

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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Received and published: 9 February 2017

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. Proposed title revision, “A 21,000 year record of organic matter markers in the WAIS Divide ice core.”

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.

All time units listed as “kyrs” will be adjusted to “kyr” in the text and figures.

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, these descriptions will also help clarify the terms organic matter markers in the manuscript. Labile OM/bioavailable carbon species are both defined as the fluorescent fraction considered to be easily altered by microorganisms, whereas recalcitrant OM refers to the chemical species that are less easily altered in the environment. We will make these edits 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.

As per this suggestion, we will make this adjustment accordingly.

5. Lines 51 and following. What “OM character” means? Chemical composition?

C2

Chemical-species or functional groups identification? Authors are requested to clarify their thought.

As mentioned above, we will provide appropriate definitions and descriptions. Chemical composition will be discussed in the manuscript as the fluorescent nature of the OM, along with specific details corresponding to higher/lower molecular weights, aromaticity, reactivity, and potential functional groups identified.

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

Could 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".

We will change this to average annual accumulation rate 0.207mweq a⁻¹ (Banta et al., 2008).

8. Lines 74-76. What means this sentence? Several other ice cores (for instance, Taylor Dome and Talos Dome, in the same Antarctic Sector; Dome C and Dome Fuji, in the inner Antarctica; Dronning Maud Land, in the Atlantic Sector; etc.), even drilled before WD ice core, constitute "equivalent paleoclimate record" to Greenland ice cores. In particular, the EDC, EDML and DF climate records were compared with the climate oscillations recorded along the NGRIP ice core in: EPICA Community Members, Oneto-one coupling of glacial climate variability in Greenland and Antarctica. Nature,

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2006, Vol. 444, 195-198, doi:10.1038/nature05301.

We acknowledge that other ice cores were investigated in Antarctica to be equivalent paleoclimate records to Greenland ice cores. We will edit the text to clarify this point, providing appropriate references, and delete the claim previously stated.

9. Line 80. Please, change "drilling solvent" with "drilling fluid".

"Drilling solvent" will be edited to "drilling fluid" in the text.

10. Line 88. Please change "combusted" with "pre-fired".

The usage of the word "combusted" to describe furnaced glassware is common in the organic matter community. "Pre-fired" is a suitable alternative and can be edited in the text.

11. Section 2.3. The correction for the absorbance measurements seems to be not clear. Authors are asked to give more information on that. Besides, the absorbance threshold seems to be quite high. If a.u. means, as I think, absorbance unit, the value $A = 0.3$ corresponds to a percentage transmittance of 50% ($A = \text{Log } 1/T$) that seems to be too low for ice-core melted water at 254 nm. Maybe, some particles were suspended or some gas bubbles were present in the melted samples during the measurements. Authors are requested to clarify this point.

We can report that all of our samples were optically dilute.

12. Line 97. Maybe the term "optically dilute" could be changed in "optically transparent" (but I do not think that this term is correct for $T\% = 50\%$).

The term "optically transparent" can be edited in the text.

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

Basic information on the setup of our analyses will be added to the manuscript.

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14. Section 2.5. Authors should here anticipate why some elements were considered in this paper (e.g., nssCa as crustal marker, ssNa as sea spray indicator, nss-SO₄ spikes to identify volcanic deposition signatures, etc.). Besides, more detail is requested in calculating the ss- and nss- fractions of Na, Ca and SO₄. Since both Na and Ca can be related to two main sources (sea spray and dust), a four-equation system is necessary to calculate the ss- and nss- fractions (particular attention has to be put in evaluating ssNa during the LGM and nss-Ca during Holocene). Finally, which sea water ratio was used for the calculation of ss-SO₄? Have the Authors used the SO₄/Na seawater ratio of 0.25 or a lower value?

The crustal marker nssCa will be highlighted in the manuscript instead of three crustal indicators, and appropriate references will be provided to strengthen why some elements were considered for this work. The sea spray indicator (ssNa) and calculation information are referenced already in the text: Bowen 1979, WAIS Divide Project Members 2013.

15. Lines 126 and 128. Authors are requested to shortly describe the characteristics of “bioavailable carbon species” and “more recalcitrant species”.

Similar to the third comment above, these descriptions will strengthen the scope of the manuscript and the usage of “organic matter markers” in the text. Labile OM/bioavailable carbon species are both defined as the fluorescent fraction considered to be easily altered by microorganisms, whereas recalcitrant OM refers to the chemical species that are less easily altered in the environment. We will make these edits in the appropriate sections.

16. 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.,

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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 not possible as only 7.5mL of each sample were available and have been used in the present analyses. It is our intention to remove this figure upon revision.

17. 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 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 de-

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rived 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 categorized to identify the chemical character of the fluorescing organic material characteristic of each climate period. RC1 Comment: "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." 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, however possible chemical species can be suggested. 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. RC1

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Comment: "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. RC1 Comment: "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. Submission of data to 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 it contains 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.

18. 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

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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 have longer emission wavelengths, therefore correspond to higher molecular weight chemical species that are potentially more aromatic than materials that fluoresce at shorter wavelengths.

19. 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).

Relationships between dust markers and temperature will be further explained regarding OM transport efficiency. Without concentrations of OM investigated for this project, we were only able to speculate on the relationships between dust concentrations and OM transport efficiency, since we cannot directly relate higher concentrations of dust to higher concentrations of OM. Thus, the OM character reported in this project was discussed in terms of the influence of dust concentrations for the different climate periods. We highlighted that different types of OM were observed for higher and lower concentrations of dust. Three dust markers were presented in this project so that the reader may see different indicators of continental influences. Trends among all three

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can be discussed in further detail upon revision, or the records of Mn and Sr can be removed so that our results focus on the influence of the nssCa dust indicator with OM character (e.g., chemical species and characteristics).

20. Lines 174 and 176. Maybe, "throughout time" is better than "throughout history".

We can make this adjustment accordingly.

21. Line 198-200. Common transport processes of dust and OM could be hypothesized 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).

Common transport processes of OM were only hypothesized, and we inferred a local South American major dust source region for Antarctica. We cannot predict the origin of our OM, but rather make hypotheses and suggestions based on our dataset. We can clarify that point for dust and continental OM from the South American southern region, and separately discuss marine origins having different pathways.

22. 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 concentrations were not performed as part of this work. Correlation values can be presented from the preliminary data that is unpublished. Preliminary data was provided in the Supplemental section and will be referenced accordingly.

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

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

24. 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 (nssCa) will be presented and only discussed in terms of the fluctuations of dust concentrations with the different OM chemical species present in different climate periods. This section will be completely revised to reflect these points.

25. 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

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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.

The authors agree. 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. The PARAFAC components C1 and C2 relative contributions can be discussed in terms of percentages relative to the other components. See above responses outlining our PARAFAC component discussion section in further detail. The sections outlining the volcanic signatures is highly speculative and will be removed upon revision.

26. 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.

27. 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

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revised to clarify that the material originated externally from the englacial ecosystem.

28. 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 OM character during the ACR, specifically for PARAFAC C2 in the deglaciation period. We can revise this section to clarify our speculation.

29. 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.

30. Line 258. Please, change "Concentrations of nss-sulfur. . ." with "Spikes in nss-SO4 concentrations. . ."

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The sections outlining volcanic activity discussed in terms of OM character will be removed.

31. 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 on this topic. Volcanic activity discussion sections will be removed accordingly.

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

This section will be revised accordingly based on all the reviewer's comments.

A revised Figure 4 is provided for consideration.

Interactive comment on Clim. Past Discuss., doi:10.5194/cp-2016-119, 2016.

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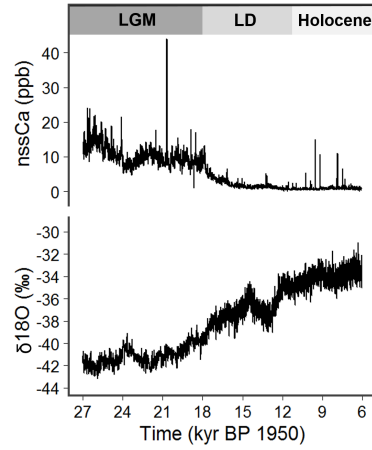


Figure 4. Trace element concentration of (top) non-sea salt calcium (nssCa; ppb), and the $\delta^{18}\text{O}$ (per mil) temperature record (WAIS Divide Project Members, 2013) from the West Antarctic Ice Sheet Divide ice core as a function of time (kyr before present 1950), dating from the Last Glacial Maximum (LGM), through the last deglaciation (LD), to the mid-Holocene.

References

WAIS Divide Project Members (2013) Onset of deglacial warming in West Antarctica driven by local orbital forcing. *Nature* 500, 440-444.

Fig. 1. Figure 4. Trace element concentration of (top) non-sea salt calcium (nssCa; ppb), and the $\delta^{18}\text{O}$ (per mil) temperature record (WAIS Divide Project Members, 2013) from the West Antarctic Ice Sheet Divide