

Dear Editor,

Please consider our revised manuscript “Organomineral nanocomposite carbon burial during Oceanic Anoxic Event 2” for publication in Biogeosciences.

Firstly, we would like to thank the reviewers for their positive feedback, constructive comments and helpful suggestions, which have allowed us to improve our manuscript. As requested by the reviewers we have made more explicit and now discuss at greater length the tie between our data and our interpretations, for example how we link the bulk data and the high resolution imaging results. We have also included a more detailed discussion of how our results compare to previous work. We further include, tabulated as supplementary information, all of the data presented in the manuscript.

Please find below our point by point response to all of the referee comments. For clarity, referee comments are reproduced in *italics*.

We look forward to your response.

Best Regards,

Dr Stefan Löhr

Anonymous Referee #1

*This paper was a great pleasure to review and an eye opener in several respects. The methods and very broad range of sophisticated experiments are at the cutting edge and appear to be thoroughly performed and are well presented. The correlation between TOC and MSA is very strong and convincing, amazingly good, in fact, for such a complex system. Thus, I was initially worried that the MSA/TOC correlations might partially be an artifact of the methodology, i.e. that the EGME method for MSA determination essentially measures organic matter surfaces, not mineral surfaces (thus creating an autocorrelation). However, this concern is dispelled by the correlation in Fig 3 between MSA before and after organic matter removal. **For this correlation, it would be useful to add evidence about the efficiency of OM removal using hydrogen peroxide (i.e., was OM entirely eliminated?).***

We note in the caption to Figure 3 that efficiency of OM removal ranged between 61 and 92%. In addition, we are making available all the data presented in the manuscript as supplementary information, including the percentage of OM removed after treatment with hydrogen peroxide.

Anonymous Referee #2

The reviewer requested that a more clear tie between data and interpretation be made, specifically they wanted these issues addressed:”

- In the manuscript they point out that 'OC is preserved mainly as sub- μm organic matter in close association with clays, rather than as discrete, μm -scale organic particles' and 'the great majority of OC is quantitatively associated with and stabilized by clay mineral surfaces' (p. 6822). However, I cannot find any discussion about quantitative estimation of their relative abundances. Thus, it is

difficult to agree with the authors claim. Isn't it possible to quantitatively estimate their ratios? In Fig. 6D, some areas (few to 10 μm in size) with high carbon content are seen. They look like discrete OM. I feel that the manuscript needs careful discussion on relative abundances of μm-size discrete OM and sub-μm size OM associated with clay minerals.

Our assessment of the relative abundance of clay-associated vs discrete OM is based on the strong bulk sample relationship between MSA and TOC, which shows an R^2 value of >0.9 in some sections. As we note in the manuscript, the strength of the relationship implies that the great majority of OM is associated with clay minerals, and that the OM is sufficiently small to meaningfully interact and associate with clays. We assume that this type of OC preservation maintains a proportionality between TOC and MSA since a mechanistic control of OC preservation by mineral surfaces should result in a reproducible relationship between these two parameters (Mayer, 1994; Keil & Mayer, 2014; Kennedy et al., 2014). Not only is discrete OM detritus too large to meaningfully interact with the clay mineral matrix, if particulate OC from pelagic sources (and unrelated to mineral surface associated OC) were an important contributor to some of the samples these would plot above the regression evident in Figure 2 (high TOC with limited surface area) indicating the presence of OC that was independent and unrelated to the MSA scaling relationship controlled by surface area. Yet samples with high TOC relative to MSA are not apparent in our dataset.

Alternatively the relationship between MSA and TOC could be simply a coincidence. However, we found this relationship repeated in each core we sampled, and it is reported from other unrelated deposits (Mayer, 1994; Kennedy et al., 2002; Blair & Aller, 2012; Kennedy et al., 2014) of varying age and depositional conditions making a coincidental scaling unlikely. Still, the correlation does not require causation, and to provide further evidence that nanocomposites were forming we directly imaged the relationship using high-resolution synchrotron and SEM imaging. This shows that rather than being concentrated in discrete particles, OM is dispersed throughout the sample, where it is associated with clays forming organo-clay aggregates. SEM images and STXM maps are consistent with our interpretation of the MSA-TOC relationship that the majority of OM is aggregated and associated with clays.

We recognize that because of the μm size of the image, establishing that any given sample is representative of the primary form of OC is problematic, and so we offer this type of data only as a proof of concept while relying on the bulk rock relations (MSA-TOC) to identify the extent of this relationship. Additionally, however, the clay-organic association is also evident in our XRD data, which shows the presence of molecular-scale OM intercalated within the expandable smectite interlayer (Figure 7), and this relationship is evident from bulk sample material.

We added a new section to the revised manuscript to further clarify these points and the rationale behind them (Page 6 Line 22 to Page 7 Line 4) :“A limitation of the small, μm -scale field of view of the high resolution images is that establishing that any given image is representative of the primary form of OC is problematic, so that we offer this type of data only as a proof of concept while relying on the bulk rock relations (MSA-TOC) to identify the extent of the organo-clay relationship. Thus, our assessment of the relative abundance of clay-associated vs discrete OM is based on

the strong bulk sample relationship between MSA and TOC, which implies that the great majority of OM is associated with clay minerals, and that the OM is sufficiently small to meaningfully interact and associate with clays (Keil and Mayer, 2014; Kennedy et al., 2014; Mayer, 1994). Not only is discrete OM detritus too large to meaningfully interact with the clay mineral matrix, if particulate OC from pelagic sources (and unrelated to mineral surface associated OC) were an important contributor to some of the samples these would plot above the regression evident in Figure 2 (high TOC with limited surface area) indicating the presence of OC that was independent and unrelated to the TOC-MSA scaling relationship. Yet samples with high TOC relative to MSA are not apparent in our dataset, and our high resolution images show an intimate, sub- μm scale association between clays and OM.”

- I am not fully convinced by the FTIR spectroscopic maps of aliphatic carbon and clay (Figs 6B and 6C) that were used to exemplify the close association between organic matter and clay minerals. In my view, the distribution of aliphatic carbon significantly differs from that of clay.

We have revised the manuscript to clarify that the FTIR spectroscopic maps show that both OM and clays are broadly distributed throughout the sample, with overlapping distributions, suggesting a close association between clay minerals and OM. The resolution of the technique is not sufficient to do better than this. What it can do, however, is rule out the presence of $> \mu\text{m}$ scale organic particles that are independent of clay minerals.

The intimate ($< 1 \mu\text{m}$) relationship between clay and organic material is further indicated in backscatter electron images, which show that OM is present throughout the sediment and is primarily present within organo-clay aggregates.

Page 6 Line 20-21 now reads: “...confirms that OC and clay minerals have overlapping distributions and are disseminated throughout the sediment where they are spatially associated ”

- The analytical position of electron microprobe analysis with EDAX (Fig. 5D) should be given in Fig. 5C. In general, electron beam expands about $3 \mu\text{m}$ in the sample surface. Because of the limit of spatial resolution of electron beam, I think that the EDAX data is not good enough to demonstrate the co-existence of organic matter and clay minerals on the sub-micrometer scale.

As reviewer 2 points out electron beams have sample interaction volumes of up to about $3 \mu\text{m}$ diameter, depending on factors such as accelerating voltage and sample composition, so that EDS analyses with sub- μm resolution are not feasible. Fortunately, sub- μm elemental analyses are not required for the point we are making here. We simply seek to demonstrate that the relatively homogeneous $\approx 5 \mu\text{m}$ size aggregates shown in Figure 5B and C, which we interpreted as organo-mineral aggregates based on petrographic and back-scatter electron contrast criteria (i.e. presence of bright, sub- μm , elongate particles morphologically consistent with clays, coated and aggregated by an amorphous, darker material interpreted to be OM), are indeed composed mainly of Si, Al, O and C. This is straightforward with the EDS since the electron beam interaction volume is confined to the relatively homogeneous aggregate. Thus it is the SEM BSE image that demonstrates the co-existence of organic matter and clay minerals at the sub-micrometer scale, the EDS analyses

simply serve as an independent confirmation that the average composition of the sub- μm materials visible in the SEM images is consistent with clays and organic matter.

We have revised Figure 5C to show more clearly the area analysed by EDS, and revised the corresponding figure caption as well.

- The regression lines shown in Fig. 2 do not run near the zero point, but they have intercepts around $200 \text{ m}^2/\text{g}$. What does the intercept mean? Attention must be paid to compare their results with their previous data (Kennedy et al., 2002, 2014; Kennedy and Wagner, 2011). For example, the 'laminated anoxic' sediments of late Cretaceous interval from the deep Ivorian Basin, Site 959 (Fig. 2B in Kennedy and Wagner, 2011), are plotted in a different field with a different slope ($\sim 0.7 \text{ mg-OC/m}^2$) compared with the data presented in this paper (Fig. 2). What does this mean? Does this indicate that mechanism governing the OM preservation is not as simple as the authors consider, and that we should think other mechanisms to explain the preservation of OM?

We have revised the manuscript to expand our discussion of the points requested by Reviewer 2, there are now two additional paragraphs at the end of the manuscript (Page 9, Line 23 to Page 10, Line 21):

“The x-axis intercepts of the Demerara Rise MSA/TOC regressions (Figure 2) are offset from zero ($\approx 200 \text{ m}^2/\text{g}$). This is similar to offsets of $\approx 260 \text{ m}^2/\text{g}$ and $\approx 290 \text{ m}^2/\text{g}$ for the anoxic/suboxic and the oxic facies, respectively, of OAE3 at ODP Site 959 (Deep Ivorian Basin; Kennedy and Wagner, 2011) and an offset of $\approx 60 \text{ m}^2/\text{g}$ for the Cretaceous Pierre Shale (Kennedy et al., 2002). This x-intercept offset implies MSA that did not acquire OM or subsequently lost OM. It has previously been interpreted to reflect loss of a more readily oxidised fraction of OM that was associated with external clay mineral surfaces and edges (which can exceed $200 \text{ m}^2/\text{g}$ in smectitic sediments) whereas OM preserved within the smectite interlayer is considered to be more refractory (Kennedy and Wagner, 2011; Kennedy et al., 2014). However, SEM observations of organoclay aggregates from Demerara Rise identify a component of OM associated with external clay surfaces, encapsulated within organoclay aggregates. The observed offsets may be the product of lower OM concentrations in the outermost zone of these aggregates. OM encapsulated by and sorbed to clays in aggregate interiors is progressively better protected relative to OM initially present closer to the aggregate exterior (Keil and Mayer, 2014), as also documented for soil organomineral aggregates (Kinyangi et al., 2006).

Finally, the slope of the MSA to TOC regression has been shown to vary as a function of the depositional environment, sediment diagenesis, and oxic versus anoxic sediments (Blair and Aller, 2012; Kennedy and Wagner, 2011). While TOC generally correlates with MSA in modern continental margin sediments, the highest OM loadings per unit MSA (slope) are found in sediments from high productivity and/or oxygen depleted settings whereas the lowest loadings are typical of sediments from higher energy settings or deep-sea deposits that are subject to long oxidant exposure times (Blair and Aller, 2012). Similar differences are apparent in ancient sediments, with higher OM loadings recorded in samples from anoxic facies (0.7 mg OC/m^2) compared to oxic and suboxic facies (0.4 mg OC/m^2) at ODP Site 959 (Kennedy and Wagner, 2011). While the ODP 959 and Demerara Rise datasets largely overlap, the

slope of the MSA to TOC regression at Demerara Rise sites ranges between 0.44 mg OC/m² (Site 1258) and 0.52 mg OC/m² (Site 1260), somewhat lower than the laminated, anoxic facies at Site 959 but greater than the oxic to suboxic facies at Site 959. Although this might indicate greater oxidant exposure at Demerara Rise relative to Site 959, comparison to modern sediments show that OM loading ratios are equally reduced in relatively higher energy, lower productivity, or lower sedimentation rate settings.”

- How are the slopes and intercepts of the MSA-OM crossplots (Fig. 2) sensitive to mineral compositions? Don't those slopes change in response to relative abundance of smectite (e.g., smectite / total clay minerals) during OAE2, when relative abundance of smectite increased?

Apart from higher temperature clay diagenesis during burial (Kennedy et al., 2014), which can be ruled out in the thermally immature sediments studied here, mineralogical changes are unlikely to influence the slope. This is because the > 100 m²/g surface areas measured here are diagnostic of smectite clay, which dominated sediment surface areas even where representing <5% of the total sediment (Ransom et al., 1998), so that the surface area contribution by other minerals is negligible in the smectite-rich Demerara Rise sediments. As discussed in the previous point, varying slopes are more typically attributed to changes in depositional conditions, i.e. energy, oxygenation, OM input etc.

In any case, and as we note in the manuscript, our data does not show an increased OC richness or smectite abundance in the non-carbonate fraction during OAE2 at Demerara Rise, although we suggest that an increase in volcanic-derived smectite at other sites may account for increased global OC burial during this period and the C isotope anomaly associated with OAE2.

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