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Climate of the Past
Discussions

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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RC3 The reviewer comments are numbered for reference. Each reply is listed below the numbered reviewer comment.

1. The first weakness of the manuscript is the use of poorly defined wording rendering difficult (sometimes obscure) the reading of the manuscript. For instance, I guess that, when saying "OM quality", you mean "fluorescent signal of the OM"? Also what is a recalcitrant OM?

Fluorescence measurements were carried out and interpreted as signatures of organic 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, as recommended by Reviewer #1. 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 the terms used more appropriately upon revision to clarify any confusion and improve compatibility with both the ice core and organic matter characterization communities.

2. Some abbreviates appear in the text without definition. For instance, what is the PARAFAC model that is already mentioned in the abstract, also please indicate what is the basic of this kind of model?

A definition of multivariate parallel factor (PARAFAC) analysis will be edited in the abstract and basic information can be provided about the analysis in the main text.

3. The abbreviates C1, C2 and C3: I guess that they refer to component 1 etc (and not to C1 carbone chain etc).

Correct. The annotation of the abbreviation is set first in Line 135, but can also be annotated in the abstract for clarity.

4. In section 2.3, please define A254 and re-define EEMs here.

A definition of A254 (absorbance at 254nm) will be provided. The acronym “EEMs” is defined in the Introduction section.

5. Section 2.4: I don’t understand the following sentence “A three component PARAFAC model was generated for the subset of samples by drEEM and the N-way toolbox scripts Âż : what is Âń drEEM Âż and N-way ?, please define.

Definitions of each can be provided along with the currently listed reference. “drEEM” is an acronym for a commonly used PARAFAC modelling tool created by Murphy et al. “Decomposition routines for Excitation Emission Matrices” version 0.1.0. The package is compatible for MATALB users, and contains a plethora of MATLAB scripts written to specifically characterize complex OM mixtures worldwide using fluorescence spectroscopy datasets.

6. Concerning units: Line 98 : what is au ?

The unit description was not provided. Absorbance units will be annotated to clarify the definition of a.u. in the text.

7. I will avoid the use of RU for Raman unit (RU is sometimes used for relative unit). Also I am not sure that the readers of CP, specially those working on ice cores, are familiar with this Raman unit ? A few words on that would help (see also my comment on Figure 2).

Raman Units (R.U.) are the technical unit from the fluorescence instrument and are appropriate for this work. A definition and explanation in a few words will be added upon revision.

8. Introduction, first paragraph (lines 31-446): This paragraph can be improved significantly, for both the wording and the cited references. Two of your co-authors have a nice expertise on the chemistry of ice cores, they certainly can also help here. From my side I would suggest to start with an overall sentence: “In addition to its water stable isotope content that provides a proxy record of past temperature (see Dansgaard et al. (1993), for instance), ice archives atmospheric information on trace gases like CO2 and CH4 encapsulated in air bubbles and chemical species trapped in the ice lattice. Numerous inorganic species trapped in ice has been used to reconstruct past chemical composition of the atmosphere, its recent change in response to growing human activities as well its past natural variability (see Legrand and Mayewski for a review).”

We appreciate the suggested wording changes and will update the text accordingly.

9. I here agree with another reviewer of the manuscript that the Nature paper from Wolff and co-workers (2006) is an excellent example that you have to mention of what was done on deep Antarctic ice cores in terms of changing sea-ice dust emission and marine biological productivity over the 8 climatic cycles. Then focus on what was done on organics saying “In contrast, as reviewed by Legrand et al. (2013), information on

the load and composition of the organic matter archived in ice are still very limited."

Indeed, we will incorporate the reference and the suggested phrasing into the revised manuscript.

10. I think you can find in this review paper relevant references that can be useful for your introduction. In particular, I suggest to report the work from Amanda Grannas made of the nature of OM in polar ice and those done on the HULIS like content of ice.

Grannas' work involved sampling snow events to test OM photoreactivity, therefore, modern events, but at some point in time, so were the WD ice core samples. Upon revision of the introduction, this may be a good addition to cite as OM in polar ice is still in its infancy.

11. Section 2.1.: line 75: WD is not at all the first Antarctic ice record available for comparison with Greenland records. Please modify the text.

The text will be modified upon revision.

12. Section 2.2: line 86: what is the difference between cracks and fractures?

This is a good question. We can revise this statement to include the difference between a section of ice that contained a break in the continuity (crack), versus a section that was broken all the way through (fracture).

13. Section 2.5: Please write a few sentences explaining why your choice was to show these inorganic species. Note that, as far as I know (and checking your fig 4), I see no reason to use three species (Mn, Sr, and Ca) for dust (except if you have in mind to discuss the ratio between the 3 in view to eventually highlight the source region, which seems not to be the case).

We will revise the manuscript to report nssCa as our dust marker for this work.

14. Figure 2: Are there any possibility of estimate from the Raman values how much is the concentration of OM? Indeed, given the scarcity of data on organics, even an order

of magnitude would be welcome here. From that and using a typical conversion factor OM/C you can estimate the TOC or DOC content of ice. Also I am surprised that the spikes shown in the fluorescence intensity during the LGM are not more commented in the text.

Regarding the Holocene peak, the authors described a series of years that correspond to that shift in fluorescence, which are 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. Upon revision of the manuscript, this Figure will be removed and an updated figure for the PARAFAC model and variation will be provided.

15. Line 184-195: I assume that “Humic-like fluorescent OM” corresponds to Humic like substances observed in the atmosphere of many regions. If correct, did you consider these species as primary emitted (with soil particles for instance) or secondary produced from oxidation of gaseous organic precursors emitted by the continental biosphere (vegetation)?

Those are good considerations and can be clarified as speculations in the discussion section accordingly. Unfortunately, our methodological limitations prevent us from differentiating the two categories, but an acknowledgement to that point can be added in the text.

16. Section 4.2: Your discussion on change of dust tracers is quite oversimplified and I would recommend you to revisit previous works done on this topic.

This section will undergo considerable revisions to highlight the usage of the dust tracers to supplement the results of the WD OM characterization work by fluorescence spectroscopy. We aim to use this information to better understand the different environmental changes over the three climate periods.

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17. Lines 255-265: This discussion is from my point of view rather confusing. It is incorrect to say that nssS concentrations are used to trace back volcanic eruptions. Only the narrow peaks of nssS are related to volcanic eruptions whereas the background nssS level in Antarctica originates in marine biogenic emissions (please revisit here the paper from Wolff et al., 2006 for instance). Also, I don't think that the wording of the following sentence makes sense ”Therefore, volcanic eruptions increase the potential for particles and chemicals to be transported to polar regions and deposited onto ice-sheets.” Please modify.

This section was purely speculative and without any experimental results connecting the OM character with volcanic activity, this section will be removed from the manuscript upon further revisions.

18. Supplementary material: Following your line 201 on a correlation between DOC and nssCa, I checked the S2 figure (extracted below) that strongly bothers me. Indeed, if the DOC unit you report is correct, DOC levels of this Antarctic ice are as high as 200 μM. If I am right that means 12*200 μg L-1 i.e. 2400 ppbC. If correct, please comment with respect to the review of Legrand et al. (CP, 2013). It is very likely that you have a large DOC contamination in this shallow WD core. Also, sorry but I don't see a good correlation in this figure between dust and DOC!!! Please comment.

Correct. The shallow WD core DOC concentration numbers are a cause for concern. We cannot validate how this data could have resulted from contamination or is a reflection of surface DOC concentrations and processes. Therefore, we will remove this information from the Supplemental Information section. Upon revising the manuscript, using only nssCa for a discussion on the dust concentration changes with climate, these Supplemental figures are no longer relevant. A discussion linking Ca and Sr to DOC concentration will no longer be a focal point of the manuscript, therefore this material will not be used.

A new Figure 4 is provided for consideration.

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

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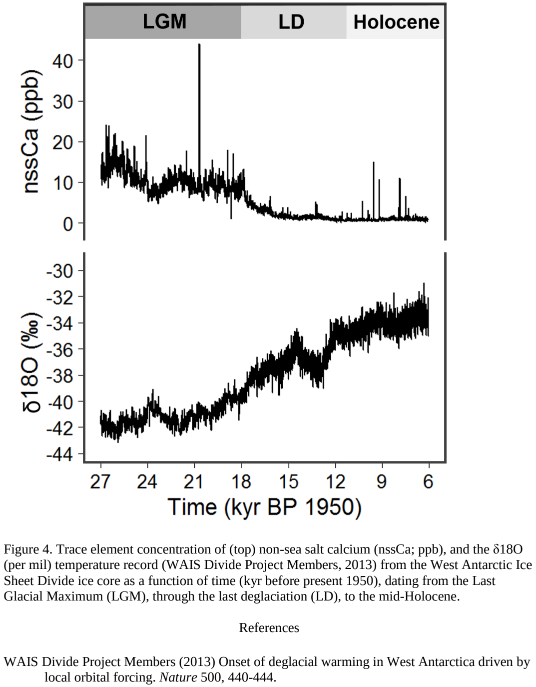

Figure 4. Trace element concentration of (top) non-sea salt calcium (nssCa; ppb), and the δ18O (per mil) temperature record (WAIS Divide Project Members, 2013) from the West Antarctic Ice Sheet Divide ice core as a function of time (kyr before present 1950), dating from the Last Glacial Maximum (LGM), 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 δ18O (per mil) temperature record (WAIS Divide Project Members, 2013) from the West Antarctic Ice Sheet Divide

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