

Interactive comment on “Evidence for vivianite formation and its contribution to long-term phosphorus retention in a recent lake sediment: a novel analytical approach” by M. Rothe et al.

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Summary

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.

C2559

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. 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. 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 cannot 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.

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

C2560

'missed' by the method presented here, due to the sieving protocol collecting only the >80 μm 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?

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)

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

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'.

P 7368: Line 10: Spelling of 'indices'.

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

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

P 7370: Line 4: Misplaced comma after 'Both'

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).

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

C2561

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?

P 7375: Line 12: Remove comma after 'of'.

P 7376: Line 21: Replace 'these' with 'this'.

P 7376: Line 28: Spelling of 'reported'.

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).

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C2562