

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

by **Jakob Vinther (Referee)**

The authors identify that samples in euxinic conditions have undergone substantial kerogenisation, while samples in 'oxic' settings have not.

Their argument that the oxic conditions are better seems apparently good on these premises. I would like to stress, though, that I am not certain about the premise of good preservation and also what constitute oxic environments.

I have two key issues:

1. Kerogenisation is not necessarily bad organic preservation. This may be a way to quench many labile organic molecules into larger macromolecules. What they mean is that the cysts have been overprinted by kerogenisation. This is not bad organic preservation per se, but not good if you want to look at the original composition of a microfossil.

We adapted the text to make a better distinction between intermolecular and intramolecular diagenetic processes accordingly to make clear what we do mean. We added a paragraph outlining that we consider better and worse molecular preservation, what we consider kerogenisation and polymerization as is explained also below:

As we mention in the text, kerogen has been defined as the sedimentary organic matter that is insoluble in common organic solvents (see Durand, B., 1980. Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen. In: Durand B., Kerogen : Insoluble Organic Matter from Sedimentary Rocks, Editions Technip, Paris 13-34). As such an organic microfossil fits in this definition of kerogen.

Kerogenisation is simply the process of diagenetic cross-linkage (see Butterfield, N. J., 1990. Organic preservation of non-mineralizing organisms and the taphonomy of the Burgess Shale. *Paleobiology* 16, 272-286). This cross linking may thus be intermolecular and intramolecular.

This definition of kerogenisation is too narrow for what we describe in the manuscript. We consider diagenetic change of the dinoflagellate cyst wall. This involves not only diagenetic cross linking (kerogenisation) but all kinds of structural changes, thus also e.g., modifying, adding and losing bonds and functional groups, changing stereochemistry.

We report on the extent to which the cyst biomacromolecule has been modified by different diagenetic regimes - indeed changes in the original structure of the microfossil biomacromolecule. In that perspective, each change away from the

original biomacromolecule is a decrease in its condition of preservation. We obtain insight in the degree of change through infrared spectroscopy, pyrolysis and thermochemolysis of the cysts and comparison with each other and an unaltered recent analogue. This shows that the cyst preserved in the environment that was subject to extensive aerobic OM mineralization underwent diagenetic changes which were different from the changes to the cysts preserved in the initially anaerobic setting. These changes not only involved diagenetic cross linkage but also addition and removal of functional groups. Unexpectedly, the cysts from the aerobic setting appear structurally more close to the recent analogue than the cysts preserved in the initially anaerobic setting. We do not mention or imply that the preservation is good or bad in an absolute sense, we only mention that the molecular structure of the cysts from the Kerguelen Plateau preserved better at molecular level than those from the Rhine Graben. And we find a reasonable explanation why this is so.

We revised the text such that this becomes more clear.

2. When the authors call the other deposit oxic I am not sure that this has been proven and in fact, I doubt it is fully oxic throughout. While it may be on the surface, almost all sediments switch to anoxic conditions quickly in the subsurface. Dinoflagellates are robust and survive initial oxic decay under almost any circumstances contrary to most other tissues. This is the reason why exceptional Konservat Lagerstätten are notoriously anoxic environments. But, this does not mean that oxic environments may not preserve extremely stable and recalcitrant biomolecules such as dinoflagellates and pollen as it will switch to anoxic conditions a few centimeters below the sediment- water interface.

We agree, we were not clear about this issue. We explain this more clearly now. The depositional setting has been oxic and considered to be an open oceanic setting with low sedimentation rate and carbon lean sediments. Oxygen penetration must have been more than a few centimeters. The oxygen exposure time must have been long and organic matter mineralization extensive. Considering the marine environment, probably the most common state is that the sediments are oxic beyond a few cm from the surface. With oceanic sedimentation rates this accounts easily for centuries to millennia of aerobic degradation which considering the low OM input from above produces OM poor oozes. In large parts of the Pacific oxygen penetration reaches even decimeters to meters below the sediment surface and even may reach the basement. Only in upwelling and shelf regions, mostly near the continental margins, this may be different but also here, bioturbation often significantly extends the oxygen exposure time of the sedimentary organic matter.

In conclusion. I would like the authors to nuance in their abstract, title and throughout the distinction between kerogenisation and in situ polymerisation with respect to preservation without it. Finally, I don't think that the dichotomy between 'euxinic' and 'oxic' is true given that sediments quickly become anoxic soon after deposition and dinoflagellates would survive the initial oxic conditions that would have been existing in the subsurface.

We elucidated that kerogenisation is diagenetic crosslinking as is in situ polymerization. The difference lies in the word polymer. A biopolymer is macromolecule that exists of repeating units of relatively simple molecules (biological monomers). In contrast to synthetic polymers small variations between the monomers are allowed (e.g. DNA, polypeptides, polysaccharides). We do not make this distinction for the above-mentioned reasons.

With respect to the preservation of organic-walled dinoflagellates there is a very strong difference in preservation potential between the different groups of dinoflagellates, with the most labile cyst types degrading under suboxic conditions and the most refractory cysts hardly degrading after millennia oxygen exposure (for a recent overview see

Zonneveld, K. A. F. Gray, D. D. Kuhn, G. and Versteegh, G. J. M., 2019. Postdepositional aerobic and anaerobic particulate organic matter degradation succession reflected by dinoflagellate cysts: The Madeira Abyssal Plain revisited. *Marine Geology* 408, 87-109).

We deliberately analysed a degradation resistant cyst species to avoid the problem that the species would have been entirely mineralized in the Kerguelen Plateau sediments. Therefore, I would focus on the nature of kerogenisation and how this complicates investigation of original biosignatures endogenous to a microfossil. Describe and discuss kerogenisation and therefore how an investigation of tissues in euxinic settings need to evaluate degrees of kerogenisation before doing other chemical analyses, such as isotope composition or more superficial chemical analyses, such as FTIR, RAMAN, TOF SIMS or similar, as they would characterise a mixed bag of molecules. This, I think, would make for an interesting comparison and a study I would find useful.

We would like to point out that this paper is not primarily on what happens with organic matter in euxenic settings and that we did FTIR.

Best wishes,

Gerard Versteegh