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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 analysis (PARAFAC) 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 will be provided. EEMs are defined in the Introduction section. Why would another definition be necessary here?

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 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 char-

acterize 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.

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).”

These revisions are greatly appreciated and will be considered at length upon editing the manuscript.

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. Âż

Indeed, we will incorporate this 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 2.2: line 86: what is the difference between cracks and fractures?

This is a good question. Is there a technical definition, or should we just revise this to list one? We can revise this statement to include the difference between a section of ice that contained a break in the continuity, versus a section that was broken all the way through.

12. 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).

The text will be revised to discuss the dust maker of Ca for clarity.

13. 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 unavailable.

14. 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.

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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