

Interactive comment on “Vivianite formation in methane-rich deep-sea sediments from the South China Sea” by Jiarui Liu et al.

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This manuscript by Liu and co-authors discusses the formation of vivianite in sediments below the SMTZ found in a core from the South China Sea. The manuscript is very well-written and structured, the results support the interpretation, and the evidence for vivianite in this depositional setting is compelling. The topic of the manuscript and the overall quality makes it suitable for publication in Biogeosciences, however, there are a number of issues that the authors need to resolve before the manuscript can be accepted. These issues mostly relate to (a) the description analytical methods and interpretation of the resulting data, (b) the interpretation of the observed geochemical profiles (in particular the suggested downward migration of the SMTZ) in the context of the wider depositional conditions, (c) the downcore record and formation of Ca-P, and

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(d) the implications the study might have for specific intervals of the geological past when oceans were anoxic, non-sulphidic (ferruginous).

I hope the authors will find my comment useful. Best regards, Christian März

Sampling of sediments: It is unclear from the text (Methods) how the core sections were processed after sectioning. They were transferred into cool storage. What happened next? Were the sections split on board and samples taken immediately? Were samples stored frozen and/or anoxic to avoid pyrite oxidation prior to freeze-drying? This is crucial for the determination of reactive Fe fractions. Sampling of pore waters: Were pore waters extracted using rhizons? Were they extracted from the closed core by drilling holes into the liner, or were they extracted from the split core surfaces? How long before pore water sampling were the sections split? This is crucial not only for methane and sulphate concentrations, but for any volatile and/or redox sensitive species, i.e., Fe²⁺, HS⁻, HPO₄²⁻. For example, pore water Fe²⁺ could precipitate as Fe (oxyhydr)oxides and adsorb pore water HPO₄²⁻.

Pore water data: In general, I am not sure if I trust the practise of inferring pore water geochemistry from neighbouring sites, especially since no further information is provided about these. How far away are these nearby sites, and were they affected by the same paleo-depositional processes as the study site? Are there distinct similarities in lithology, sedimentation rates etc that would warrant the “import” of pore water data from these sites? Some of this information can be extracted/inferred from Figure 2 but should be explained in the text as well. Also the methods of pore water sampling and data generation at these nearby sites should be explained.

SMTZ definition: From each of the nearby sites, there are only 1-2 methane data available just below the SMTZ. It should be highlighted in the text that (whether?) this is sufficient to define the SMTZ position. I would also shift the upper boundary of the SMTZ upwards, to the depth where the first methane-free sample was encountered.

Iron extraction: Please cite a reference that defines Fe phases extracted by an anoxic

0.5M HCL solution. I am not actually sure this extraction method has been well-calibrated using different Fe minerals.

Appropriate description of methods: Lots of data are shown (AVS, pyrite, S isotopes, Fe-bound P, Ca-P etc) that are not covered in the Methods section at all. Even if they were published before, a brief account of how these data were generated is required in this manuscript. Were the analyses conducted on splits of exactly the same samples, or nearby samples, or were samples taken at different times? I would also defer from making speculations about what certain data would look like if they had been generated (e.g., pore water HPO₄²⁻).

The Ca-P fraction: A lot of Ca-P is found below the SMTZ, more than Fe-bound P. This is not discussed sufficiently. Is part of the HPO₄²⁻ that is (tentatively) liberated in the SMTZ precipitated as authigenic apatite? Is this supported by pore water Ca and F profiles (if not at this sites, maybe at the nearby sites)? And could the formation of Ca-P be related to the sulphidisation front that consumed part of the Fe-AOM-derived Fe²⁺ and precipitated it as AVS? In other words, does the activity of a sulphidisation front put a constraint on how much Fe(II) phosphate can precipitate below the SMTZ? Are there any estimates of the kinetics of these potentially competing authigenic processes of Fe²⁺ removal from the sub-SMTZ pore waters? This would be very interesting, as it would allow to better link the rate of HS⁻ production in the SMTZ (which is largely controlled by sulphate diffusion from above and methane delivery from below), the amount of reactive Fe oxides beneath the SMTZ, and the potential to form different authigenic P phases beneath the SMTZ.

“Deepening” of the SMTZ: The suggestion of a previously shallower SMTZ in section 5.1 comes out of the blue, without any specific reasoning for why the authors think this was the case. I do not necessarily disagree with this hypothesis, but the authors need to give some supporting arguments, e.g., maybe the fact that pyrite exists above the SMTZ (although this could also be formed by organoclastic sulphate reduction). They then need to better develop how such a deepening of the SMTZ would have affected all

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of the described geochemical parameters, and if observations agree with expectations. Finally, they need to relate the migration to the SMTZ to depositional/environmental processes – if it was not caused by changes in sedimentation rate, was it changes in methane flux from below?

Missing reference: Please cite März et al. (2008, 2018) (both Marine Geology) when stating that a lot of the vivianite is likely finely disseminated. In general, wherever the authors speculate about the wide-spread occurrence of vivianite in methane-rich continental margin sediments, they need to cite the new study by März et al. (2018) (Marine Geology) that comes to exactly the same conclusion.

Vivianite to Ca-P sink switching: When looking at the Ca-P profile, one cannot help but notice that there is an increase to higher values from the SMTZ to the bottom of the core, while Fe-P and vivianite seem to decrease in parallel. This raises the question of the long-term stability of vivianite in the sedimentary record, and its use as paleo SMTZ marker. In fact, vivianite is hardly ever found in older sediments/sedimentary rocks where carbonate fluorapatite is by far the dominant mineral, so there is a strong argument that vivianite is (at least partly) transformed into something else, maybe authigenic apatite?

Importance of findings to the geological past: The link between vivianite formation below the SMTZ in Fe-AOM affected sediments and the potential importance of these processes in the pre-GOE oceans is not well-developed. The actual effects of Fe(II) phosphate formation in an Fe-rich ocean are not discussed at all, only the potential importance of Fe-AOM is mentioned (which is not wrong, but also does not reflect the main story of the research presented here). It would be much more interesting to develop what impact Fe(II) phosphate formation under ferruginous conditions might have had on the marine P cycle. These considerations do not only apply to the pre-GOE ocean; as first proposed by März et al. (2008) (GCA) and further developed by Poulton and Canfield (2011) (Elements), ferruginous conditions existed periodically in the Mesozoic (and probably throughout the Phanerozoic) as well. And as März et

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al. (2008) (GCA) pointed out, the precipitation of Fe(II) phosphates occurred under ferruginous conditions during the deposition of Cretaceous black shales on Demerara Rise, sequestering P from the water column and putting a constraint on the anoxia-productivity feedback loop. While we still do not understand enough about the details, and potential effects, of Fe(II) phosphate formation under ferruginous conditions, these earlier studies should be referenced appropriately.

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