

Response to the interactive comment on “Better molecular preservation of organic matter in an oxic than in a sulphidic depositional environment: evidence from *Thalassiphora pelagica* (Dinoflagellata, Eocene) cysts by Gerard J. M. Versteegh et al.”

by **Morgan Raven (Referee)**

In this manuscript, the authors present a detailed characterization of dinoflagellate cyst walls that were deposited in oxic versus sulfidic sediments. This data directly inform a critical and timely knowledge gap, as they address the chemical mechanisms driving organic matter preservation as well as taphonomic issues. The dataset will be a significant contribution and I support its eventual publication in BGD. Before that point, however, I encourage the authors to significantly expand their discussion of the broader implications of their results, especially relating to selective biases in the fossil record and the importance of organic matter sulfurization versus other aspects of preservation under anoxic conditions.

We considerably expanded the manuscript taking these suggestions into account. However, we like to stress that the paper is not about the selective bias due to sulfurization alone. It rather highlights the differences in modification of refractory organic matter (dinosporin) between an aerobic and an anaerobic setting. To do this we present new information on the aerobic setting and add this to the published information already available for the anaerobic setting.

Specific notes:

Broadly speaking, many paragraphs would benefit from the addition of a clear concluding sentence, summarizing the main point or argument arising from the preceding results. Such sentences have been added.

Figure 2: One key thing the reader needs to assess here is whether the green line or the black line is more similar to the blue line, which is difficult to do in this arrangement. Consider rearranging your figure so the blue line is common among the sections. The common line also appears stretched at different scales, making it particularly difficult to cross compare the green vs blue lines. We revised this figure completely and also remeasured spectra.

Line 49 – Please revise this sentence: “in the absence of reactive Fe, which has the potential to outcompete organic molecules for reactive polysulfides and limit organic matter sulfurization”.

Done

Line 51 – , which Done

Line 69 – To broaden the accessibility of your results, provide a description of the key aspects of pelagica cyst composition here. Why is this organism relatively resistant to aerobic degradation, and what does that mean for the interpretation of your results? We added a few lines on the aerobic and anaerobic degradation of dinoflagellate cysts. Since cysts sensitive to aerobic degradation degrade quickly (Zonneveld et al., 2019 and references therein) only resistant cysts remain in aerobic settings. The resistance means that we can do this comparison. In any other case, the cysts would be gone from the Kerguelen sample.

Line 74 – I'm not sure what you mean by “the addition of carboxylic acids by early sulfurization of the cysts.” To what molecule is the reduced sulfur being added? What is the source of the carboxylic acids? [Has been explained now.](#)

Line 83 – For both sites, please provide a description of the environment, including a summary of what is known about sedimentation rates. How do the burial ages of these samples differ? What other sedimentological differences exist between the sites? (e.g., clays vs biogenic silica, overall TOC, water depth etc). This information is critical to holistically assess the possible drivers of variation between the two sites. I would hope to see this section substantially expanded. [This section has been expanded now and a description of age, sedimentation rate, redox environment, TOC content and general environmental setting is now present.](#)

Line 85 –Please provide a complete description of the processing of the reducing cysts here. The 2007 paper is behind a paywall and not available to all of your readers. [Info has been added.](#)

Line 110 – Either write out the description of your conditions in sentences or use a table. [Done](#)

Line 112 – What internal standards were used to verify and track retention times? Were any of the identified compounds in your table 1 confirmed with authentic standards? Inclusion of such standards would significantly enhance confidence in the contents of Tables 1+2. [A mixture of n-alkane standards was used to calibrate the retention times. Over the years we produced a considerable library of compounds, spectra and relative retention times. During this period again and again, pyrolysis products were checked with internal standards \(such as n-alkanes, n-alcohols, n-carboxylic acids, a wide range of linear and cyclic isoprenoids, alkylated aromatics, carbohydrates, polycyclic aromatics. Identification is based this accumulated knowledge. We made this more clear in the text](#)

Line 114 – The paywall, again: please make your methods self-contained to this manuscript. [Information has been added](#)

Line 122 – I would find this information (band definitions, minima, etc) more useful in table format. A lot of your section 4.1.1 reads like results rather than discussion; consider moving that results interpretation up to this point. This will also allow your discussion section to focus on the exciting takeaways rather than more routine IDs. [We moved section 4.1.1. into the results section. As a result the former result section largely became obsolete and has been removed. We therefore also refrain from adding a table.](#)

Line 159 – marked absence of absorptions by CH3 – this seems important and is highlighted in Figure 4, but the significance of this observation is not really discussed. What does this mean? [We elaborated more on this issue.](#)

Section 4.1.1 – Reads like results. [see reply to remark for line 122](#)

Line 204-207 – There are multiple sentences starting with “this” or “it” in this section, which makes it difficult to precisely follow the argument. Please revise for clarity. [Done](#).

Line 205 – please revise sentence “and which for its absence in recent cysts we at- tribute” [Done](#)

Line 207 – What else is known about this rapid C=O addition phenomenon? What is the proposed mechanism? (It is an oxic phenomenon?) **We rephrased the sentence so that it is clear now this is an oxic mechanism.**

Line 213 – I like the way this is set up, and I agree chemical processes are likely dominant. But, there are also geological / sedimentological processes that may differ between the sites, most notably sedimentation rate and the composition of surrounding sediments. Please address these potential differences and explain why they do not explain the contrasts in cyst composition you observe. **A good point. We now provide a more thorough explanation of the geological settings and their implications.**

Line 218 – sentence: “Specifically, the Rhine Graben pelagica lack the absorption feature at 718cm-1 and thus appear to lack long chains of algaenan, contrasting pelagica from the Kerguelan Plateau.” **Could not find this in the pdf**

Section 4.1.3 – Please add a concluding sentence to this section that summarizes your case for how FTIR spectra show that redox differences in the sedimentary environment are the key driver of differences in Figure 2. **We added a small concluding paragraph to what is now 4.2**

Line 213 “A further alteration in the same direction as the differences” is unclear. Please be as specific as possible about what observations you’re talking about. **The section has been rewritten**

Line 220 – sentence more like: “GC-MS results are consistent with the results of FTIR analyses, which suggest that differences in depositional environment are associated with differences in molecular structure” **OK, changed**

Line 225-227 – Please revise this sentence to clearly explain which group of alkanes were bound by which mechanism and where those pools ended up in your analytical flow. **Done**

Line 235 – define “it” (in “its presence”) their? **Done**

Line 239 – Consider driving home this point “sulfurization may thus eliminate/consume carbohydrate hydroxy groups from the cyst walls, leaving __”. Indications for the molecular selectivity of sulfurization reactions seems like a significant aspect of your results - please discuss further. **In this case the text is about the oxidized cysts from the Kerguelan Plateau. Here the diagenetic processes presumably removed the hydroxyl groups of the carbohydrate, so that their methylation upon thermochemolysis with TMAH did not occur to such an extent.**

When you find that sulfurized materials are richer in long-chain aliphatics, what does that mean for the relative importance of carbohydrate vs. lipid sulfurization? **We do not think that we can draw a conclusion on this right away. The depositional environment of the Rhine Graben was such that large amounts of lipids must have reached the sea floor and were stored in the sediment. this kind of environment typically develops into a source rock for oil and gas. For the kerguelen plateau, these lipids have probably already been degraded during their transport through the oxic water column to the sediment floor.**

Line 240 – define which sample you are discussing in this paragraph. **Done**

Line 249 – don't stop! You've set up some really exciting observations (e.g., Fig. 8) and this feels as though their implications haven't been fully fleshed out yet. Please also clarify your final sentence – how exactly do you see aliphatic content fitting into the sulfurization story? [We added a paragraph just before the conclusions clarifying this in more detail.](#)

Can you say anything further about the signature of sulfurization in the geologic record? How cyst sulfurization would bias the interpretation of fossils? Which general categories of molecules would be most susceptible to alteration (e.g., carbohydrates, maybe lipids less so)? Many of these ideas seem to be hidden within the text but would benefit from being explicitly stated.

[We now discuss these questions in the manuscript.](#)

The cyst sulphurisation is only apparent on molecular level, not visible at microscopic level and as such does not provide bias. Furthermore, the cysts belong intrinsically to the more refractory organic matter and the sulphurisation does not increase their preservation and therefore presence in the fossil record.

Our study does not provide an answer to the type of molecules that is most vulnerable to sulphurisation, it rather describes how the dinoflagellate cyst wall gets modified differently in different environments. The kind of interactions in both environments that are apparent are polymerization reactions with linear aliphatics, simply since these are not available in the initial biomacromolecule. [We did implement answers to these questions in the revised manuscript.](#)

Finally, I would strongly advocate for the authors to include at least a rough quantification of the sulfur content of these samples, for example by combustion elemental analyzer or x-rays. Sulfur-to-carbon molar ratios would be extremely valuable for the identification of similar processes in other environments. Sulfur quantification would also allow you to assess to what extent sulfurization can explain the alteration of your bulk organic matter or whether some other aspect of a reducing environment might have been the main driver (for example, you could compare whether the sulfur addition is sufficient to account for the loss of hydroxyl functional groups that you observe.)

[We agree that it would be interesting to do these analyses. However, how interesting the questions that may be attacked we consider our non-quantitative study not suited to efficiently attack these questions and therefore the proposed analyses beyond the scope of this paper.](#)