

Dear Prof. Fischer,

Thank you for handling the review of our submission. We have found the reviewer comments to provoke much discussion and thought. We appreciate the time taken in their reviews.

The following are the reviewer comments and our responses in point by point form. We present the Reviewer general comments in entirety then our responses immediately below. The specific comments are answered after each reviewer comment. For clarity, we begin all of our comments with, 'AU>>', and end with, '<<'. Revised or additional passages in the manuscript are shown here (in italics) for easy comparison. A list of the references we cite is provided at the end of this document.

We have moved much of the material that was in the Supplementary Online Material (SOM) into the main text with some exceptions, which we hope will be acceptable. We have kept the step-by-step guide to the triple mass balance in the SOM as it is a bit pedantic for the main text and we have also kept all SOM tables in the SOM.

Joe Melton, Hinrich Schaefer, Michael Whiticar

=====

Anonymous Referee #1

The paper presents a new and higher resolved ice core record of  $d_{13}CH_4$  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 ( $\delta D-CH_4$  from Sowers 2006 and  $14CH_4$  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  $CH_4$  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)

AU>> Reviewer #1, Thank-you for your review.

The Pakitsoq data outside of the transition has lower sampling density and could also have a higher spread between sample measurements. A mismatch between Pakitsoq and EDML is definitely possible but is not necessarily an indicator for bad data quality. The important point is a qualitative agreement between the two data sets: both show a trend towards more negative  $\delta^{13}\text{CH}_4$  value prior to, and after, the rapid  $[\text{CH}_4]$  increase. This finding is pertinent despite the complications that render a quantitative comparison between the two data sets difficult. These are greater uncertainties in the age scales outside the rapid transitions in climate and atmospheric chemistry, the existence of an inter-hemispheric gradient with currently unknown magnitude and trend and the possibility of inter-lab offsets, i.e. a bias in either data set. We note that any bias (assuming the reviewer refers to measurement bias) would either increase or decrease the offset between the datasets but generally leave the pattern unchanged. All of these uncertainties are now discussed in the manuscript. (The EDML record comes up more in the reviewer's comments and will be discussed again later in this response).

New MS text:

*“Comparing the combined Pákitsoq  $\delta^{13}\text{CH}_4$  dataset to the published records from the EDML core (Fischer et al. 2008) and GISP2 (Sowers, 2010) shows good agreement in the Preboreal period with all records showing a general pattern towards more  $^{13}\text{C}$ -depleted values as the PB progresses (Fig 2). Looking at the YD period, there is a greater divergence between the Pákitsoq and EDML records (Fischer et al. 2008) with the Pákitsoq values generally more  $^{13}\text{C}$ -depleted (and possibly with higher scatter than in the PB period). This could indicate that the inter-hemispheric  $\delta^{13}\text{CH}_4$  gradient was greater in the YD than in the PB period. However any interpretations of the magnitude of offset between datasets should be tempered by uncertainties due to the inter-laboratory offset between the measurement labs. The inter-laboratory offset could be influenced by several factors including blank corrections, standard gases, and instrumental drift corrections. However, an inter-laboratory offset would result in a constant offset that influences the magnitude of the offset between datasets, but not the general pattern of each dataset. As a result we will limit our discussion to the general pattern displayed by each dataset and not attempt to interpret the magnitude or changes in offset between datasets. “*

>>

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  $\text{CO}_2$  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 Pakitsq/EDML data are due to a methane concentration dependent offset based on blank contribution.

AU>> We felt that the reference to the detailed description of the blank correction in Schaefer and Whiticar (2007) would be sufficient. We have now expanded this discussion in the revised MS. Yes, the full diagnosis of the  $\delta^{13}\text{CH}_4$  value was done for the new setup following Schaefer & Whiticar (2007). Since the value found was not distinguishable from the one found by Schaefer & Whiticar (2007), i.e. atmospheric signal, we did not go into further details in the initial version of this MS. A brief discussion of a possible bias introduced by the blanks is included in the comparison to EDML (see above).

Revised MS text:

*"The blank contribution was at most ~5% of the sample signal, while more commonly <3%. Blanks were measured every two to four samples and consistently yielded a contaminant value with atmospheric  $\delta^{13}\text{CH}_4$ . Following Schaefer & Whiticar (2007) sample  $\delta^{13}\text{CH}_4$  was corrected in an isotope mass balance approach using the  $\text{CH}_4$  concentration based upon  $m/z$  44 peak height."*

>>

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  $\text{CH}_4$  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.

AU>> The reviewer is absolutely correct, our approach has an inherent limitation of the system being under constrained. Our approach necessarily simplifies things a lot, an unfortunate but unavoidable situation. However, it should be noted that we have taken a more rigorous approach than is common by conducting sensitivity tests with different representative source values, investigating the changes in source isotope values due to changing environmental and climatic conditions, etc. We have made revisions to further make evident the assumptions and simplifications of our approach

Revised MS (added paragraph):

*"Obviously several simplifications and assumptions are intrinsic to the triple mass balance approach including: constant and representative source isotope values through the transition, constant sink isotopic fractionation (the sink strength can vary, it just changes the magnitude of the  $\text{CH}_4$  increase), and the assumption that the  $\text{CH}_4$  increase can be represented adequately by the contribution of three or less sources. Representative source isotope values could also have changed from modern values and are investigated in Section 3.4."*

>>

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  $\delta^{13}\text{C}_{\text{CH}_4}$  values.

AU>>Ok, the handling editor has directed us to do the same.  
>>

Specific

p 3288 L 9-12: It is not straightforward to compare the EDML and Pakitsq records. Fischer et al. 2008 did only correct their data for gravitational settling (via  $15\text{N}$ ). No correction was applied for the concentration effect during the rapid rise of  $\text{CH}_4$  (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 Pakitsq 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 Pakitsq 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.

AU>> Yes, it is definitely fairly complicated to compare EDML and Greenland records. We are aware that the Fischer et al. dataset has not been corrected for diffusion fractionation. However, we, like the reviewer, found that only 1 data point is sufficiently close to the transition to require a closer look. We have expanded the description of how the onset of the transition (and therefore the necessity for diffusion correction) was determined for both Pakitsq and EDML. This documents why we think that the questionable EDML data point should not be corrected. However, we have also included a discussion of Buizert (2011) and his correction to that datum and the implications for our study. Below is a description of how we determined the point was not requiring correction and then the revised MS text (which is in two parts in the MS).

We defined the start of the concentration rise as the inflection point in the GISP2  $\delta^{15}\text{N}$  record, which is coincident with the last low  $\text{CH}_4$  concentration measurement in the GISP2 record. Since Severinghaus et al. (1998) showed the  $\text{CH}_4$  concentration increase to occur 0 - 30 yrs after this inflection, this is a pretty solid way to set the start of the  $[\text{CH}_4]$  increase. Then to put the EDML and GISP2 records on a common (Pakitsq) timescale, we matched the records using the rapid  $\text{CH}_4$  increase at the end of the YD. Given  $[\text{CH}_4]$  is globally reasonably well-mixed, this is a common technique for matching timescales. As a reminder, all data in our paper is present on a common Pakitsq timescale, which is pinned to a YD termination date of 11.570 ka BP (Friedrich et al. 1999) for the  $\delta^{15}\text{N}$  inflection point. Hence our gas age values in the MS are not the exact same as those on either the GISP2 or EDML timescales.

When we matched the EDML  $\text{CH}_4$  to the GISP2  $\text{CH}_4$  (and placed them both on the Pak timescale) we found that we had to shift the Fischer et al. (2010) dataset

134 years older (we did not scale it (compress or expand the timescale), just a simple linear addition). With the shift of 134 years, the point that was at 11.715 ka BP (GICC05 EDML gas age) becomes 11.581 ka BP (Påkitsoq common timescale). This puts the point before (older than) the [CH<sub>4</sub>] increase (again set at 11.570 ka BP (Friedrich et al. 1999)). Since the concentration rise occurs after this data point, we found no need for the diffusion correction at the point suggested by the reviewer, since it was not within the rapid concentration increase. Our approach has the advantage that we are not attempting to divine an inflection point in the sparse EDML [CH<sub>4</sub>] record (EPICA Community Members 2006) but instead using the slope of the rapid [CH<sub>4</sub>] increase (which has many more points). Finding the exact point of the EDML [CH<sub>4</sub>] rise is further hampered by no good gas phase indicator like the d<sub>15</sub>N record in Greenland.

Naturally, some caution is due here as this EDML point is very close to the transition. It is then prudent to discuss if the point was actually within the transition (due to errors in the age-scale transformation, age-depth scale creation, etc.). In that case, a correction should be applied and it would be in the direction suggested by the reviewer, making the move towards more positive d<sub>13</sub>CH<sub>4</sub> values smaller than it appears as presented in the MS (which includes only the original gravitational correction). However, that would not necessarily provide evidence contrary to our findings. As the result would be a plateau in the long-term depletion trend that coincides with the [CH<sub>4</sub>] rise (as the EDML point after the CH<sub>4</sub> transition is decidedly not requiring diffusion correction so would remain as is). One could argue that such a plateau itself is indicative of different source/isotope dynamics during the [CH<sub>4</sub>] rise than during the YD. Especially so when considering that the EDML point in the Preboreal may not have captured the most enriched value of the reversal that Påkitsoq data suggests and the actual inter-hemispheric d<sub>13</sub>CH<sub>4</sub> gradient could have changed over the course of the transition.

Further higher resolution and sampling density future datasets will help to further pin down the time of concentration rise and help to decrease uncertainty. However, the datasets are not presently available so we must operate with the material we have. This is one of the reasons we have emphasized in our MS that our work would benefit from further datasets and studies. We have included a discussion of the possible diffusion correction of this EDML data point in the revised MS below.

Revised MS text (added further description of converting to Påkitsoq timescale):

*“The absolute gas age scale (GISP2 depth to calendar age) used is that of Schaefer et al. (2006). This age scale differs from the common GISP2 gas age scale of Brook et al (2000) by fixing the date of the YD termination to  $11,570 \pm 0$  yr BP on the basis of tree ring records (Friedrich et al., 1999). All literature datasets presented in this study are converted to this age scale. The EDML dataset was converted to the Påkitsoq timescale by performing a linear regression on both of the GISP2 and EDML [CH<sub>4</sub>] records during only the abrupt [CH<sub>4</sub>] increase, and adjusting the EDML gas ages to allow the lines to overlap. This fitting and placement on the Påkitsoq timescale required*

*an addition of 134 years (no compression or expansion of the timescale was performed) to the GICC05 age of EDML points.”*

Revised MS text (discussion of EDML point diffusion correction):

*“One of the EDML  $\delta^{13}\text{CH}_4$  data points has a mean gas age (on the Pákitsoq timescale) of little more than a decade prior to the initiation of the rapid  $\text{CH}_4$  transition. While we feel that our age determination is based upon the best approach available (see Section 2.2.5), given uncertainty in gas ages, it is possible that the EDML sample falls within the abrupt  $\text{CH}_4$  transition. If so, that data point would require correction for diffusion fractionation, giving a possible correction of between 0 and almost 1‰ (Buizert, 2011). Where exactly in that range the appropriate correction lies depends on how well the exact start of the abrupt  $[\text{CH}_4]$  rise can be determined. The Greenland records (GISP2 and Pákitsoq) have an advantage with detailed  $[\text{CH}_4]$  and  $\delta^{15}\text{N}$  records (Severinghaus et al. 1998) while the EDML  $[\text{CH}_4]$  record is relatively sparse (EPICA Community Members 2006) and lacking a good gas phase indicator of the initiation of the warming event. Regardless, Buizert (2011) applied diffusion correction to the data point in question, which creates a plateau in the EDML  $\delta^{13}\text{CH}_4$  record during the YD-PB, rather than a  $^{13}\text{C}$ -enrichment. However, the next younger EDML datum is clearly younger than our maximum  $\delta^{13}\text{CH}_4$  suggesting that the enrichment trend is simply not resolved in EDML. Yet, even a plateau would still mark a disruption of the long-term  $^{13}\text{C}$ -depletion trend that initiates at the start of the deglaciation (Fischer et al. 2008), indicating different source/isotope dynamics during the  $[\text{CH}_4]$  rise than during the YD.*

*We conclude that a trend to higher  $\delta^{13}\text{CH}_4$  during the  $[\text{CH}_4]$  increase of the YD-PB is a statistically significant feature measured using three different extraction and analytical techniques. The feature is also possibly evident in ice from a different location and measured with an independent set-up. Thus while our record has higher uncertainty given the necessity of applying a contaminated samples filter, it appears that the observed  $^{13}\text{C}$ -enrichment trend is robust enough to allow further interpretation.”*

>>

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

AU>>FID – added this to the MS

>>

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

AU>>This is covered by the expansion of the description of the blank correction that we detailed in our response to the general reviewer comments.

>>

p 3293 L 5: What is the difference between “reference gases” and “air standards”?  
Tell us which gases have been used (origin,  $\text{CH}_4$  concentration)

AU>> Added. Reference gases are serial dilutions of  $\text{CH}_4$  gas in  $\text{N}_2$  while air

standards are air samples of known composition.

Revised text:

*“Sample [CH<sub>4</sub>] for this data filter are derived by calculation against calibration curves from reference gases (serial dilutions of CH<sub>4</sub> gas in N<sub>2</sub>) and air standards (1033 ppb methane (balance ultra zero air) purchased from Airgas Incorporated and calibrated at Washington State University against standard tanks previously calibrated at NOAA CMDL)(Petrenko et al., 2006) using the IRMS m/z 44 ion peak height (derived from the ice sample <sup>12</sup>CH<sub>4</sub>) and air content of the ice.”*

>>

L 7: Please cite the method to determine the air content.

AU>>Added as to MS text as:

*“The air content of the δ<sup>13</sup>CH<sub>4</sub> ice samples is determined via parallel samples that were measured with GC at OSU as described in Brook et al. (2000) and (2005) from pressure in the sample loop and ice sample volume.”*

>>

L 10: What is the precision for [CH<sub>4</sub>] air measurements?

AU>> The precision given is for ice measurements (original MS p. 3292 l .23). The precision for air content measurements was not determined.

L 22: I suggest to elaborate on the applied corrections here (move from the supporting online material)

AU>> Following the reviewer and editors’ suggestion, we moved this all to the main text

>>

P 3296 L16: Please account for the general concerns stated above.

AU>> Assumedly this is the concern about the diffusion correction to the point in the Fischer et al. (2010) dataset. Please see that discussion above.

>>

L 29: This is not cited correctly. A <sup>13</sup>C enrichment was not found to be evident by Schaefer et al 2006. On the contrary, they stated: “there is no significant change in d<sup>13</sup>CH<sub>4</sub> 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).

AU>> We do not say that the authors of Schaefer et al. 2006 state that it is evident. In our original MS we write, ‘*The authors did not state a trend because the start of the transition was represented by samples from only one field season, introducing the*

*possibility of a sampling bias'* (line 22 p3296 ). We contend that a trend is evident in their data measured at UVic (which is plotted in several of the figures in this MS) and qualitatively also in the NIWA data presented in that study (we have added a sentence acknowledging that the enrichment in the latter is not statistically significant). To further clarify we have added to the reference the figure number of the Schaefer et al. paper that shows the evident  $^{13}\text{C}$  enrichment in both the NIWA and UVic measured samples.

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

AU>>We believe the reviewer is referring to the limitations of the triple mass balance approach(?). Here is the revised text addressing that concern:

*“Obviously several simplifications and assumptions are intrinsic to the triple mass balance approach including: constant and representative source isotope values through the transition, constant sink isotopic fractionation (the sink strength can vary, it just changes the magnitude of the  $\text{CH}_4$  increase), and the assumption that the  $\text{CH}_4$  increase can be represented adequately by the contribution of three or less sources. “*

>>

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).

AU>>Thanks, fixed in all equations.

>>

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

AU>>Yes, that is why we conducted several sensitivity tests (particularly Section 3.4.2). These sensitivity tests show it to be unlikely that another source could satisfy the triple mass balance as well as a combination of fire and thermokarst lakes.

Added into MS for clarity:

*“Representative source isotope values could also have changed from modern values and are investigated in Section 3.4.”*

>>

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

AU>> We have added in the labels from the table into the main text to make it clearer.

>>

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



AU>> Within the MS we have added in a discussion around the EDML point requiring/not diffusion correction and how that influences uncertainty also the limitations of the triple mass balance approach. Within the conclusions we have Revised the MS text:

*“We present a new  $\delta^{13}\text{CH}_4$  dataset measured from Pákitsoq ice covering the YD-PB transition. A  $^{13}\text{C}$ -enrichment trend across the transition is evident and well exceeds measurement uncertainty. The trend is also evident in previously published Pákitsoq measurements (Schaefer et al., 2006) using different experimental setups (Ferretti et al., 2005; Schaefer et al., 2006). While not unambiguous due to dating uncertainty, it appears that a similar disruption of the long-term deglaciation  $^{13}\text{C}$ -depletion trend occurred in the presently available Antarctica  $\delta^{13}\text{CH}_4$  record (Fischer et al., 2008). “*

>>

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

AU>>Thanks, we have added that.

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”.

AU>>See discussion in the general comments section.

>>

P16 Fig S3: Define excess CH4

AU>>The definition can be found in the figure caption as ‘Excess CH4 is defined as the difference between Pákitsoq IRMS-derived [CH4] and GISP2 (Brook et al. 2000)’

>>

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

AU>>The same as the new d13C dataset. Only the new measurements were plotted to make the plot easier to read. We have added a note making it clear they were treated identically.

>>

=====

Anonymous Referee #2

General comments

Melton et al., present a very interesting d13C record of atmospheric CH4 over the dramatic YD-Preboreal transition. A problem they have to deal with is that Pákitsoq CH4 record is altered by unknown (?) processes. Generally there is excess CH4 with occasional large spikes. The methods section compares the data to existing data and here the “reliable” data points are handpicked. This is not a problem per se, the authors present evidence that there is no systematic shift by the contaminant over

the time period of interest. I believe that the shift in the isotopes they see is reliable but it could be systematically offset from the true value. The discussion of the data can be much more straight forward starting by stating at the beginning that the record is altered and that date have to be selected following by the arguments that the shift in the isotope ratios is reliable. A lot of the methods section can go to the supplement. What I am not so convinced of is that there is no constant offset by the contaminant.

AU>>Reviewer #2, Thank you for your review.

We appreciate the reviewer's concern about data quality and we are pleased that he/she agrees with the filtering approach and the conclusion that a systematic offset can be ruled out. We have added a section discussing the possibility of a constant offset and its implications for the conclusions.

Revised MS text:

*“Comparing the combined Pâkitsoq  $\delta^{13}\text{CH}_4$  dataset to the published records from the EDML core (Fischer et al. 2008) and GISP2 (Sowers, 2010) shows good agreement in the Preboreal period with all records showing a general pattern towards more  $^{13}\text{C}$ -depleted values as the PB progresses (Fig 2). Looking at the YD period, there is a greater divergence between the Pâkitsoq and EDML records (Fischer et al. 2008) with the Pâkitsoq values generally more  $^{13}\text{C}$ -depleted (and possibly with higher scatter than in the PB period). This could indicate that the inter-hemispheric  $\delta^{13}\text{CH}_4$  gradient was greater in the YD than in the PB period. However any interpretations of the magnitude of offset between datasets should be tempered by uncertainties due to 1) higher uncertainties in the age-scales outside the rapid transitions, and 2) the inter-laboratory offset between the measurement labs. The inter-laboratory offset could be influenced by several factors including blank corrections, standard gases, and instrumental drift corrections. However, an inter-laboratory offset would result in a constant offset that influences the magnitude of the offset between datasets, but not the general pattern of each dataset. As a result we will limit our discussion to the general pattern displayed by each dataset and not attempt to interpret the magnitude or changes in offset between datasets.”*

We feel that all the other discussion points requested by the reviewer are already presented in the manuscript, although the exact order and flow is subject to personal preference.

As for the reviewer's request to move material to the supplement, it is at odds with recommendations of the editor and we have followed his direction.

>>

The finding that thermokarst lakes and biomass burning are the dominant sources changing over the transition is conflicting with earlier findings. This has to be discussed in depth. What is missing specifically is the finding based on the pole to pole gradient (Chappellaz et al., 1997; Dällenbach et al., 2000) that there was a large

increase in tropical sources at the YD transition. Further the documented change in the gradient may be important for the interpretation of the data and it should be taken into account.

AU>> We actually do compare our results to estimates of inter-hemispheric gradients (orig MS p.3305 l.23):

‘Thermokarst lake emissions into the Northern Hemisphere are consistent with the increase in inter-hemispheric [CH<sub>4</sub>] gradient between the averages of the YD and PB periods (Brook et al., 2000; Dällenbach et al., 2000), although the latter may not be indicative of the short term transition dynamics.’

Note the Chappellaz et al. (1997) paper is not referenced in our MS because the paper does not provide a YD inter-hemispheric concentration gradient (IHG) estimate, only PB.

We urge caution in the comparison of our results to those of Brook et al. (2000) and Dällenbach et al., 2000 because those papers compare changes in the IHG over much longer time periods than considered in our paper.

However, that does not mean that the combined results of Chappellaz et al., Dällenbach et al., and Brook et al. contradict our findings as suggested by the reviewer. Dällenbach et al. (2000) report a YD (11.63 – 12.5 ka BP) IHG of 26±9 ppb and Chappellaz et al. (1997) reports an IHG for the Preboreal (11.5 – 9.5 ka BP) of 44±7 ppb. The modeling based on these findings shows an increase in tropical sources, but also an unexpectedly large rise in high latitude sources so that their proportion in the total source increases. This is consistent with our conclusion that thermokarst lakes increased their CH<sub>4</sub> emissions over the course of the YD-PB transition.

>>

The manuscript should be restructured focusing more on the results and setting the new finding into context to previously published estimates. As the authors state on page 3310, line 1: This data needs to be confirmed and I could not agree more.

AU>> The reviewer is not specific in his request which independent estimates should be considered. We have provided discussions using independently published ice core methane concentration and isotope data, as well as modeling based on these. Further, we compare to bottom up estimates and modeling of certain emissions to critically evaluate the plausibility of our findings. We discuss evidence that supports our findings as well as evidence that is not consistent. We caution that an approach where the Pakitsoq record can only be used to support previous findings but not challenge them would be poor scholarship.

As the reviewer notes, our conclusions would be strengthened from further independent confirmations, as is the case with any study.

>>

### Specific comments

Page 3290, lines 7-12: Wetlands in higher latitudes should be discussed here. They are a player on at glacial interglacial transitions.

AU>> The role of northern peatland/wetlands is discussed extensively (Section 3.4.1). However, it is important to note that our paper does not focus on glacial-interglacial transitions but on a rapid climate transition, which occurs much more abruptly.

>>

Page 3290, lines 13-21: Recent evidence point to methane released below 200m below surface not reaching the ocean surface. Solomon, E. et al., I.: Considerable methane fluxes to the atmosphere from hydrocarbon seeps in the gulf of Mexico, Nature Geosci, 2, 561-565, 2009.

AU>> We assume the reviewer refers to pg. 3289? Although we agree with the detail raised by the reviewer, we find that an in depth discussion of clathrate methane dynamics (and by extension of the two competing hypotheses) is not suitable for a general introduction. A literature review on the various emission types is beyond the scope of this paper.

>>

Page 3291, lines 7-9: Where is the 5% blank originating from? 5% is quite a lot. How was the blank determined?

AU>> Added information to MS about how blank was determined in response to Reviewer #1 (also see Schaefer & Whiticar 2007). 5% is only the maximum seen across all sample runs. The more typical values were consistently below 3%. The blank contamination was atmospheric air (or at least that was its isotope value, thus assumedly small leaks in the system).

>>

Page 3291, lines 29: Why is it not possible to take the atmospheric variations into account by using the NOAA network data?

AU>> It is possible, however the amount of error involved would not result in a net reduction. The unknown offset between locations would not be an improvement over the unknown seasonal cycle.

Revised MS text:

*“The seasonal change in  $\delta^{13}\text{CH}_4$  is  $\pm 0.11\text{‰}$  on the nearby Olympic Peninsula during the period from 1988 to 1995 (Quay et al., 1999). However, due to unknown offsets in  $\delta^{13}\text{CH}_4$  between Victoria and Olympic Peninsula, we do not correct for inter- or intra-annual variability.”*

>>

Page 3292, line 24 and elsewhere: Eurocore and GISP2 are not the same thing! Eurocore is a core drilled by a European conglomerate at Summit in 1989, a few meters away from where GRIP was drilled later. GISP2 was drilled 30km to the west of GRIP. What is referred to as Summit today is actually not Summit but where the old GISP2 was located.

AU>> Sorry, "GISP2" accidentally got inserted in front of Eurocore when the text should read: "Greenland Eurocore". This has been corrected.

Revised MS:

*"This CH<sub>4</sub> concentration agrees reasonably well with measurements made with a conventional GC-FID from the Greenland Eurocore 235 (724 ± 5 ppbv) for ~217 yr BP (Etheridge et al., 1998)."*

>>

Page 3298, equations: add that sum DeltaQn=1.

AU>> It doesn't necessarily sum to 1. This actually forms one of the quality control steps for the triple mass balance. Any combination that sums outside of 1.0±0.1 was considered to be an unlikely source combination and therefore rejected. From the revised MS text:

*We impose two criteria on the mass balance calculation's source combinations to identify valid scenarios. First, the calculated cumulative isotope values,  $\delta(^{13}\text{C}, \text{D}, ^{14}\text{C}) \hat{\uparrow}_c$ , must reproduce the ice isotope records within their respective uncertainties, which are chosen to be the reported analytical precision for  $\delta^{13}\text{CH}_4 \hat{\uparrow}_p$ ,  $\delta\text{D-CH}_4 \hat{\uparrow}_p$ , and  $^{14}\text{CH}_4$  i.e.,  $\pm 0.3\%$  of  $\delta^{13}\text{CH}_4 \hat{\uparrow}_p$ ,  $\pm 4\%$  of  $\delta\text{D-CH}_4 \hat{\uparrow}_p$ , and  $\pm 10\%$  of  $^{14}\text{CH}_4 \hat{\uparrow}_p$ , the latter an approximate conversion of the reported value (~1 pMC; Petrenko et al. (2009) to  $\Delta$ -notation. Second, the fractional contribution from each source,  $\Delta Q_1$ ,  $\Delta Q_2$ , and  $\Delta Q_3$ , must sum to  $1.0 \pm 0.1$  (the closer to one, the more probable).*

>>

Section 3.4.4: I cannot follow here. The authors hint that the conclusions in those papers are incompatible with their findings. If so they have to discuss why this is.

AU>> No, these papers are not incompatible with our results at all. These papers did not address the transition investigated in our paper so their results are not comparable (indeed the Lassey et al. paper looks at the 20<sup>th</sup> century).

We simply include these other possible representative stable isotope values to demonstrate the robustness of our conclusion. Essentially, the choice of a 'representative' stable isotope value is based upon expert opinion. We are using the work of Lassey et al and Fischer et al. to show that even choosing different representative values for the sources and sinks does not change the main conclusions of our work.

Revised MS (new sentence for enhanced clarity):

*“While both Lassey et al. (2007) and Fischer et al. (2008) address different time scales than ours and thus have no direct bearing on our conclusions, they demonstrate the sensitivity of the triple mass balance results to different representative source isotope values.”*

>>

Page 3305, lines 3-13: CO has a lifetime of 2 months in the atmosphere. Therefore the Antarctic CO data show at most increased biomass burning in the southern hemisphere but not globally.

AU>> Yes, it is correct that the CO record is likely dominated by a southern hemisphere signal. We are simply pointing out, as did the Wang et al. paper, that the Antarctic CO record shows similarity with the tropical charcoal record. Thus the CO record has some connection/correlation with a proxy for fire. We also use the CO record to compare with the Antarctic  $\delta^{13}\text{C}_{\text{CH}_4}$  record of Ferretti et al. The comparison between these two records (Wang et al. and Ferretti et al.) shows that the  $\delta^{13}\text{C}_{\text{CH}_4}$ -based estimates of biomass burning  $\text{CH}_4$  emissions is supported by the CO record, which also is similar to the tropical charcoal record. We make no claim that the Ferretti number is global, nor the Wang number.

For further clarity we have changed p.3305, line 7 to read: “although CO has a short atmospheric residence time and is governed by southern hemisphere processes, recent results...”

>>

Section 3.5.1: The deuterium discussion can be removed down to citing Bock et al., 2010.

AU>> We prefer to keep the entire discussion in place. The possibility of changes in deuterium values should be highlighted as it has not figured much in the literature (there is no deuterium analogue to the papers of Schaefer and Whiticar where they investigate possible shifts in the representative isotope values back in time).

>>

Technical corrections Page 3297, line 22: Either write “epsilon = alpha-1” or add that epsilon is in ‰

AU>> We have added to (p. 3297 l. 20):

*“Epsilon is calculated from the fractional proportion of each sink (including the highly fractionating atomic chlorine in the marine boundary layer (MBL) sink) and its ratio of the rate coefficients,  $\alpha$ , for each isotope as  $\epsilon = 10^3(\alpha - 1)$  in units of per mille.”*

Epsilon is not ‘alpha -1’, but ‘ $10^3(\alpha - 1)$ ’, which puts it in ‰.

>>

=====

## References:

- Brook, E. J., Harder, S., Severinghaus, J., Steig, E. J., and Sucher, C. M.: On the origin and timing of rapid changes in atmospheric methane during the last glacial period, *Global Biogeochemical Cycles*, 14, 559-572, 2000.
- Chappellaz, J., Blunier, T., Kints, S., Dällenbach, A., Barnola, J.-M., Schwander, J., Raynaud, D., and Stauffer, B.: Changes in the atmospheric CH<sub>4</sub> gradient between Greenland and Antarctica during the holocene, *Journal of Geophysical Research*, 102, 15,987-915,997, 1997.
- Dällenbach, A., Blunier, T., Flückiger, J., Stauffer, B., Chappellaz, J., and Raynaud, D.: Changes in the atmospheric CH<sub>4</sub> gradient between Greenland and Antarctica during the Last Glacial and the transition to the Holocene, *Geophysical Research Letters*, 27, 1005-1008, 2000.
- EPICA Community Members: One-to-one coupling of glacial climate variability in Greenland and Antarctica, *Nature*, 444, 195-198, 10.1038/Nature05301, 2006.
- Fischer, H., Behrens, M., Bock, M., Richter, U., Schmitt, J., Loulergue, L., Chappellaz, J., Spahni, R., Blunier, T., Leuenberger, M., and Stocker, T. F.: Changing boreal methane sources and constant biomass burning during the last termination, *Nature*, 452, 10.1038/nature06825, 2008.
- Friedrich, M., Kromer, B., Spurk, M., Hoffman, J., and Kaiser, K. F.: Paleo-environment and radiocarbon calibration as derived from Late Glacial/Early Holocene tree-ring chronologies, *Quaternary International*, 61, 27-39, 1999.
- Lassey, K. R., Etheridge, D. M., Lowe, D. C., Smith, A. M., and Ferretti, D. F.: Centennial evolution of the atmospheric methane budget: What do the carbon isotopes tell us?, *Atmospheric Chemistry and Physics*, 7, 2119-2139, 2007.
- Schaefer, H., Whiticar, M. J., Brook, E. J., Petrenko, V., Ferretti, D. F., and Severinghaus, J.: Ice record of  $\delta^{13}\text{C}$  for atmospheric CH<sub>4</sub> across the Younger Dryas-Preboreal transition, *Science*, 313, 1109-1112, 2006.
- Schaefer, H., and Whiticar, M. J.: Measurement of stable carbon isotope ratio of methane in ice samples, *Organic Geochemistry*, 38, 216-226, 2007.
- Schaefer, H., and Whiticar, M. J.: Potential glacial-interglacial changes in stable carbon isotope ratios of methane sources and sink fractionation, *Global Biogeochemical Cycles*, 22, 10.1029/2006GB002889, 2008.
- Severinghaus, J., Sowers, T., Brook, E. J., Alley, R. B., and Bender, M.: Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice, *Nature*, 391, 141-146, 1998.