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Interactive comment on "A 21,000 year record of organic matter quality in the WAIS Divide ice core" *by* Juliana D'Andrilli et al.

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RC1

The reviewer comments are numbered for reference. Each reply is listed below the numbered reviewer comment.

1.Title and text. The term "organic matter quality" seems to be not adequate to describe the measurements here reported. Really, just fluorescence measurements were carried out and interpreted as signatures of some classes of organic components-like markers. I'd suggest the term "organic matter markers" or "organic fluorescent components".

Fluorescence measurements were carried out and interpreted as signatures of organic

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components. The chemical nature of the fluorescent fraction of the organic matter was surveyed using a fluorescent technique, thus organic matter markers is an appropriate alternative for the title and text. In the organic matter community, the words/phrases quality, composition, and chemical nature are interchangeably used to infer the same meaning from fluorescent measurements. We aim to define organic matter markers appropriately in the text to clarify any confusion and improve compatibility with both the ice core and organic matter characterization communities.

2. Line 17 and several other points. Usually, time unit is expressed as “kyr” and not as “kyrs”. Please, correct in the text and figures.

We will make this adjustment accordingly.

3. Lines 20-22. Here or in the “Results” section, Authors should clarify what They mean with the terms “labile microbial OM”, “recalcitrant OM”, “bioavailable carbon species” etc. A very short description of these terms could help the reader in better understanding the different biological significance and the different availability in carbon exchange between cryosphere and other ecosystems.

Towards the point mentioned earlier, the descriptions of labile (easily altered) and recalcitrant (less easily altered) descriptions will also help clarify the terms organic matter markers in the manuscript. We will make this edit in the appropriate sections.

4. Line 32. Please, cite also Wolff et al., Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles. Nature, 2006, Vol. 440, 491-496, doi:10.1038/nature04614.

We will make this adjustment accordingly.

5. Lines 51 and following. What “OM character” means? Chemical composition? Chemical-species or functional groups identification? Authors are requested to clarify their thought.

We will provide descriptions as already mentioned above.

6. Line 55. Even methane formed in anaerobic conditions is a strong forcing factor in the warming climate.

Would the reviewer clarify what is meant by this comment? We describe the release of organic material upon melting of polar ice and the potential for it to be metabolized to carbon dioxide, thus increasing greenhouse concentrations in the environment. Indeed, the anaerobic production of methane is also a strong forcing factor in a warming climate. We have only inferred aerobic production of carbon dioxide in this sentence. Is the reviewer describing the potential for methane to be produced under anaerobic conditions in the ice, and then released as gas?

7. Line 72. Since snow density is variable, it is better to express the mean accumulation rate as cm or mm “water equivalent”.

The accumulation rate is provided as cm per year. What is the significance of using “water equivalent”?

8. Line 80. Please, change “drilling solvent” with “drilling fluid”.

We will make this adjustment.

9. Line 88. Please change “combusted” with “pre-fired”.

The usage of combusted to describe furnace glassware is common in the organic matter community. What is the significance of using “pre-fired” instead?

10. Section 2.4. Even if a reference is cited, Authors are requested to give some basic information about the PARAFAC multivariate analysis.

This section was truncated upon a previous revision. Basic information can be provided. 11. Lines 126 and 128. Authors are requested to shortly describe the characteristics of “bioavailable carbon species” and “more recalcitrant species”.

We will describe these phrases in further detail to clarify.

12. Lines 129-131. This early Holocene peak of fluorescent mater is interesting, as well as the larger peak around 21-22 kyr BP. Authors do not discuss these two features in the temporal profile of the WD ice core. I'd like to know the Author interpretation on these large depositions of organic fluorescent compounds, even if as a tentative hypothesis. It should be very interesting to perform some qualitative analysis (e.g., by HPLC-MS measurements) on these samples in order to clarify the nature of the fluorescent compounds.

The fluorescent peaks were discussed as intensity shifts in each climate period, and do not directly correspond with large depositions of organic fluorescent compounds. Rather, the quantum yields of specific fluorescing material is represented, along with the hypotheses that both fluorescing material and concentration of organic material may be contributing to shifts in fluorescence intensities. Large deposition events of organic material cannot be linked to shifts in fluorescence intensities. This point can be clarified further in the text. Regarding the Holocene peak, the authors described a series of years that correspond to that shift in fluorescence, again not related to one event or year. Any anomalies, increases, or even decreases in chemical concentrations, dust, etc. in the WD data set were surveyed to support a tentative hypothesis for this signature, however, none were identified. Further analyses of these samples is unavailable.

13. Lines 132 and following. I surely do not want to minimize the contribution of the PARAFAC analysis, but I have to note that the result of its application is quite basic. From Figure S1, the separation of the fluorescent bands at 420 nm Em and 300 nm Em is very clear even without any multi-parametric analysis. The only significant result is the identification of two fluorescent components C1 and C2 at short Em and Ex wavelength. However, the two components are just attributed to two large organic compound classes (amino acid-like fluorescent compounds), without a more specific characterization. Besides, the C1 and C2 fluorescent components are not clearly differentiated in terms of biological origin: C1 is attributed to tyrosine-like fluorescent

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compounds associated to “microbial processing in aquatic environment”, while C2 is described as a fluorescent signature overlapping “between tyrosine- and tryptophan-like” fluorescent compounds. At line 177-178, Authors just report that C2 containing tryptophan-like fluorescence could represent “intact dissolved proteins ....freshly derived from microorganisms”. Authors are requested to better organize, in the present section, the discussion on the possible origin of these components and to enlighten the biological and environmental differences. In conclusion, the PARAFAC analysis seems to be not able to “resolve the representative subset of samples into individual OM fluorescing components”, as the Authors assessed at lines 132-133. Even the comparison with the OpenFluor database components did not give significant matches (if I have well understood lines 153-155).

The separation of the fluorescent bands at 420 nm Em and 300 nm Em is very clear even without any multi-parametric analysis. This is correct, however Figure S1 highlights examples of different types of fluorescing organic matter, so it was our intention to show notably obvious differences from the WD core. The WD core fluorescent data set comprised a small fraction of material fluorescing in Figure S1 (b), thus we needed to apply a statistical tool, PARAFAC analysis, to decompose the EEMs into individual fluorescing components, even for fluorescing material at lower Ex/Em wavelength pairs. The significant result is that PARAFAC was used as a multiparametric tool to decompose the EEMs data set into three fluorescing components. That information was subsequently used to identify the chemical character of the fluorescing organic material in each climate period. “Besides, the C1 and C2 fluorescent components are not clearly differentiated in terms of biological origin: C1 is attributed to tyrosine-like fluorescent compounds associated to “microbial processing in aquatic environment”, while C2 is described as a fluorescent signature overlapping “between tyrosine- and tryptophan-like” fluorescent compounds.” That is the correct interpretation and C1 and C2 fluorescing components cannot be clearly differentiated in terms of biological origin using this fluorescence technique. More specific characterization of C1 and C2 fluorescing components cannot be determined using this bulk analytical technique. This

can be clarified in the text. The chemical species associated with PARAFAC C1 and C2 were discussed in the text providing a bulk representation of the organic materials present throughout 21,000 years. This sets the foundation for future work, a point which can also be clarified in the text. “Authors are requested to better organize, in the present section, the discussion on the possible origin of these components and to enlighten the biological and environmental differences.” The discussion on the possible origin based on these data is present in the manuscript, highlighting environmental differences over time. “In conclusion, the PARAFAC analysis seems to be not able to “resolve the representative subset of samples into individual OM fluorescing components”, as the Authors assessed at lines 132-133. Even the comparison with the OpenFluor database components did not give significant matches (if I have well understood lines 153-155).” The authors disagree. The PARAFAC analysis resolved the representative subset of samples into the only individual OM fluorescing components that were present in the samples. PARAFAC analysis is capable of producing brilliant results of the data set asked of it. With most EEMs resulting in the example provided in Figure S1, it was not surprising to have the low Ex/Em wavelength fluorescent components modeled as two individual components C1 and C2, prior to C3. The order of the modeled components describes the variation in the data set, and was statistically validated with the drEEM program in MATLAB. The OpenFluor database contains various data sets from samples collected around the world. OpenFluor is not a requirement, and is currently still in its growing phases. Scientists are encouraged to upload their PARAFAC datasets upon publication, but it is not required, thus the database is does not encompass all possible fluorescent component data. OpenFluor matches with the dataset describe PARAFAC components that have been identified in other ecosystems. A match or no match describes unique data worth reporting. We felt it was interesting to report that organic material from 6,000 to 27,000 years ago did not match any of the uploaded PARAFAC data currently in the database. Our dataset is the first of its kind from a continuous Antarctic ice core, thus we stress the importance of its upload to OpenFluor upon publication, which in turn will better serve the fluorescent community.

14. Lines 142-143. The terms “red/blue shifted to longer/shorter Em wavelengths” are repetitions. Please, change in “Em-wavelength red/blue shifted” or “shifted to longer/shorter Em wavelengths”. Authors should clarify the statistical significance of these shifts (especially from LGM to LD) and anticipate the consequent biological meaning (especially from LGM-LD to Holocene). Besides, which is the meaning of the red or blue shifts? When blue (red) shift occurs, is the C2 component a marker of tyrosine-like (tryptophan-like) fluorescent compounds?

We can make this adjustment accordingly to clarify the chemical meaning regarding organic matter characterization. A red shift in C2 describes organic matter markers that share similar chemical nature with tryptophan-like species, whereas a blue shift describes more tyrosine-like material.

15. Section 3.2. The relationship between glacial cycles and atmospheric deposition of dust in Antarctica is a very relevant and largely discussed topic in ice core studies. Here, the Authors have to take for granted the inverse relationship between site temperature and dust deposition (by citing the most relevant references) and anticipate the discussion on the possible relationships among temperature, dust and biological activity (or OM transport efficiency), as revealed by the fluorescence temporal profile. At this purpose, Authors should choose the preferred dust indicator among the possible dust markers measured along the WD ice core (nss-Ca, Mn and Sr), also basing on the correlations between the elements (lines 165-166).

The preferred dust indicator of nss-Ca will be highlighted in the discussion section to improve clarity. We will also extend our observations to discuss relationships among temperature, dust, and biological activity relevant to organic matter characterization.

16. Lines 174 and 176. Maybe, “throughout time” is better than “throughout history”.

We can make this adjustment accordingly.

17. Line 198-200. Common transport processes of dust and OM could be hypothe-

sized only if dust and OM originated from the same continental areas. In LGM, Southern South America was supposed to be the major dust source area for Antarctica. In LD and, especially, Holocene, even Australia could have played a significant role. Therefore, Authors implicitly suppose that OM was originated in these continental regions. For OM originated by marine sectors (C1, C2?, part of C3), the relationship with dust transport processes cannot be considered significant because they can follow very different pathways (e.g., implying different meridional or zonal atmospheric circulation modes).

We can clarify this point in the text accordingly.

18. Lines 200-201. Authors here refer on relationships between dissolved organic carbon and dust markers. I suppose DOC measurements were not performed as part of this paper (see following sentence in the text). Authors should give more information on that or cite some reference.

DOC concentration measurements were not performed as a part of this paper. Some of our preliminary data include DOC concentrations of the upper firn layers of the WD ice core, which were measured simultaneously with concentrations of nssCa and Sr. We can provide information on how dust and DOC concentrations relate, however do not have this information for the main project.

19. Line 204. I think Authors refer to Figure 4.

Indeed, we did. Thank you. We can make this edit.

20. Lines 205-212. This part has to be completely revised. The complex relationship between dust deposition in Antarctic ice cores and climatic cycles cannot be discussed in this form in this paper and, how I have already pointed out, has been (and will be) the topic for several specific papers. Authors are requested to report the major literature references about LGM-LD-Holocene dust/climate pattern and focus the discussion on the relationship among climate, dust (possibly) and OM fluorescent markers. Besides,

I have to note that the detail in the discussion on the behavior of OM data and dust profiles along the WD ice core is not so high to appreciate specific differences in nss-Ca, Mn and Sr profiles. Therefore, since the three dust-marker profiles were not singularly discussed and differentiated, I'd suggest to replot Figure 4 with just one dust marker (maybe, nss-Ca).

One dust marker will be presented and discussed relevant to the transport of organic matter.

21. Section 4.3. Even this section has to be largely revised. Authors assume a series of speculations to correlate changes of OM fluorescent markers to changes in climatic and environmental conditions, as evaluated by changes in sea-ice coverage (by ss-Na – Authors could add the ss-Na profile in figure 4), dust production and transport (by dust markers) and volcanic eruption frequency (by nss-SO4 spikes) in the LGM, LD and Holocene. However, no reliable comparison among the different time profiles is shown. In particular, while dust and sea ice markers show a progressive decreasing during the LD, the OM fluorescent profile shows an abrupt change (at about 18.5 kyr BP) from high LGM values and very low LD and Holocene levels. All the discussion is too elemental and also the changes in C1 and C2 relative contributions are not clearly interpreted. From the data here reported, I can just see that OM fluorescent markers are high in the LGM, when dust and sea spray are high. However, there is not experimental evidence on which climatic or environmental factors (more efficient meridional or zonal atmospheric transport, larger sea ice coverage, higher input from continental areas, larger emissions from marine biota, etc.) could have driven the OM deposition at the WD site. Finally, the relationship between volcanic activity (as recorded by the nss-SO4 spikes along the WD ice core) and OM fluorescent markers is, in my opinion, really unsustainable. Volcanic signatures in Antarctic ice core are mainly related to long range atmospheric (especially stratospheric) transport of SO2 emitted during eruptions occurred at hemispheric scale and it is really difficult to correlate changes in WD OM to sporadic, short-time and widespread volcanic emissions without a strong experimental

evidence.

Agreed. The co-registered geochemical WD dataset were used to speculate on the origin of the OM characterized by fluorescence spectroscopy. No direct comparisons were reported because none were available for this project; that was beyond the scope of this work. We can clarify this point in the manuscript. Further comments will be organized for the formal response letter.

22. Lines 225-226. What this sentence means? What is compared to the open ocean?

The authors meant to state a comparison of more to less sea-ice extent. We can revise this accordingly.

23. Lines 233-234. Authors are requested to better discuss the red shift of the C2 component, explaining which amino acid-like components increases its contribution to fluorescent OM and at which biological source can be attributed. What "external environments" means?

The red shift clarification will be added as stated above. "External environments" will be revised to clarify that the material originated externally from the englacial ecosystem.

24. Lines 237-243. The pattern of the OM fluorescent markers during the ACR is not visible in Figure 3 (neither in Figure 2). This part is merely speculative and not supported by experimental evidences.

Correct. The dust record was used in Figure 4 as a discussion point to speculate on the variation in organic matter during the ACR, specifically for PARAFAC C2 in the deglaciation.

25. Lines 244-250. How can the Authors explain the very low levels of OM fluorescent markers during the Holocene, when climatic conditions should promote higher terrestrial and marine biological productivity? Which could be the significance of the large spike in OM fluorescent profile (Figure 2) at about 10 kyr BP?

This is a great question, however, it is the intensities that are plotted in Figure 2, thus neither describing high or low levels of OM fluorescent markers, merely just their fluorescent intensities. Fluorescent intensities can be linked to highly or lowly fluorescent material and also chemical concentrations. Without chemical concentrations of OM, we can only speculate to that point. Higher terrestrial and marine biological productivity during the Holocene, as we may assume in the warmest climate for this project, may result in higher fluorescence intensities and different fluorescing OM chemical species in the environment, however, if they are not transported to the WD core, we have no way to detect them with these methods in englacial ice. We cannot discount that carbon productivity is reportedly higher in the Holocene, however, that does not ensure efficient transport of materials to Antarctica. We can thus report our findings and discuss these ideas with the need for future investigations that could answer such questions.

26. Lines 261-262. Authors are requested to clarify how volcanic activity can stimulate OM production. How is calculated the percentage of the fluorescent OM attributed to the volcanic activity? The relationship between volcanic activity and OM deposition at WD site is, in my opinion, not plausible and not supported by experimental data (at least, by experimental data here reported). Have the Authors measured OM fluorescent peaks in ice core sections with volcanic depositions? In absence of experimental support, the discussion about the volcanic activity and OM fluorescent markers should be removed from the manuscript.

Indeed, we do not have experimental support, merely just speculations here.

27. Conclusions section. This part should be changed accordingly to the changes suggested along the different manuscript sections.

This section will be revised accordingly.

All other comments will be addressed in our formal response letter. This response was provided by the lead author based on conversations with a subset of coauthors.

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