

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 would like to express our gratitude to R2. Most of the points raised here were also raised by R1, we have attempted to cross reference between our responses to prevent repetition. We reply to each of the reviewer's comments in turn and aim to revise the manuscript accordingly.

R2.1). Comment: Although other pore-water chemical compositions (PH, PO₄³⁻, Ca²⁺ etc.) is lacking, a simple geochemical calculation on what's kind of minerals (FeS, CFA, Mg₃(PO₄)₂, Fe₃(PO₄)₂) are expected to precipitated in/above/under SMTZ can make the P-cycle in methane-rich environments more clearer.

Reply: Pore water chemistry is essential to conduct a comprehensive series of calcu-

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lations on mineral precipitation in marine sediments. As discussed in R1.1, we lack robust pore water data and thus we draw on PHREEQC calculations of pore water saturation indexes from other sites (Egger et al., 2015a, Baltic Sea, Fig. S8; März et al., 2018, open marine margins) to address this comment.

Hydroxyapatite saturation indexes above 0 suggest that the steady supply of phosphate from reductive dissolution of Fe-oxides creates thermodynamically favorable conditions for carbonate fluorapatite (CFA) precipitation around the SMTZ, whereas CFA formation appears to be a minor sink for pore water phosphate below the SMTZ (März et al., 2018). Higher saturation indexes for vivianite are typically obtained below the SMTZ. Here, the upward flux of Fe^{2+} from iron reduction and downward flux of phosphate from the reductive dissolution of Fe-oxides create favorable geochemical conditions for vivianite precipitation below the SMTZ, consistent with the vivianite distribution observed at Site 973-4. The solubility product constant pK_{sp} ($-\log K_{\text{sp}}$) of Mg phosphate is 24, while the pK_{sp} of vivianite is 36 (Nriagu, 1972), making the former mineral more soluble. Moreover, Mg concentrations are typically up to three orders of magnitude higher than those of Fe in marine sediments (e.g. Hu et al., 2015, Site D-5). Consequently, Mg phosphate precipitation is unlikely. Rather, Mg^{2+} is more likely to be co-precipitated with vivianite, forming Mg-rich vivianite below the SMTZ.

Besides phosphate minerals, Fe sulfides are enriched in and above the SMTZ. Pyrite is a common mineral in marine sediments where dissolved sulfide, produced by either organoclastic sulfate reduction (above the SMTZ) or sulfate driven anaerobic oxidation of methane (within the SMTZ), is trapped by Fe-oxides, forming Fe monosulfide. Fe monosulfides are gradually converted to pyrite as a permanent sink for sulfur. The acid volatile sulfur peak at ~ 900 cm depth contains large amounts of Fe monosulfides, and is referred to as the sulfidization front (S-front). The dissolved Fe is sourced either from the reductive dissolution of Fe-oxides by sulfide at the same depth or iron reduction at depth. Consequently, the formation of Fe sulfide is modulated by sulfate penetration depth.

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R2.2). Comment: Why vivianite is only observed/common under SMTZ (Fig 7a) instead of forming in/above SMTZ. What's the concentration of HPO_4^{3-} are expected when the Mg-rich vivianite is observed (Fig. 4) (The KSP of $\text{Mg}_3(\text{PO}_4)_2$ are three orders of magnitude higher than $\text{Ca}_3(\text{PO}_4)_2$, but the $[\text{Mg}^{2+}]$ in pore-water are one orders of magnitude higher than $[\text{Ca}^{2+}]$). Vivianite is lack in ancient record. Would the vivianite formed here be convert to $\text{Ca}_3(\text{PO}_4)_2$ further or what's kind of condition where the vivianite can be preserved in sedimentary record and further served as a proxy for methane rich environment or Fe-AOM activity? In Fig 6, vivianite is only observed in the depth of 747 m? Why there is no vivianite below the 900 cm depth according to the XRF result? There is an inconsistent of vivianite content between the XRF and handpick method.

Reply: We did not identify any macro-vivianite within or above the SMTZ. Generally, vivianite is unstable in the presence of sulfide that is produced by sulfate reduction in/above the SMTZ, and is readily converted to pyrite (Berner, 1981). Previous studies suggest that phosphate concentrations are higher than $\sim 100 \mu\text{mol/L}$ in the SMTZ when potential vivianite is observed, so that enhanced phosphate flux could create favorable geochemical conditions for vivianite precipitation below the SMTZ (e.g. Egger et al., 2015; März et al., 2008, 2018). Dissolved Mg concentrations at a nearby site range from 48.4 to 37.7 mmol/L, while dissolved Ca concentrations decrease linearly from the sediment surface to the SMTZ (12.5–2.5 mmol/L) where most of the dissolved Ca is consumed (Ye et al., 2016; Site B). Empirically, Ca tends to be precipitated as CFA independently, while Mg tends to be co-precipitated with vivianite rather than forming Mg phosphate (see R2.1).

Vivianite is apparently lacking in deep-time records. Whether this is an artifact of inefficient surveys and/or non-diagnostic extraction protocols remains to be shown. Generally, authigenic Ca-P concentrations increase with burial depth, likely due to the transfer of P from more labile forms into authigenic apatite, so called sink switching. Sink switching is considered to be the dominant process of apatite authigenesis in marine

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sediments worldwide (e.g. Ruttenger and Berner, 1993; Slomp et al., 1996). Therefore, it is possible that vivianite formed at Site 973-4 is partly converted to authigenic apatite at depth. However, as we stressed in R1.8, the relationship between apatite and vivianite abundances is not straightforward and the details of vivianite preservation and potential transformation remain fundamental unanswered questions.

Finally, there is some element of misunderstanding concerning the origin of the questioned data. Figure 6 displays XRD data derived from handpicked Fe-rich silicates (the grey to green mineral aggregates), whereas the XRD-derived data sourced from handpicked vivianite aggregates is shown in Figure 5a. Vivianite aggregates are only identified below the SMTZ. The vivianite found in the aggregates of Fe-rich silicates at 747 cm depth is intriguing, however, it is not surprising that XRD reveals mineral phases that evade detection optically. As discussed in R1.6, we argue that SMTZ was once shallower and speculate that the vivianite observed at 747 cm was precipitated beneath the SMTZ when it was closer to the sediment water interface. The subsequent downward migration of SMTZ would then be expected to have converted most of the vivianite to iron sulfide erasing the shallow vivianite record. Exactly why the vivianite at 747 cm survived sulfidization is uncertain, however, the textual association with Fe-silicates implies that these phases may have armored the vivianite, preventing conversion to sulfide.

R2.3). Comment: Another concern is the recognition of the current and previous SMTZ. Either porewater or sediment has its own validity in revealing the characteristics and mechanisms of seepage. For example, the geochemical data obtained from the solid fraction of sediments and from authigenic carbonates provide time-averaged information on biogeochemical processes on a timescale of years to centuries. Sediment pore waters and seep-dwelling fauna, on the other hand, provide information on much shorter timescales, spanning from days to months. This issue need to be considered and discussed in discussion. One needs to mention the nature of the seeps. It is well known that seeps are heterogeneous both in time and space. I would find interest-

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ing that they describe in a few words the inherent nature of seeps in the introduction section and consequently highlight their findings in the discussion section. The shift of former and current SMTZ is exactly caused by the varying of flux of fluids.

Reply: We agree with R2, and reiterate that pore water and solid phase data resolve processes acting on different timescales. We have discussed this in R1.6. If we had reliable pore water sulfate and methane data, this would constrain the depth of current SMTZ, reflecting seep activity on a timescale of days to years. Solid phase imprints, such as those seen at ~6–9 m depth (Figs. 7–9), reflect sulfate driven AOM in a SMTZ that has been more-or-less static over decadal to millennial time-scales. Given the constant sedimentation rate at Site 973-4, the position of the SMTZ is controlled by flux of methane-rich fluids from depth. The long-term migration of SMTZ has altered the solid phase records and controlled the distribution of vivianite, creating the mineralogical and geochemical distribution profiles we observe today.

Sincerely, on behalf of all authors,

Jiarui Liu

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