Interactive comment on “Enrichment in $^{13}$C of atmospheric CH$_4$ during the Younger Dryas termination” by J. R. Melton et al.

Anonymous Referee #1

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Review Melton et al. Climate of the Past

General The paper presents a new and higher resolved ice core record of d13CH4 over the Younger Dryas – Preboreal transition compared to what exists (Schaefer et al. 2006 and Fischer et al. 2008). Schaefer et al did not interpret a trend in their data and Fischer et al showed only 2 data points for the rapid event discussed here. The new data set is interpreted using a mass balance approach including additional information from other published work (dD-CH4 from Sowers 2006 and 14CH4 from Petrenko et al. 2009). The conclusion drawn by the authors is new and sheds additional light on the methane inventory during the investigated transition. Limitations due to data quality, firn processes and Pakitsoq in situ CH4 production are discussed extensively, nevertheless I recommend to include additional information (specified below).
The contribution is well within the scope of “Climate of the Past” and I think the paper can be accepted after some revisions.

General concerns:

The 13C increase during the actual transition from the Younger Dryas (YD) to the Preboreal (PB) seems to be a robust feature. Nevertheless, the Pakitsoq data outside the transition (as indicated in Figure 1) do not show a clear picture, challenging the robustness of the data. Specifically, there is an apparent mismatch of the Pakitsoq / EDML data sets which seems to start at the end of the YD-PB transition and increases further back in time. Could an interhemispheric gradient evolve? Is one of the datasets biased? These questions should at least be pointed out, and are not even mentioned in the manuscript. (See specific comment on abstract)

The authors state that blanks are corrected as described in Schaefer and Whiticar 2007 (p.3291 L.7-9). Observed blanks are quite high (∼3%) and it should be elaborated how the blank correction is performed. Is there a blank measurement for each sample? Which isotope value is used for the blank correction? (I assume the same as in Schaefer and Whiticar 2007? Was it determined again after the implementation of the post combustion trapping of CO2 as introduced by Melton et al. 2011 (ChemGeo)? According to the latter publication this seems not to be the case, and should be clarified in a final version of this paper). Possibly this can help to rule out that the differences in Pakitsoq/EDML data are due to a methane concentration dependent offset based on blank contribution.

While the triple mass balance approach is elegant, it should be mentioned that it simplifies things a lot. If all sources are allowed to change simultaneously (in strength and isotopes) and atmospheric lifetime of CH4 is allowed to increase with increasing concentration alternative solutions are possible. I see, that these cannot be quantified as the system is under-determined. However, it should be mentioned as a limitation of the approach.
I feel that a good portion of the supporting online material could be placed in the main text. This is especially true for the corrections to the d13CH4 values.

Specific

p 3288 L 9-12: It is not straightforward to compare the EDML and Pakitsoq records. Fischer et al. 2008 did only correct their data for gravitational settling (via 15N). No correction was applied for the concentration effect during the rapid rise of CH4 (YD termination). Such a correction would shift the data point at the start of the YD termination towards a heavier number. This does not falsify the Pakitsoq data but is also not confirming the robustness of the new data as mentioned in the abstract. In the light of the diverging trends at older dates the differences of the datasets should be discussed in the paper. The GISP2 record (Sowers 2010) is in line with the youngest Pakitsoq and EDML data but unfortunately it ends in the Preboreal. Concerning the trend of the data presented in Schaefer et al. 2006 see my comment on page 3296 line 29.

p 3290 L 13+14: What were the detectors of the used GC systems (field / OSU)?

p 3291 L 7-9: Please elaborate on the blank correction.

p 3293 L 5: What is the difference between “reference gases” and “air standards”? Tell us which gases have been used (origin, CH4 concentration) L 7: Please cite the method to determine the air content. L 10: What is the precision for [CH4] air measurements? L 22: I suggest to elaborate on the applied corrections here (move from the supporting online material)

P 3296 L16: Please account for the general concerns stated above. L 29: This is not cited correctly. A 13C enrichment was not found to be evident by Schaefer et al 2006. On the contrary, they stated: “there is no significant change in d13CH4 across the YD-PB transition ” and “Slight variations fall within the envelope of uncertainty.” This is true for the data measured at University of Victoria and NIWA (Ferretti).

P 3298 L 11: You could elaborate on limitations of the approach here.

C1971
L 19-21: Formulas: A subscript “c” is missing for the cumulative isotope values of the mixed sources. (This also the case in the supporting online material).

P 3299 L15: In reality also source signatures might have changed.

P 3301 sections 3.4.x: Please indicate which sensitivity test corresponds to which “scenario description” in table S6.

P 3308 Please update the conclusions according to the comments made above.

P 3324: Fig. 3: insert “of additional emissions” after “values”

Supporting Online Material

p2. line 32: I do not agree: The Fischer 2008 data point at the start of the YD-PB transition is likely influenced by the “diffusion fractionation”.

P16 Fig S3: Define excess CH4

P17 Fig S4: How did you treat the older Schaefer data?

Interactive comment on Clim. Past Discuss., 7, 3287, 2011.