

## 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 FeSx, 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 FeSx 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 FeSx 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

( $\text{FeS}_x$ ) (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 ( $MS_{\text{sample}}$  [ $\text{m}^3 \text{ kg}^{-1}$ ]) 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  $MS_{\text{sample}}$  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 diamagnetic, 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  $MS_{\text{sample}}$  values ranged from  $1.7 \times 10^{-7}$  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  $MS_{\text{sample}}$  for the contribution of paramagnetic  $\text{FeS}_x$ , we assumed all sulphur (see Table 1) to be present as  $\text{FeS}$  in the high-density samples. Accordingly, high-density samples contained between 4 and 21 weight as % of total  $\text{FeS}$ . Assuming a paramagnetic mass specific susceptibility of  $\text{FeS}$ , 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  $\text{FeS}$  to the measured mass specific susceptibility and  $c_{\text{FeS}}$  is the content of  $\text{FeS}$  [weight as % of total] in a high-density sample.

The  $\text{FeS}$ -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  $\text{FeS}$  correction. This is because paramagnetic vivianite

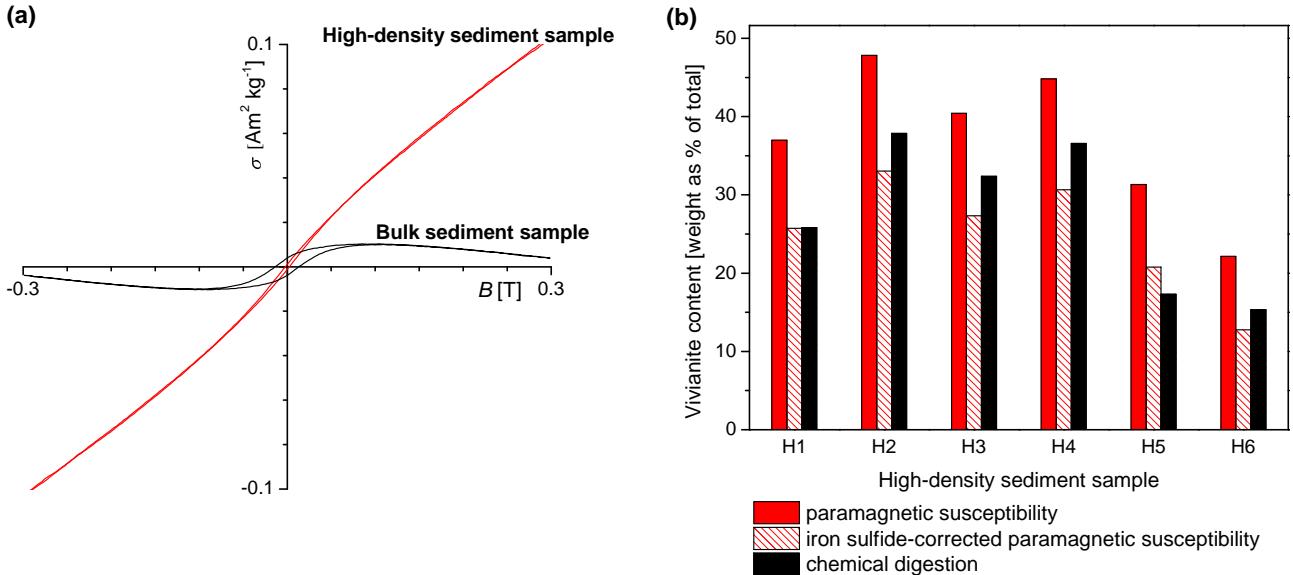


Fig. 5. (a) Magnetization  $\sigma$  [ $\text{Am}^2 \text{ kg}^{-1}$ ] versus magnetic field  $B$  [ T], peak value  $B = 0.3$  T of a high-density sample, and a bulk sediment sample from 10 cm sediment depth. The positive slope of the high-density sample at higher magnetic fields indicates enrichment 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.

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  $\text{FeS}$  to be chosen. Tabled values for  $\text{FeS}$  and  $\text{FeS}_2$  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 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  $\text{SiO}_2$  and  $\text{CaCO}_3$  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  $\text{SiO}_2$  and  $\text{CaCO}_3$  than vivianite, the correspondent weakening of the positive magnetisation was negligible. The contribution of paramagnetic  $\text{FeS}_x$  to the measured positive magnetisation of high-density samples was significant (Fig. 5b) when assuming all sulphur to be present as  $\text{FeS}$ . For the susceptibility correction we used the  $MS_{\text{FeS}}$  value given by Lide (2004). The  $\text{FeS}$ -correction could account for the overestimation of the vivianite content derived from uncorrected magnetic susceptibility data. The  $\text{FeS}$ -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  $\mu$ 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-sulution 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 extractions 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  $10 \mu\text{m}$  diameter which we interpreted as vivianite. These would be ‘‘missed’’ by the method presented here, due to the sieving protocol collecting only the  $> 80 \mu\text{m}$  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  $80 \mu\text{m}$  revealed a majority of quartz and carbonate phases, and to a much lesser extend 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.

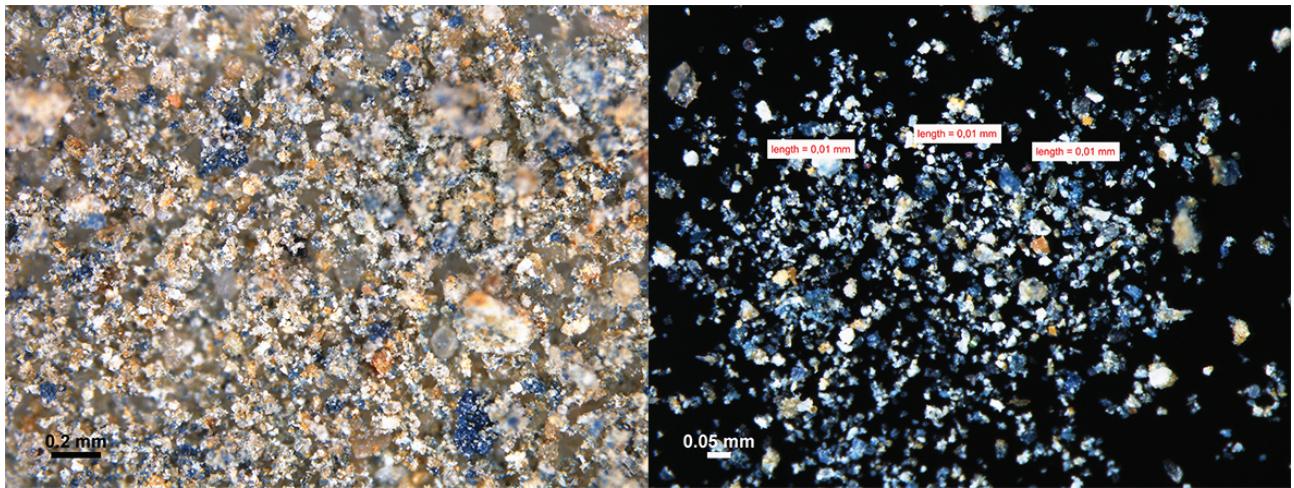


Fig. A. Reflected-light microscopic images of a high-density sample from Lake Arendsee. A sieving step was not applied. Many small-sized ( $< 40 \mu\text{m}$ ) vivianite nodules (blue appearance) are present.

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 Fe<sup>2+</sup> 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 Fe<sup>2+</sup> ( $a_{\text{Fe}^{2+}}$ ) 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 FeSx 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<sub>α</sub>-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<sub>4</sub>). 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<sup>3+</sup>:Fe<sup>2+</sup> 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*

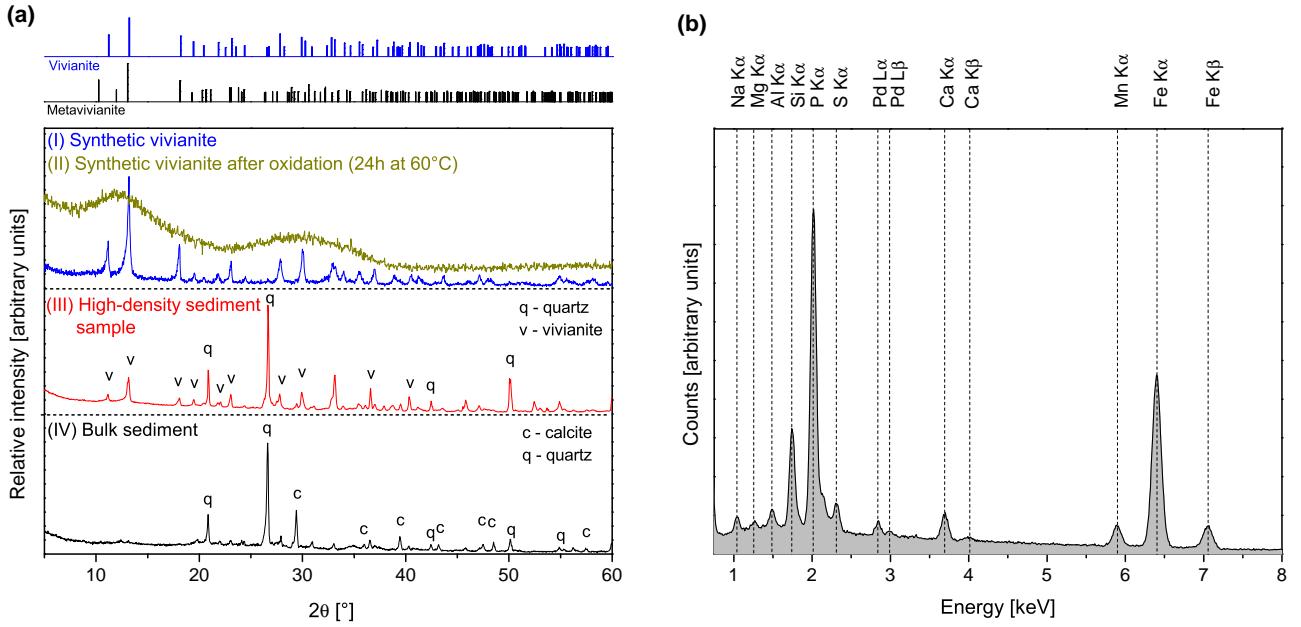


Fig. 4. (a) XRD patterns of (I) synthetic vivianite, (II) synthetic vivianite after oxidation at 60°C for 24 h, (III) high-density sample, and (IV) bulk sediment. Characteristic reflexes of vivianite could only be observed after heavy-liquid separation in the high-density sample (II). The line patterns 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-Glienicker. The correspondent atomic Fe:P ratio is 1.49. Note that elemental peaks of carbon and oxygen were omitted.

*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).*

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 porespaces. 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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