

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

Anonymous Referee #2

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Liu et al characterized the distribution and mineralogy of iron-phosphate minerals in methane-rich deep-sea sediments from the South China Sea. They demonstrated the pervasive presence of vivianite authigenesis below the current SMTZ, which is thought to be caused by the downward migration of the former SMTZ where vivianite formation occurred. The data were used to provide insights into Fe-AOM in today's ocean and potentially in the early Earth. The manuscript is definitely suitable for publication in Biogeosciences, systematic and of broad relevance and interest for the geosciences community. I have a few comments for the authors to consider during revision.

Please find below my comments and concerns for the authors to consider during revision:

1). Although other pore-water chemical compositions (PH,PO4³⁻,Ca²⁺ etc.) is lacking,

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a simple geochemical calculation on what's kind of minerals (FeS , CFA, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Fe}_3(\text{PO}_4)_2$) are expected to precipitated in/above/under SMTZ can make the P-cycle in methane-rich environments more clearer.

2). 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 an 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.

3). Another concern is the recognition of the current and previous SMTZ. Either pore-water 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.

4). Along with 3), 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 interesting 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.

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