

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 CaCO_3 ?

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 CaCO_3 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.

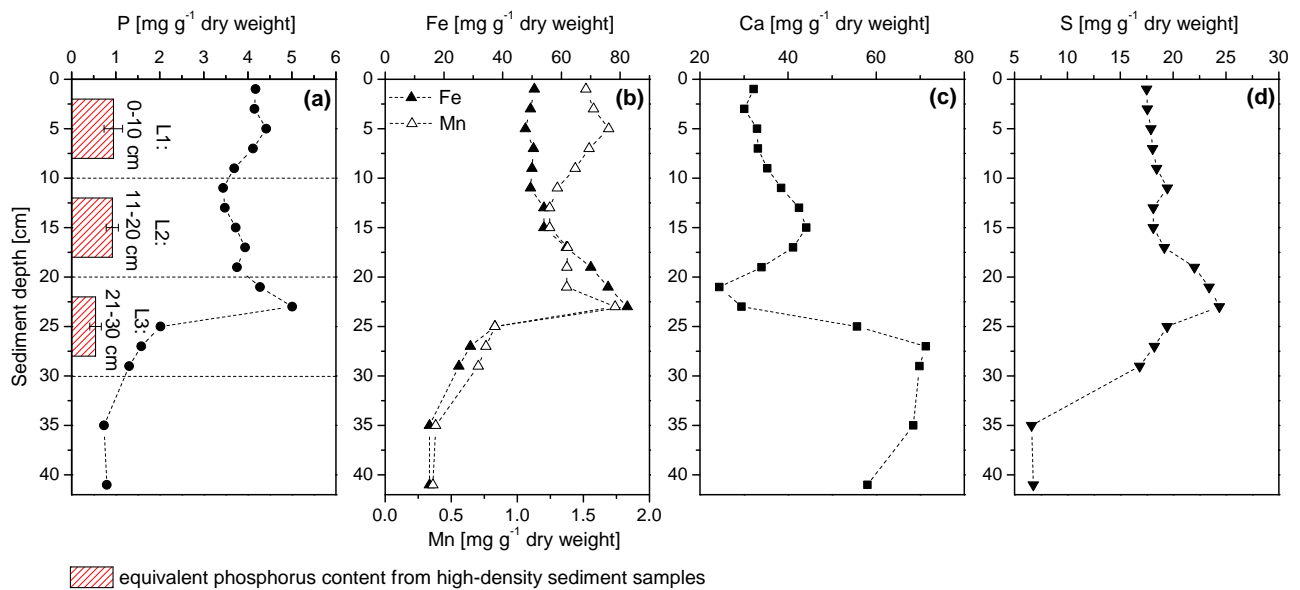


Fig. 6. Sediment stratigraphs of (a) phosphorus (P), (b) iron (Fe) and manganese (Mn), (c) calcium (Ca) and (d) sulphur (S) of Lake Groß-Glienicke from May 2013. Bar charts in graph (a) represent the equivalent P content analysed in the high-density samples from depth layers L1, L2 and L3. Error bars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

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 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...]

References

Deneke, R. and Mischke, U.: Welche Bedeutung haben Planktonuntersuchungen im Rahmen der Seentherapie? Fallbeispiel: Kombinierte hypolimnische Belüftung und Phosphatfällung im Groß-Glienicker See (Berlin),

in: Verfahren zur Sanierung und Restaurierung stehender Gewässer, edited by: Jaeger, D. and Koschel, R., Gustav Fischer Verlag, 226–238, 1995.