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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.

Anonymous Referee #1

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Comments to the paper J. D'Andrilli et al. A 21,000 year record of organic matter quality in the WAIS Divide ice core.

General Comments

The paper is concerning the stratigraphy of some organic matter markers (fluorescence signatures) along ice core sections from the WAIS Divide ice core (West Antarctica) covering the LGM, Last Transition and early-mid Holocene climatic periods. The topic is very interesting for ice core scientific community because measurements of organic matter (OM) or OM markers, as well as organic carbon, are very scarce in Antarctic ice cores and every new record, especially if obtained at high resolution, is useful in understanding the complex interactions between biological activity and climatic changes. However, the manuscript presents several weak points and, in my opinion, a deep re-

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vision is necessary before it can be accepted for publication on Climate of the Past journal. The main criticisms are discussed in the “Specific and minor Comments” section end are concerning: 1. the results of the PARAFAC method; 2. the relationship between C1, C2 and C3 PARAFAC components with the different climatic periods; 3. the relationship between OM markers and dust deposition; 4. the relationship between the OM markers and volcanic activity. Besides, some methodological aspects have to be clarified. As a conclusion, in my opinion, the manuscript is not ready to be accepted for publication on CP in this form, but I’d like to encourage the Authors to re-submit a new improved version because their high-resolution measurements of OM markers are potentially very interesting in the paleoclimate studies.

Specific and minor comments.

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”.

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

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.

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.

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

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

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

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, One-to-one coupling of glacial climate variability in Greenland and Antarctica. Nature, 2006, Vol. 444, 195-198, doi:10.1038/nature05301.

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

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

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 = 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.

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%).

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

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 taking into account the possible contribution of frost flowers as sea salt source?

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

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.

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

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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 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).

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?

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).

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

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 MO 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).

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.

Line 204. I think Authors refer to Figure 4.

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).

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.

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

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?

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.

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?

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

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.

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

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