

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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We thank Dr. März for his comments and insight. His requests have helped to clarify the text and highlight omissions from our initial submission. We reply to each of his comments in turn and aim to revise the manuscript accordingly.

R1.1). Comment (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

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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⁻.

Reply: We acknowledge this oversight and agree that more detail should be included to clarify how the sediments/pore waters were handled and collected. We intend to clarify this in the amended manuscript.

After sectioning on board, the cores were stored below 4 °C. Half-cores were then split and subsampled immediately after the cruise. Sub-samples were stored frozen (–20 °C) prior to freeze-drying. The obvious peak of Fe-oxides at ~900 cm depth (Fig. 8a) may include part of acid volatile sulfur (AVS) pool since AVS oxidizes to dithionite- and oxalate-extractable Fe phases during freeze-drying or exposure to air. It is difficult, however, to quantify the influence of pyrite oxidation on the reactive Fe distributions at Site 973-4.

Unfortunately, the pore waters were not immediately extracted; instead, they were extracted several months later via centrifugation of previously frozen sub-samples. Consequently, the pore water chemistry of Site 973-4 (Fig. 2b) is more likely to reflect post-recovery oxidation or contamination rather than sediment-housed processes. For example, volatile sulfide lost and/or sulfate distributions could be modified by sulfide oxidation. Alternatively, as R1 suggests, precipitation of dissolved Fe could influence the distributions of Fe-sensitive species. It is for this reason that we opted to deemphasize the importance of the published pore water chemistry in favor of proximal published data (Fig. 2b; see R1.2).

R1.2). Comment (pore water data and SMTZ definition): 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

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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. 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. Also the methods of pore water sampling and data generation at these nearby sites should be explained.

Reply: We agree with R1’s concerns but, given the complications concerning the quality of the pore water data at Site 973-4 (See R1.1), we believe that synthesizing pore water data from the surrounding sites is likely to be more representative. We stress that we do not advocate this approach to replace pore water analysis but, in its absence, we argue that pore water data from nearby sites when combined with solid-phase distributions from Site 973-4 allow to estimate an approximate position of the SMTZ that satisfies for the purposes of our manuscript.

Sites from which we obtained pore water data are separated from Site 973-4 by a few kilometers. These sites are lithologically similar and dominated by silty clay. Unfortunately, age constraints and sedimentation rates are lacking at the other sites. The pore water chemistry from the combined sites, however, is analogous, indicating that each site was likely affected by the same depositional process(es). Solid phase distributions at Site 973-4 support this inference. At the sulfidization front, sulfide is known to diffuse out of the SMTZ promoting reductive dissolution of Fe-oxides and the sequestration of elemental sulfur and Fe monosulfides ($3\text{H}_2\text{S} + 2\text{FeOOH} \rightarrow \text{S}_0 + 2\text{FeS} + 4\text{H}_2\text{O}$). At Site 973-4 there are two pronounced peaks of elemental sulfur at 730 and 880 cm depth, while AVS concentrations reach their maximum at ~900 cm depth (Fig. 9b). Accordingly, we combine these site-specific solid-phase records, with the “imported” pore water data to infer the SMTZ is currently around 700–880 cm depth at Site 973-4.

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As R1 suggested, however, the first methane-free samples appear at 640 cm depth right above the SMTZ. Considering the first elemental sulfur peak at 730 cm depth, we stress that it is more appropriate to define the upper boundary of the SMTZ as a rough depth for the purposes of our manuscript, i.e. around 700 cm depth.

Given following discussion, and the need to draw on the data of others, we agree with R1 that the pertinent details of pore water sampling and analysis should also be included in the manuscript. Clarifying text to rectify this oversight is: Pore water extraction from Site DH-CL11 was conducted on shore via centrifugation, exploiting sample aliquots that had been immediately taken and stored under vacuum at -80°C (Lin et al., 2017). Pore water samples from Site B and Site HD319 were collected immediately after recovery by vacuum extraction (Lu et al., 2012; Ye et al., 2016). The extracted pore water at these three sites was preserved in cryogenic vials at 4°C prior to sulfate analysis by ion chromatography. Methane concentrations at these three sites were determined via sediment plug sampling and gas chromatographic analysis of the resultant headspace gas (Lin et al., 2017; Lu et al., 2012; Ye et al., 2016).

R1.3). Comment (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.

Reply: The extraction method with anoxic 0.5 M HCl solution was adopted from Holmkvist et al. 2011 and 2014 (GCA). More than 97% of amorphous iron (hydro)oxides and ferrihydrite can be extracted, while other Fe-oxides minerals are apparently recalcitrant to this extractant (Wallmann et al., 1993, Limnology and Oceanography; Haese et al., 1997, GCA). Compared to the more well-known dithionite method (e.g. Poulton and Canfield, 2005), the HCl method has not been well calibrated. Therefore, we will ensure the relevant references are included in the manuscript but intend to refer dithionite-extractable Fe as Fe-oxides. These data will be used for the ensuing discussion.

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R1.4). Comment (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⁻).

Reply: Following R1's advice, a brief description of how the various published datasets were generated will be included in the amended manuscript. This will be appended to the existing methods section. The clarifying text requested by R1 is: Additional published data (e.g., Fig. 9) was determined following established protocols and full methodological details are provided in the respective papers. Accordingly, only a brief description is provided here. Acid volatile sulfide was liberated via HCl distillation and trapped by zinc acetate, its concentration was then determined spectrophotometrically (Zhang et al., 2014). Pyrite aggregates were handpicked from the coarse-fraction (> 65 μm) with its abundance expressed relative to the coarse grains. The sulfur isotopic composition of handpicked pyrite was determined directly using a Delta V Plus isotope ratio mass spectrometer (IRMS; Lin et al., 2015). The solid-phase distribution of P was revealed through the SEDEX sequential extraction scheme (Ruttenberg, 1992). Iron-bound P and Ca-P were extracted by citrate-bicarbonate-dithionite and Na-acetate buffer, respectively (Zhang et al., 2018b). The carbon isotopic composition of total inorganic carbon was determined after treatment with phosphoric acid using a Finnigan MAT-252 IRMS (Ou, 2013). Finally, magnetic susceptibility was investigated using a MFK1-FA kappameter (Lin et al., 2017a).

All analyses were conducted on splits of exactly the same samples from the same core which was obtained from a cruise in 2011. Although test date is different for each analysis, all the sediment samples were kept frozen before analyses. Following R1's advice, speculations will be removed from an amended manuscript.

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R1.5). Comment (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 site, 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.

Reply: This is an interesting point, and one that warrants inclusion in the discussion of the amended manuscript, albeit still speculative due to the lack of appropriate data.

As pointed out by R1, authigenic Ca-P is the major P sink at Site 973-4 (~55%), in agreement with its globally estimated importance. Indeed, Ca-P concentrations are much higher than Fe-bound P throughout the studied core. It is well known that a steady supply of phosphate, fueled by the reductive dissolution of Fe-oxides, fosters thermodynamically favorable conditions capable of promoting apatite authigenesis in proximity to the SMTZ (Egger et al., 2015a, Fig. S8; März et al., 2018). Thus, as suggested by R1, it is possible that some of the SMTZ-sourced phosphate is consumed and precipitated as authigenic apatite, providing the other necessary chemical constituents are available. While there are no reliable pore water data from Site 973-4 (R1.1), dissolved Ca²⁺ concentrations from Site B are consistent with ongoing apatite authigenesis, with a linear down-core decrease from the sediment-water interface to the upper SMTZ (12.5–2.5 mM) where most of the Ca²⁺ has been consumed (Ye et al., 2016). To our knowledge, however, there are no available dissolved F⁻ and PO₄

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data to unequivocally confirm apatite precipitation rather than other calcium-harboring phases.

Vivianite formation below the SMTZ depends on PO₄ and Fe²⁺ availability, which we suggest are mainly supplied from PO₄ liberation in the SMTZ and the upward flux of Fe²⁺ from iron reduction at depth. Kinetics notwithstanding, providing there is sufficient Ca²⁺ and F⁻ apatite will remove PO₄ competing and effectively limiting vivianite precipitation. At Site 973-4 vivianite occurs below ~900 cm depth suggesting that even if apatite authigenesis is a competing process, Ca²⁺ and F⁻ might have been consumed at this depth. Importantly, vivianite authigenesis occurs below the sulfidization front (~900 cm) implying that FeS precipitation is kinetically favored relative to vivianite precipitation right below the SMTZ. We speculate, therefore, that the pore water chemistry and the activity of sulfidization front will influence the depth of vivianite formation. Intensified activity at the sulfidization front would liberate more phosphate, however, the extra sulfide flux may serve to nullify the ascent of Fe²⁺ from depth, especially as highly reactive iron is consumed, preventing vivianite formation or forcing it to occur in deeper sediment-layers.

Unfortunately, we do not have the data to definitively test the hypothesized competing role of apatite and FeS authigenesis in vivianite precipitation. However, any process that serves to deplete pore water PO₄ and Fe²⁺ will hypothetically compete with vivianite formation. Future work in/around the study area should focus on generating comprehensive pore water and solid phase data sets analyses, coupled with reactive transport modeling, to better link the rate of HS⁻ production in the SMTZ, the amount of reactive Fe-oxides beneath the SMTZ, and the potential to form different authigenic P phases beneath the SMTZ.

R1.6). Comment (“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

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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 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?

Reply: Following R1’s advice the following discussion is warranted. If we accept that the current SMTZ is around 700–880 cm depth based on the arguments presented in R1.2, we can speculate on the SMTZ migration at our site. The preservation of Fe-oxides and absence of pyrite below the SMTZ were most likely caused by the rapid upward migration of the SMTZ from below 14 m (i.e. deeper than the core) to the middle of our core. The short exposure of Fe-oxide minerals to sulfidic conditions led to incomplete reduction and sulfidization (März et al., 2018). After migrating, the SMTZ has varied around 560–880 cm, leaving pronounced imprints on the pyrite, Fe-oxide, Fe-silicate, total inorganic carbon and magnetic susceptibility profiles (Figs. 7–9). It should be noted that pyrite formed by organoclastic sulfate reduction usually features more negative $\delta^{34}\text{S}$ values (–50 per mill) such as those seen at ~300–560 cm depth. Whereas, the $\delta^{34}\text{S}$ excursion seen at ~560–880 cm depth is best explained by sulfate driven AOM activity at and above the current SMTZ. Assimilating these observations, we suggest that the SMTZ might have slowly migrated downward from ~560–700 cm to its current position at ~700–880 cm depth.

This migration pattern may explain why we observed vivianite at 747 cm depth (Fig. 6). The paleo-SMTZ may be a little shallower (e.g. ~560–700 cm depth) allowing vivianite precipitation at shallower depths (e.g. 747 cm depth). However, we speculate that most the vivianite formed at/around the current SMTZ was readily converted to Fe-sulfide phases via reaction with H₂S during the downward migration of the SMTZ, concentrating vivianite below the current SMTZ. If the SMTZ continued to descend within the sediment, we would expect that the pronounced solid-phase imprints ob-

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served at ~560–880 cm would also descend to deeper sediments below the current SMTZ.

Given that the sedimentation rate at Site 973-4 is almost constant over the duration of the core (Fig. 2a), we attribute the SMTZ migration pattern to a change in the methane flux from depth. During sea-level low stands around the Last Glacial Maximum, the low hydrostatic pressure would destabilize the underlying methane clathrates, enhancing methane fluxes while promoting a rapid upward migration of the SMTZ (Borowski et al., 1996). The subsequent Holocene sea-level rise diminished methane fluxes and might have instigated a slow downward migration of the SMTZ to its current position. Our study further supports recent findings that the SMTZ needs to be fixed at a specific sediment interval (i.e. ~560–880 cm depth) for thousands of years to allow for the development of significant authigenic Fe(II) phosphate mineral enrichments below the SMTZ (März et al., 2018).

R1.7). Comment (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.

Reply: We apologize for the omission of the reviewer's most recent work. We had submitted our paper before the 2018 study had been formally published. As suggested, in our manuscript, we will cite März et al., 2008 and 2018 to fully credit the importance of finely disseminated vivianite in methane-rich continental margin settings.

R1.8). Comment (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 sedi-

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ments/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?

Reply: The question concerning vivianite's longevity in the sedimentary record is a good one and, indeed, an outstanding question that needs to be addressed more generally. Unfortunately, in the context of the available data, we cannot unequivocally test this hypothesis and thus opt to expand the discussion to encompass the available observations and interpretations. However, given the ambiguity, we also elect to "tone-down" our language to convey uncertainty in the amended manuscript.

The increase in Ca-P concentrations noted by R1 may reflect the conversion of labile P-species into authigenic apatite, so-called sink switching. Sink switching is considered to be the dominant global process of apatite authigenesis in marine sediments (e.g. Rüttenberg and Berner, 1993; Slomp et al., 1996). Whether vivianite is converted to authigenic apatite at depth, while possible, remains an open question. Moreover, if it were a simple conversion then one would predict a linear increase in apatite with a concomitant decrease in vivianite. Closer inspection of the relevant solid phase records reveals that this is not the case and, in fact, the relationship between apatite and vivianite concentrations is ambiguous and largely decoupled at Site 973-4.

Alternatively, the "increase" in authigenic Ca-P from the SMTZ to the bottom of the core may reflect non-vivianite-related apatite authigenesis at depth. Upward fluxes of Ca²⁺ and F⁻ to the SMTZ have been observed in continental margin settings (e.g. Clemens et al., 2016, IODP 353; März et al., 2018), which would provide the necessary chemical constituents to promote sub-SMTZ apatite authigenesis. As discussed in R1.5, if apatite is a more favorable phosphate sink, then precipitation of this mineral phase could hypothetically curtail vivianite authigenesis. In this scenario, although the two phosphate phases are linked, they are linked through Ca²⁺ (and F⁻) availability rather than stability and conversion of one phase to another.

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The apparent decrease in vivianite with depth could also be completely decoupled from apatite authigenesis. For example, vivianite is sensitive to oxic conditions, thus it is possible that vivianite in deep-time records was oxidized to Fe-oxides (e.g. hematite; Berner, 1981), Fe(III) phosphate (e.g. koninckite; März et al., 2008, Marine Geology) or some other unknown phases during tectonic uplift. It provides another clue for future research that vivianite may be partly preserved as pseudomorphs (e.g. metavivianite) or with special markers in P-bearing sedimentary rocks. However, the perceived absence of vivianite in aged sedimentary archives could equally be an artifact of insufficient surveys. Our work, as well as that of R1 (März et al., 2018), has shown that vivianite is likely a finely disseminated phase and thus may have escaped detection in many studies. Moreover, typically employed extraction schemes co-extract vivianite, meaning that Fe-P in deep time records could have been wrongly ascribed, and could be vivianite (c.f., März et al., 2008, GCA).

Future work, targeting long cores coupling aqueous- and solid-phase analysis, is required to definitively test our hypotheses linking vivianite authigenesis and Fe-AOM activity, as well as to examine the long-term stability of vivianite in the sedimentary record. More routine application of XRD and modification of solid-phase extraction protocols is also necessary (pers. comm. S. Poulton, 2018) to answer questions relating to the geological significance of vivianite.

R1.9). Comment (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

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by Poulton and Canfield (2011) (Elements), ferruginous conditions existed periodically in the Mesozoic (and probably throughout the Phanerozoic) as well. And as März et 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.

Reply: These are interesting and valid points. As detailed by R1, the seawater chemistry was vastly different between ancient oceans and their modern counterparts. In our original manuscript, we specifically referred to the predominantly ferruginous state of pre-GOE oceans, yet we concede that ferruginous conditions were also a periodic feature post-GOE oceans (März et al., 2008; Poulton and Canfield, 2011). The latter scenario is subtly different from the former, however, due to ingrowth of the seawater sulfate reservoir (Canfield et al., 2000). Accordingly, we welcome the opportunity to extend the discussion, fortifying the stance of others while more completely developing our hypotheses concerning the importance of vivianite, and its wider role in P-cycling in ancient oceans.

Where basal waters are oxygenated, we expect a similar pore water pattern to that observed at Site 973-4 or other modern open marine settings (Fig. 10), where vivianite is dominantly formed below the SMTZ. If oxygen concentrations drop, however, vivianite authigenesis is expected to be different with implications for P-cycling and productivity. These intricacies, however, remain to be fully explored.

Under ferruginous (anoxic and Fe²⁺-rich) conditions dissolved phosphate would be adsorbed to and/or co-precipitated with Fe-oxides (März et al., 2008), or even precipitated as vivianite directly if Fe²⁺ and PO₄ concentrations were sufficiently high (Dijkstra et al., 2018b). This P shuttle is (at least) partially eradicated if euxinic conditions develop in the water column caused by sulfidization of Fe-oxides and/or vivianite presumably

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governed by particle settling kinetics. After settling, the fate of the P-rich Fe-oxides and vivianite particles would be dictated by the prevailing conditions in the diagenetic environment. Under sulfate limited conditions P removed from the water column is likely to be retained in the sediment-pile, throttling productivity via a negative feedback (März et al., 2008). When sulfate is available, however, reductive dissolution of Fe-oxides will liberate phosphate to the pore water which may be lost or retained dependent on the locus of dissolution and the availability of other important dissolved species (Ca^{2+} , Fe^{2+} , Mg^{2+} , F-) and reductants (e.g., OM, CH_4).

Applying these principles to our understanding of Earth History is somewhat speculative but nonetheless interesting, with broad implications for P-cycling. In the largely low-sulfate ferruginous oceans prior to the GOE, the development of euxinia would have been scarce, enhancing phosphate shuttling to the sediment. If this phosphate was efficiently retained on a global-scale, then phosphate availability in these ancient oceans would have been low, especially considering the reduction in oxidative weathering (Reinhard et al., 2017). By contrast, throughout Earth's history euxinic marine environments have become more prevalent – a consequence of rising sulfate concentrations. As discussed, euxinic conditions promote P recycling and its return to the water column; whereas P is more recalcitrant in ferruginous environments. In a simple sense, therefore, euxinic conditions are touted to be quasi self-sustaining (via a productivity feedback) whereas ferruginous conditions are not. In a wider Earth System sense, however, these gross generalizations may not be valid, and warrant further investigation. Sustained euxinia, for example, could lower sulfate inventories causing the development of ferruginous conditions if S/FeHR ratios drop below 2 (e.g., Poulton and Canfield., 2011). Furthermore, unless reactive iron enrichments are solely derived from hydrothermal emanations, simple mass balance constraints dictate that sedimentary iron enrichments are unlikely to occur throughout an anoxic ocean and the source region must be depleted in reactive iron. Consequently, to understand the global effects of oxygen deficiency on P-cycling we must more completely understand the local controls on P-cycling and how oxygen deficiency developed on an event-by-event basis

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to successfully integrate these processes in an Earth system model.

Sincerely, on behalf of all authors,

Jiarui Liu

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