COD). The synthetic vivianite powder changed its colour from dark blue to orange-brown and lost its characteristic diffraction pattern upon heating at 60 °C for 24 h (Fig. 4a).

p. 7370, line 3-16: we rephrased this paragraph:

[Magnetic hysteresis measurements showed that in comparison to bulk sediment, the high-density samples were enriched with paramagnetica such as vivianite and iron sulfides (FeS_x) (Fig. 5a). Both bulk sediment and high-density samples contained ferrimagnetic material, most probably magnetite, recognized by the opening of the hysteresis loops.]

The vivianite content ($c_{\text{vivianite}}$ [weight as % of total]) in high-density samples was estimated by comparing the measured paramagnetic mass specific susceptibility of a high-density sample (MS_{sample} [$\text{m}^3 \text{kg}^{-1}$]) with the value given for vivianite, of $MS_{\text{vivianite}} = 1.05 \times 10^{-6} \text{ m}^3 \text{kg}^{-1}$ (Minyuk et al., 2013). The MS_{sample} values were calculated from the slope of the linear increasing part of the hysteresis loops after magnetic saturation of ferrimagnetic minerals. The relative vivianite content in a high-density sample is then given as follows:

$$c_{\text{vivianite}} = \frac{MS_{\text{sample}}}{MS_{\text{vivianite}}} \times 100. \quad (3)$$

This calculation is valid assuming that: (1) the contribution of diamagnetica, such as calcium carbonate and quartz, to the overall measured magnetic susceptibility is small, and (2) vivianite is the only paramagnetic material present in the high-density samples. Our MS_{sample} values ranged from 1.7×10^{-7} to $3.6 \times 10^{-7} \text{ m}^3 \text{kg}^{-1}$, which is equivalent to a relative vivianite content of 22 to 48 weight as % of total. Theses values exceeded the maximum vivianite content based upon the amount of

P present in the high-density samples (Fig. 5b). To correct MS_{sample} for the contribution of paramagnetic FeS_x , we assumed all sulphur (see Table 1) to be present as FeS in the high-density samples. Accordingly, high-density samples contained between 4 and 21 weight as % of total FeS. Assuming a paramagnetic mass specific susceptibility of FeS, of $MS_{FeS} = 1.54 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$ (Lide, 2004), equation (1) can be re-written as follows:

$$\begin{aligned} c_{\text{vivanite}} &= \frac{(MS_{\text{sample}} - MS_{\text{sample, FeS}})}{MS_{\text{vivanite}}} \times 100 \\ &= \frac{(MS_{\text{sample}} - (MS_{FeS} \times c_{FeS}))}{MS_{\text{vivanite}}} \times 100, \end{aligned} \quad (4)$$

where $MS_{\text{sample, FeS}} [\text{m}^3 \text{ kg}^{-1}]$ is the contribution of paramagnetic FeS to the measured mass specific susceptibility and c_{FeS} is the content of FeS [weight as % of total] in a high-density sample. The FeS-corrected vivianite content in high-density samples ranged between 13 and 33 weight as % of total. These values were, except for sample H5, 1 to 15% lower than the vivianite content derived from chemical digestion (Fig. 5b).

p. 7368, line 15: “decreased” has been replaced by “increased”

p. 7368, line 23-28: we added a reference here

p. 7371, line 6: we added the following sentence here:

The course of manganese resembled that of Fe but showed an increasing trend above 12 cm sediment depth (Fig. 6b).

p. 7371, line 6: “burial” has been replaced by “content”

p. 7371, line 14-19: we rephrased this paragraph:

[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 lose 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_2 and FeS might have been oxidised and altered to amorphous phases (Hjorth, 2004).*

p. 7372, line 30- p. 7373, line 16: we rephrased this paragraph:

Provided that the the weakening of the measured positive magnetisation due to the presence of diamagnetic Si and Ca compounds is small, the vivianite content can be determined from paramagnetic susceptibility. This assumption is valid, since the values of the diamagnetic mass specific susceptibility of SiO_2 and $CaCO_3$ are more than two orders of magnitude smaller than that of vivianite (Lide, 2004). Even if high-density samples contained 3-5 times more diamagnetic SiO_2 and $CaCO_3$ than vivianite, the correspondent weakening of the positive magnetisation was negligible. The contribution of paramagnetic FeS_x to the measured positive magnetisation of high-density samples was significant

(Fig. 5b) when assuming all sulphur to be present as FeS. For the susceptibility correction we used the MS_{FeS} value given by Lide (2004). The FeS-correction could account for the overestimation of the vivianite content derived from uncorrected magnetic susceptibility data. The FeS-corrected vivianite contents were, except for one sample, lower than values derived from chemical digestion. However, it is important to note, that the relative changes in vivianite content between different high-density samples were determined similarly by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods (Fig. 5b). Considering the range of a factor of two for the mass specific magnetic susceptibility of vivianite (Minyuk et al., 2013), the vivianite contents determined by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods match acceptably.

p. 7373, line 28: we added the following sentence here:

The sieving step was applied in order to maximize the enrichment of vivianite nodules in high-density samples and minimize the relative amount of small sized ($< 80 \mu\text{m}$) Si and Ca compounds at the same time.

p. 7373, line 31: we added the following sentence here:

Assuming an increase in total sedimentary P due to the artificial application of Fe during lake restoration of 2.5 mg g^{-1} in the upper 20 cm of the sediment in comparison to sediment layers deposited prior to the in-lake measure, vivianite formation could explain about 40 % of this increase.

p. 7376, line 7-9: we rephrased this sentence:

[The Fe] and Mn [content is elevated throughout the upper 23 cm of the sediment (Fig. 6b), because there has been a continuous cycling of] both elements between their dissolved and particulate forms [at the SWI after the Fe application.] This feature reflects the change in redox conditions in the hypolimnion and at the SWI after the Fe supplement, i.e. the sediment surface has become more oxidised.

p. 7376, line 27-29: we rephrased this sentence:

Hydrophic, 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).

p. 7377, line 11-13: we rephrased this sentence:

[At our study site at Lake Groß-Glienicke, formation of vivianite was triggered by an artificial Fe supplement, and explains] 20 % of total P in sediment layers deposited [after the in-lake measure.]

Figure 4a:

We added reference line patterns of vivianite and metavivianite which use data from the Crystallography Open Database. We included a XRD pattern of heated synthetic vivianite powder in the upper panel.

Figure 5b:

We included data derived from iron sulfide-corrected paramagnetic susceptibility.

Figure 6b:

We included the stratigraph of manganese.

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