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

1. Line 88. When I have investigated the use of 'septa sealed vials', I find a contaminant fluorescent signal coming from the septa, which in my tests has always been fluorescent. Can the authors confirm that their septa sealed amber glass vials produced zero fluorescence blanks?

We cannot confirm that our septa sealed amber glass vials produced zero fluorescence blanks. We specifically selected septa seals made with Teflon to avoid any carbon and

fluorescent contamination. What type of septa produce fluorescence? What kind of fluorescent signal was detected? If we had fluorescent contaminants originating in our septa, wouldn't that signal be consistent across all our samples? We will edit the text to clarify Teflon septa sealed amber glass vials.

2. Line 89-90. Following on from my previous comment, were the blanks run just on the melting system, or the melting system and amber glass vials? It is not clear at present.

Blanks were run through the melting system. Blanks were not collected into the discrete sample vials individually, however we have run blanks on combusted amber vials and do not report fluorescence. This will be clarified in the text. Blanks were also run through the melting system into a targeted ultraviolet biological sensor (TUBS) spectrofluorometer, which uses an excitation wavelength of 224nm and collects emission from 280-400nm. All readings of blanks through this unit showed no fluorescence within the 280-400nm emission range, characteristic of dissolved organic material.

3. Line 97. What was the actual absorbance values? These should be plotted as a time series, as A254 is used as a surrogate for DOC in terrestrial systems. It would be interesting for the reader to see this data and for the authors to compare values to other terrestrial systems (e.g. rivers, groundwaters).

All absorbance values were measured below the MQ Water blank run on each day, therefore no values can be used to interrogate the quantity of DOC.

4. Line 106-107. Were the data also processed to remove Rayleigh-Tyndall scatter? How were the Raman and Rayleigh-Tyndall scatter lines processed? Were they replaced by zeros, by NaN (not a number) or was data interpolated? All of these effects can have subtle influence on the resultant PARAFAC model, so it is good to report them.

The EEMS were post-processed to remove the Rayleigh-Tyndall scattering using a MATLAB script of smootheem.m in drEEM version 0.1.0; Murphy et al. 2014. A reference can be added to the text to clarify the smoothing technique to remove each scattering effect.

5. Lines 108-110. The authors must specify what they did for sample classification, normalisation and subset selection. It will be different from Cawley et al (2012), which is just one fluorescence case study, and on pulp mills, so not really very relevant to this research.

We will revise this section to include further details on the procedure for sample classification, normalization, and subset selection prior to PARAFAC modeling. A representative data set was used for PARAFAC modeling, not the entire dataset, so this information will be included to assist others in the same situation.

6. Lines 108-110. Somewhere in this section the authors must quote the value of the standard(s) that they were using. This could be the Raman intensity of Milli-Q water at a specific wavelength, or the intensity of quinine sulphate standards run using the same instrument configuration, or an International Humic Substances Standard, or a tryptophan or tyrosine standard.

The Raman intensity of the MQ Water at a specific wavelength will be provided upon revision.

7. Lines 110-111. More detail is needed on the PARAFAC model, to allow the reader to assess its strength in modelling the data. It is crucial in this paper, as the PARAFAC model is the crux of the whole analysis and interpretation. 1. One would expect to see the core consistency value given. A 'passable' model could be considered have a value of >90%, and a good model a score of >99%. 2. It would be very informative to know why the authors chose a 3 component model over a 2 or 4 component model – did the 4 component model try to model noise, for example? Or did it model a plausible 4th component, but with a low core consistency. 3. The percentage of the data fitted by each component is very valuable information, especially if compared with that from a two and four component model. 4. And finally, a split-half analysis is very useful,

especially if the authors perform a split half analysis using randomly split datasets and a split half analysis with LGM data in one dataset and Holocene data in the other. If the split half analysis fails on the latter test, then it tells you that the LGM and Holocene need different PARAFAC models.

1. The core consistency value can be provided. 2. We will explain the rationale for a 3 component model over a 2 or 4 component model. 3. We can report the percentage of the data fitted by each component to strengthen our argument for a 3 component model. 4. Split half analysis was used for this PARAFAC model and will be reported in the text upon revision.

8. Line 126-127. Amino-acid like fluorescence is too general. Only tryptophan and tyrosine have aromatic groups which fluoresce, and even then, without independent amino acid analyses to confirm their presence, one can never be sure that these compounds are responsible for the fluorescence. If the fluorescence is from an amino acids source, then C1 and C2 look most like a 'tyrosine-like' compound. Tyrosine would excite at both âĹij225 nm and âĹij275 nm and emit at about 310 nm. But the molecular structure is such that you must observe both the 225 and 275 nm excitation of the 310 nm emission, not just one or the other, as you show in Figure 3. Supplemental Figure 1 confirms the absence of a âĹij275 nm excitation peak. Therefore C1 and C2 are not 'tyrosine-like' or 'tryptophan-like'. Model compounds and contaminants that exhibit a single peak in this general region include simple phenols such as cresol (see Aiken, 2014 in Coble et al. (eds) Aquatic Organic Matter Fluorescence), PAHs such as fluorene (Ferretto et al 2014, DOI:10.1016/j.chemosphere.2013.12.087) and aviation fuel (see Baker et al. 2014, Encyc. Anal. Chem. DOI: 10.1002/9780470027318.a9412).

This information will be clarified in the revised text. 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. Specifically, we will address the potential for monolignol fluorescence as remarked by Aiken in the Aquatic Organic Matter Fluorescence Book

(2014). Appropriate references regarding the fluorescent nature of the potential chemical species present will be included.

9. Line 128. The reference to 'recalcitrant species' is speculative. It would be better to specify the excitation and emission wavelengths of this peak or peaks. I am not aware of fluorescence in this region being recalcitrant – instead bio- and photo- degradation studies show that it is degradable (for example, Osburn et al and Stedmon and Cory, both in Coble et al 2014).

We can correct our usage of 'recalcitrant' in this manuscript, report the excitation and emission wavelengths of the peak/peaks, and cite the appropriate references.

10. Line 129 and Figure 2. There is almost no meaning in 'total OM fluorescence intensities'. Each fluorophore has a different fluorescence efficiency. For example, in this study, you identify three fluorescent components, but each will have a different amount of emitted fluorescence per g C present. So, summing the three is meaningless. It is particularly relevant as low molecular weight compounds such as tryptophan-like and tyrosine-like compounds (argued to be C1 and C2 here) have less chance of their emitted fluorescence being reabsorbed within the molecule, and they therefore have relatively high fluorescence efficiency. In contract, fulvic-like compounds (arguably C3 here) can reabsorb their emitted fluorescence, resulting in a much lower fluorescence efficiency. Figure 2 is therefore just meaningless and instead each PARAFAC component score (C1, C2, C3) needs to be presented.

This is a good point, however, this figure was created to provide a complete record of OM information that tracks relative fluorescent changes of the samples with depth. Removing this figure removes a complete record of all our samples. Using a subset of the samples to build a PARAFAC model created a limitation in the way we can present the depth profile. With our current PARAFAC model, samples were selected as a representative OM character subset of the entire record, not specifically organized to balance how many samples were included in each climate period. It was more informative to

categorize the OM chemical fluorescence into specific groups prior to modeling, rather than to group the climate periods. With statistical outlier testing, it was very challenging to keep a balanced data set in each climate period, thus the most informative results were produced from the categorized subset PARAFAC model. To investigate how the PARAFAC model would shift based on climate periods, three separate PARAFAC models were generated, which produced somewhat redundant results to our original PARAFAC model, and again had large groupings of outliers in some climate periods. However, the changes in PARAFAC component 2 over time were captured using this method, thus added to this work in Figure 3b. These results will be clarified in the text.

11. Line 134 and Figure 3. The PARAFAC scores for C1, C2 and C3 need to be presented in Figure 3. At the moment, no raw data from the PARAFAC model is presented in the paper, yet this is the main focus. The reader has no way of seeing the data and judging its nature e.g. variability over time. Just drawing some PARAFAC model EEMs over an x-y plot would be unacceptable to the fluorescent organic matter research community.

See comment above regarding the subset of samples and how that does not best represent tracking fluorescence intensities over time. We intend to produce a new figure tracking the percentages of each PARAFAC component for our model to show the relative changes. Reporting the 1,191 EEMs would show the variability of fluorescent chemical species over time, however that was unreasonable for this work. The PARAFAC model best represents this variability of the entire record, and then is discussed in terms of the types of chemical nature that is characteristic of each climate period.

12. Line 134-136. This observation needs quantification (see comment above).

That information can be provided upon revision.

13. Line 137-139. As in my earlier comment, you cannot have just one of the two excitation peaks that 'tyrosine-like' compounds excite at, and then call it 'tyrosine-like'.

We can address this by discussing the types of chemical species that would fluoresce in that region. See above comments.

14. Line 139-145. There is most fluorescence at 310 nm, so this is not 'tryptophan-like' at all, as this would also have a peak at 350 nm. More fundamentally, there is a line through the EEM at 310nm which cannot be real. Is this an artefact of the design process of Figure 2, or is it in the actual PARAFAC model? If the latter, it means the model is not correctly modelling the data. Is there anything instrumental e.g. physical filters that change over at 310 nm that could be the cause of this artefact? Is it still present in the 2 component model?

Yes, this feature was present in the 2 component model. The best explanation of this feature is that PARAFAC is doing a great job modelling the EEMs it was given. We acknowledge that challenging qualitative fluorescence data also is modeled as well in PARAFAC, if the samples were not reported as outliers. A discussion on the "unusual" feature of this fluorescence will be discussed in further detail.

15. Line 142. If you performed a single PARAFAC model, then the location of the modelled fluorescence can't change over time. So how can the location of the peak 'move' from LGM to Holocene? Is this from extra PARAFAC analyses that the reader doesn't know about? Or is it a subjective analysis of the original EEMs?

Extra PARAFAC analyses were performed and can be explained more clearly in the text (see comment above for details). It was not a subjective analysis of the original EEMs.

16. Line 145-150. I would disagree with this interpretation. This fluorescence is typical of 'peak A' and 'peak C' compounds. A peak 'M' fluorescence would be blue shifted compared to 'peak A', and in your component C3 there are two peaks and they both have the same emission wavelengths.

The manuscript will be revised to correct for peaks A and C result reporting and dis-

cussion of Holocene OM chemical fluorescence.

17. Lines 153-155. The fact that no one else has reported your fluorescence peaks is either very exciting or very worrying. It would suggest that what you are seeing is not anything that has been reported before e.g. you are not seeing 'tyrosine-like' fluorescence, and by implication, you can't definitively interpret it as a microbial signal.

Of the data available in the OpenFluor database, a repository of a selection of samples (not every fluorescent study completed), our results showed no matches with other PARAFAC components. This is reasonable given the scope of the project and the great volume of samples spanning 6,000 to 27,000 years ago from ice. Yes, we agree that what we are seeing is not anything that has been reported before. We also agree that your suggestion as the correct interpretation of the PARAFAC components would not distinctly be tyrosine-like or tryptophan-like, thus the interpretation of a microbial signal is not definitive. These interpretations will be edited accordingly upon revision.

18. Line 160 and Figure 4. The authors state that Figure 4 shows the 'PARAFAC components', but there is just one line. What is this? Is it C1, or C2, or C3? All three components must be shown individually, here and in Figure 3.

The PARAFAC components determined in each climate period are provided on the same graph for your convenience. The black line refers to the δ18O record. This figure will be edited considerable to show the nssCa and δ18O record only.

19. Line 175. C1 and C2 PARAFAC model scores need to be plotted in Figure 3. Line 184. C3 PARAFAC model scores need to be plotted in Figure 3.

Model scores can be provided.

20. Line 189-191. This observation is unremarkable, as all humic and fulvic substances standards have a higher fluorescence intensity at the short excitation wavelength (see examples in Aiken (2014)).

Correct. We can adjust this appropriately and provide the reference.

21. Line 191. It sounds like you are saying that there are plants and soil in the ice? I'm sure you don't mean that?

Yes, thank you. This was an error in phrasing and can be corrected upon revision.

22. Line 214. No fluorescence data over time is presented (except for the total fluorescence, which is not meaningful). So this section is speculative.

Correct. Please see comments above addressing our explanations and routes for revision.

New fluorescent figures (Figs 2 and 3) are provided for consideration.

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

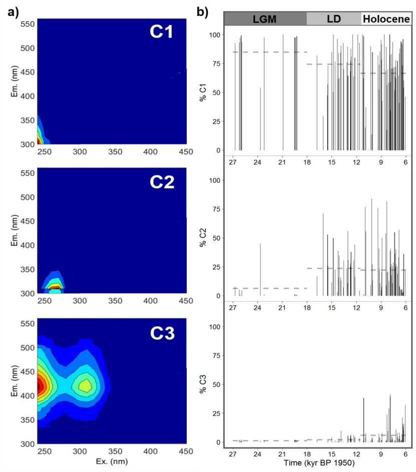

Figure 2. PARAFAC analysis results for West Antarctic Ice Sheet Divide ice core organic matter showing a) components 1, 2, and 3 (C1, C2, and C3) and b) the fluorescence percentage of each component contributing to the overall fluorescence signature over the Last Glacial Maximum (LGM), last deglaciation (LD), and Holocene climate periods as a function of time (kyr before present 1950). Average fluorescence percentages (gray dashed lines) are provided for each component, separately calculated for each climate period. Fluorescent data were reported in Raman Units. Note: C3 average fluorescence percentages ranged from 0-2% in the LGM and LD, and did not correspond to resolved fluorophores.

Fig. 1. Figure 2. PARAFAC analysis results for West Antarctic Ice Sheet Divide ice core organic matter showing a) components 1, 2, and 3 (C1, C2, and C3) and b) the fluorescence percentage of each component c

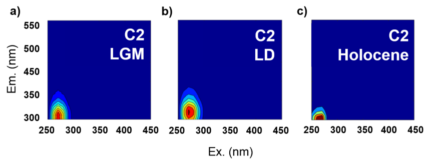

Figure 3. PARAFAC analysis results of component 2 (C2) variation with climate periods a) Last Glacial Maximum (LGM), b) last deglaciation (LD), and c) Holocene. Components 1 and 3 from the PARAFAC model in Figure 2 showed no variability over time.

Fig. 2. Figure 3. PARAFAC analysis results of component 2 (C2) variation with climate periods a) Last Glacial Maximum (LGM), b) last deglaciation (LD), and c) Holocene. Components 1 and 3 from the PARAFAC mo