

# Interactive comment on “NGRIP CH<sub>4</sub> concentration from 120 to 10 kyr before present and its relation to a $\delta^{15}\text{N}$ temperature reconstruction from the same ice core” by M. Baumgartner et al.

Answers to H. Schaefer (Referee)

## GENERAL COMMENTS

Baumgartner et al. present new measurements of past atmospheric methane (CH<sub>4</sub>) concentration from the NGRIP ice core. The new data set is combined with older published and unpublished data to provide a complete high resolution record of CH<sub>4</sub> atmospheric evolution over the entire last glacial period. This time series is analysed together with nitrogen isotopes ( $\delta^{15}\text{N}$ ), a temperature record for the drill site derived from the latter, as well as pCH<sub>4</sub> and pCO<sub>2</sub> records from Antarctica. The study derives the climate sensitivity of CH<sub>4</sub> and uses established approaches to study the inter-polar gradient in pCH<sub>4</sub> and the lead/lag relationship with local temperature. The main contribution of the study is to provide a complete picture for these parameters over the course of the last glacial that gives interesting insights into geographical patterns of CH<sub>4</sub> emissions under varying climatic conditions. This is a good contribution to our understanding of the methane cycle and suitable for publication in CoP. There are some minor points that should be addressed as detailed below. In addition, I think that the discussion of CO<sub>2</sub> effects needs a real overhaul. I think that the authors' support for a CO<sub>2</sub>-CH<sub>4</sub> link is based on selective use of evidence, such as not quantifying the potential signal in the defined climate sensitivity  $\mu$  and examining only specific time windows. The CO<sub>2</sub>-CH<sub>4</sub> link should be analysed in a robust manner or left out altogether. In contrast, the findings on trends in inter-polar concentration gradient and lead/lag relationships with temperature make this study a valuable contribution.

*Thank you very much for your constructive review comments. It improved the quality of the manuscript and reduced the length of the discussion part.*

*The two most important changes we applied for the revised version of the manuscript concern the discussion chapter 4:*

- *On the suggestion of the reviewers, we provided a new figure which shows the methane to NGRIP temperature sensitivity as a function of age together with NGRIP methane and temperature amplitudes. We further subtracted the normalised northern summer insolation from the sensitivity to reveal remaining features.*
- *We removed the discussion about the influence of carbon dioxide on methane emissions (section 4.3, including Figs. 8 and 9) since concerns were raised about this section by all of the three reviewers. While the comparison of baseline trends should be investigated in the future, it does not concern the main topic of the paper. The CO<sub>2</sub> effect on the methane to NGRIP temperature sensitivity is hardly visible after subtracting insolation and is thus speculative and certainly does not deserve a full section of discussion.*

*In the following, the specific comments are answered point by point.*

## DETAILED COMMENTS

**Abstract:** the main findings of the study could be spelled out more clearly, while currently there is strong emphasis on reporting specific numbers of individual results. For example, the identification of CH<sub>4</sub> lags for periods with low increase rates and implied geographical source shifts are worth mentioning here. Another solid finding is the evolution of rIPD throughout the last glacial.

*Thank you for your suggestion. We have rewritten and extended the last part of the abstract as follows: 'These events generally have small methane increase rates and we hypothesise that the lag is caused by pronounced northward displacement of the source regions from stadial to interstadial. We further show that the relative inter-polar concentration difference (rIPD) of methane is about 4.5% for the stadials between DO event 18 and 20, which is in the same order as in the stadials before and after DO event 2 around the Last Glacial Maximum. The rIPD of methane remains relatively stable throughout the full last glacial, with a tendency for elevated values during interstadial compared to stadial periods.'*

*We also updated the conclusions accordingly.*

**Page 4659, lines 26-27:** A possible reference would be: Mariotti, A. Atmospheric nitrogen is a reliable standard for natural <sup>15</sup>N abundance measurements. *Nature* 303, 685–687 (1983).

*Reference inserted.*

**Methods:** there should be a reference to the data table in supplementary material. Also, as the lead-lag determinations use actual d<sup>15</sup>N data a methods description for those analyses must be presented. This can take the form of a reference and a quick summary, but e.g. the reproducibility should be mentioned so that the reader can evaluate the choice of 1-sigma exceeded for the start of a T-increase.

*A reference to table 1 is given on page 4662, line 2. We see no need for an additional reference. Regarding d<sup>15</sup>N, we would like to refrain from a description on analytical methods. This paper publishes CH<sub>4</sub> data only, the d<sup>15</sup>N are published in Kindler et al. (2013) and references therein. The only important information, which is 1 sigma uncertainty, is given directly at the place where lead-lags are determined (see your second comment below).*

**Page 4661, lines 8 and 9:** completely air free ice is notoriously hard to produce. If the authors have evidence that their blank ice indeed contains zero CH<sub>4</sub> than this would be a good place to mention it. Otherwise, it should be pointed out that residual CH<sub>4</sub> from the blank ice would lead to an overestimation of the blank correction, which may affect comparability with measurements from other labs, such as LGGE.

*We use large grain crystal ice grown over 4 weeks at the University of Bern with a zonal melting-refreezing method, which is visually bubble free. But we agree that completely air free ice is hard to produce, which makes it extremely difficult to design a realistic blank scenario for a melt-refreeze extraction. We added: 'Note that the air free ice is produced at the University of Bern and may still contain minute amounts of CH<sub>4</sub>, which potentially leads to an overestimation of the blank correction and has to be kept in mind when comparing the data to results from other labs.'*

**Page 4661, lines 26 and following:** the authors could point out that the remeasurements themselves allow for quantification of CH<sub>4</sub> increases during D-Os (if I read Fig. 1 correctly), thus reducing uncertainty from splicing data sets.

*We added the following sentences at the end of line 28: 'The remeasurements ensure consistency within the entire NGRIP CH<sub>4</sub> data set, which has been obtained by splicing various different data sets. Amongst others this is crucial for quantification of CH<sub>4</sub> amplitudes at the onset of DO events (section 3.2).'*

**Page 4662, lines 1 and following; as well as supplementary table: there needs to be a complete documentation on analytical precision. It may be fair to apply the same precision to all Bern measurements as is done in the supplementary table, but this should be stated and the concerned data sets listed. Yet, Schilt et al. quote Flueckiger et al. (2004) for their methods, implying a sigma value of 10 ppbv. For LGGE data, it must be clear what precision is assigned to individual data sets and why. Most of the LGGE data were published quoting 1 sigma values between 8 and 11 ppbv. The unpublished LGGE data of the present study were measured during the same time periods as the latter, so a similar precision is likely. There seems to be some confusion on the use of standard deviation and standard error as 1-sigma. This becomes relevant for assigning lead-lag times, where the start of an increase is defined as 3-sigma exceeded. Are the lead-lag findings robust in light of differing precision of the various data sets?**

*Concerning the confusion of 1-sigma used for standard deviation as well as standard error, we replaced the only appearance of sigma in the meaning of standard error (page 4662, line 5) by '95% confidence'. The appearance of sigma in the manuscript is thus consistently connected to standard deviation. We further added '1-sigma' on page 4661, line 15, after 5.9 ppbv to clarify this issue.*

*The 10 ppbv estimate for CH<sub>4</sub> precision applied in earlier studies was a rather crude and conservative estimate, which has been assumed due to the lack of reproducibility measurements on natural ice. Our extensive set of reproducibility measurements described in the manuscript confidently determines the precision of the Bern melt-refreeze system on NGRIP ice (1-sigma=5.9 ppbv). Other ice cores like EDML (see Baumgartner et al. 2012, Biogeosciences) and TALDICE of EDC (unpublished data) show a precision very close to this value. Since no major changes occurred to the Bern melt-refreeze system during the last years, we are convinced that the same uncertainty applies to the data by Flückiger et al., (2004), Huber et al. (2006), and Schilt et al., (2010). For LGGE measurements the precision for natural ice samples is also better than the 10 ppbv, as visible from duplicate and triplicate measurements on natural ice (see page 4661, lines 24-25). We therefore think that it is a very reasonable assumption to apply the 1-sigma uncertainty of 5.9 ppbv to all the measurements. The various data sets do not show differing precisions, but the value of the precision is now precisely determined. We added the following sentence on page 4662, line 19: 'Note that we apply the same analytical precision of 5.9 ppbv (1-sigma), as deduced from the 107 reproducibility measurements of this study, to all the existing NGRIP data. The 10 ppbv estimate assumed in previous studies (Chappellaz et al., 1997; Capron et al., 2010, 2012; Schilt et al., 2010; Huber et al., 2006; Flückiger et al., 2004) , which was based on LGGE reproducibility measurements on artificial bubble-free ice samples, is therefore replaced by the 5.9 ppbv precisely determined from natural ice samples.'*

**Page 4664, lines 20 & 21: this would be a good place to say explicitly why it is useful to not just compare CH<sub>4</sub>-variability magnitudes between D-O events but to scale them to temperature.**

*We replaced the first sentence of Sect. 3.2, i.e. Page 4664, lines 20 & 21, by: 'The unambiguous attribution of the stadial-interstadial CH<sub>4</sub> increases to Greenland temperature increases strongly suggests that northern CH<sub>4</sub> sources substantially increase emissions as a reaction to abrupt northern warming. Scaling the CH<sub>4</sub> amplitudes by NGRIP temperature amplitudes reveals by how much the variability seen in the CH<sub>4</sub> increases is directly determined by the variability in the mean stadial-interstadial warmings and allows us to separate other important effects such as changes in seasonality or wetland extent on total CH<sub>4</sub> emissions.'*

**Page 4666, lines 8-10: this deserves a reference or two.**

*We cited Brook et al. (1996) and Flückiger et al. (2004). These references already existed in the reference list of the discussion version of the manuscript.*

**Page 4667, lines 8-11: here it is important for the reader to have the information on d15N analytical methods.**

*The 1 sigma uncertainty of 0.02 permil for the d15N specified by Huber et al., (2006) and also used by Kindler et al. (2013) is given on line 11. To our opinion, to provide information on d15N analytical methods is beyond the scope of this discussion. Note that the Kindler paper is a companion paper currently in review in CPD. Accordingly, we feel it is not necessary to explain all the details again in this paper.*

**Page 4671, lines 14 and following: I suggest moving this technical information to the start of the section and discussing the results afterwards (although I appreciate the note on a conservative interpretation of the results).**

*We moved lines 14-22 on page 4671 forward to line 4.*

**Page 4672, lines 4 & 5: please provide a reference or show a plot of the relevant temperature and insolation data. It would be helpful to mention that Greenland temperature variations are not just uncorrelated with insolation at 30 degN but also at 65 degN (Flueckiger et al., 2004).**

*We now show the NGRIP CH4 and temperature as a function of time in a separate new figure along with the sensitivity mu and insolation.*

**Page 4672, lines 5-13: as a side note, should the range quoted in line 9 be “5-15degC”? More importantly, I don’t see the value of the experiment performed here. Instead of randomly swapping temperature values between events, a more sensible test would be to correlate just the CH4 magnitude for each event with insolation. If the authors’ claim in lines 11-13 was true, then mu (sensitivity) should be fairly constant for all events and temperature would be orbitally controlled after all.**

*Indeed we meant 5-15degC, this was a typing error. The value of the experiment is to show that the CH4 and temperature amplitudes are not completely decoupled. You are right that the formulation on lines 11-13 was misleading. In agreement with the comment by the first reviewer, Eric Wolff, we made the following changes:*

*We replaced lines 5-13 on page 4672 by: ‘However, CH4 increases also correlate with temperature increases ( $R=0.36$ ), which themselves are not influenced by orbital parameters ( $R=-0.03$ ). This temperature effect thus obscures the orbital signal in the CH4 amplitudes ( $R=0.66$ ). It is the sensitivity mu, which seems more directly linked to the insolation ( $R=0.72$ ).’*

*Related to this subject we inserted on page 4665: ‘Figure 3 shows that CH4 amplitudes tend to increase with increasing amplitude in temperature. For example, if we take the average of  $\Delta CH4$  for  $\Delta T < 10^\circ C$  it is substantially smaller than the average of CH4 for  $\Delta T > 10^\circ C$ . Apparently, on the average, a higher NGRIP temperature amplitude is favourable for CH4 emissions.’*

**Section 4.2: this section lays out the fundamentals for influences on mu. However, there is also a lot of discussion on possible factors controlling the variability that is rather speculative (which is okay) and is completely disconnected to the later explanations for the same observations given in section 4.4. (e.g., low mu results from a stronger source displacement). I recommend that the discussion on mu-variability be presented in one coherent section. A possible option may be to restrict 4.2. to the basics and refer to 4.4. for a complete discussion of mu-variability.**

*The idea of stronger source replacement originates from the discussion on lead-lag, therefore we would like to keep the structure in section 4.4 as is. Since we now deleted section 4.3 (see answers to later comments), section 4.4 is better connected to section 4.2.*

**Page 4674, lines 14 & 15: this would be true for salt marshes. I guess the hypothesis is based on the concept that higher sea level raises groundwater levels in coastal lowlands**

**and so creates new wetland areas that are not subject to marine flooding and salt water intrusion.**

*This sounds reasonable, a higher effect might be expected from the groundwater level rise. Sea level is now discussed in the paragraph about minor influences on mu, after having subtracted the insolation.*

**Page 4674, lines 22 & 23: In Fig. 7d the time markers for D-O events are placed on the summer insolation curve and not on the spring curve, despite the fact that the evolution in mu seems to correlate with the latter. When placing the time markers on the spring curve one sees that there are simply no data for mu during the minima at 100 and 120 ka BP. Therefore, I think that the whole section (starting page 4674, line 16) on the coevolution, or perceived lack thereof, between mu and insolation is missing the point. Insolation seems to explain pretty much the complete observed variability in mu. This has implications for the discussion of the CO<sub>2</sub>-CH<sub>4</sub> link (see comments below). It is still valuable to discuss potential other factors such as shut-down of boreal sources, but it should be clear that this is done only for completeness of the argument and not because there is need for additional controls on mu.**

*To be more objective regarding which insolation curve should be used, we now have calculated the insolation at each latitude and day and found that for 30°N the best correlation to mu is given on 6 June. Therefore, we now show 6 June insolation and removed JJA and AMJ insolation in Fig. 7D.*

*You are right about the lack of data in the mu minima around 100 kyr and 120 kyr, this is indeed problematic. We deleted 'and minima' on page 4674, line 16 and removed the regression line for the mu minima in Fig. 7C. We further replaced the sentence on page 4674 starting on line 22 and ending on line 25 by: 'The lack of DO events around the insolation minima at 96 kyrBP and 117 kyrBP makes it impossible to compare the trend of the mu minima to the insolation minima over the full last glacial. However, the minimum of mu around 72 kyrBP appears to be lower than the minimum around 48 kyrBP, which is in line with the increase in the two corresponding insolation minima. We therefore conclude that insolation alone is able to explain a very large part of the variability in mu.'*

*We then continue with the minor factors, which could also influence mu. The discussion about Termination 1 and sea level (lines 1-15 on page 4674) now also joined this new paragraph.*

**Page 4675, lines 17-19: my reading of Singarayer et al. (2011) is that the one third difference can be attributed to CO<sub>2</sub> fertilisation alone, as opposed to CO<sub>2</sub> climate forcing as well (compare runs "All" and "All\_FixCO<sub>2</sub>" in their Fig. 3). If the effect really is that high, would it not be apparent when comparing mu, CO<sub>2</sub> and insolation throughout the last glacial?**

*You are right, this was a mistake in the manuscript. After Singarayer et al. (2011) the one third difference can be attributed to CO<sub>2</sub> fertilisation alone.*

*Indeed this appears to be high, however, also the absolute CO<sub>2</sub> concentration change over Termination 1 is with 80 ppmv very high. To avoid confusion, one has to keep in mind that Singarayer et al., 2011 are not able to simulate millennial scale variability. Their statement refers to the difference between Preboreal Holocene and LGM concentration levels. Assuming a PB-LGM CH<sub>4</sub> difference of 350 ppbv leads to a CH<sub>4</sub>toCO<sub>2</sub> sensitivity of  $350/3/80=1.46\text{ppbv/ppmv}$ , which is well in range with the estimates calculated after Melton et al., 2013. As described in section 4.3 and shown in Fig. 9, such an effect is visible and fully in range with the CH<sub>4</sub>/CO<sub>2</sub> concentration baselines, in particular during MIS3. The effect on mu might be rather small, we would expect that it depends on the absolute level of CO<sub>2</sub> at the onset of a DO event.*

**Page 4675, lines 19 and following: the modern-day maximum CO<sub>2</sub> sensitivity may be lower than at the LGM when low pCO<sub>2</sub> may become limiting for NPP and small changes**

could have a greater impact ( a point made on page 4676, lines 19-21). However, for a robust assessment whether there is a CO<sub>2</sub>-CH<sub>4</sub> link one should use the minimum postulated sensitivity and test whether a corresponding signal can be detected in  $\mu$  after accounting for insolation changes.

*We now decided to remove section 4.3 from the manuscript (see answers below).*

**Page 4676, lines 4 and following:** I find the concept of correlating pCH<sub>4</sub> and pCO<sub>2</sub> as illustrated in Fig. 8 throughout the last glacial period problematic. Yes, the correlation coefficients are impressive, but what would we get when correlating pCH<sub>4</sub> with parameters like pN<sub>2</sub>O or dust flux, despite the complete lack of a causal link? Evidence that I would find convincing is a trend in  $\mu$  during the last glacial or maybe a step change in  $\mu$  at the time of the MIS5-4 transition. Neither is discernible in Fig. 3. I am worried that Fig. 8 shows a co-evolution that has no information on causality and is therefore misleading. If the derived sensitivities would be clearly below the Melton et al. values I would accept this as a negative result, but as is I strongly recommend omitting the whole paragraph and Fig. 8.

*Figure 8 and section 4.3. 'Coupling of CH<sub>4</sub> and CO<sub>2</sub> concentrations' are no longer part of the manuscript.*

**Page 4676, lines 21-25:** in fact, if pCO<sub>2</sub> has any discernible influence on CH<sub>4</sub>, how would this NOT be expressed in  $\mu$ ? Further, there is no evidence for slowly decreasing  $\mu$  values (see Fig. 3), while the slowly decreasing maximum values can be explained by insolation alone. At least, the authors never attempt to show otherwise. There should be a discussion of the fact that Fig. 3 shows no trend in  $\mu$  during the glacial, despite a steady decrease in pCO<sub>2</sub>. This also rules out a climate effect of CO<sub>2</sub> (and other GHGs) on  $\mu$ . For a robust test of the CO<sub>2</sub>-CH<sub>4</sub> hypothesis,  $\mu$  should be normalised for insolation and the correlation between residuals and pCO<sub>2</sub> investigated. This would allow for an independent test of the findings by Singarayer et al. and Melton et al. If the authors proceed with a discussion of the CO<sub>2</sub>-CH<sub>4</sub> link I see this as the minimum requirement.

*We do not proceed with the discussion of the CO<sub>2</sub>-CH<sub>4</sub> link.  $\mu$  has now been normalised for insolation, shown in the new figure created for the revised version. The residuals indeed appear to be relatively constant, although there might be a small remaining decrease (hardly significant) from 90 kyr to 20 kyr. Of course YD/PB is still outstandingly high. Apparently, the residuals for DO events older than 100 kyr are negative. We have to keep in mind that using this scenario of normalisation uncertainties in the age scale arise, which are probably most pronounced for the oldest ages.*

*We do not think that Fig. 3 is suitable for a discussion of trends over the glacial. Actually, also the overall steady decrease in pCO<sub>2</sub> itself might be questioned (see comment by first reviewer, Eric Wolff). He argues that there is no long term trend in pCO<sub>2</sub>. Indeed one might identify a first plateau between 120 and 80 kyr, and a second plateau from 70-35 kyr. From 35 to 20 kyr, there is a need for more CO<sub>2</sub> data.*

**Page 4676, lines 26 and following:** this whole argument of correlated trends of pCH<sub>4</sub> and pCO<sub>2</sub> during and between D-O events is based on selective use of evidence. Is there an objective criterion to present the chosen time windows but not others? What is the relative occurrence (or duration) of times with co-correlation of pCO<sub>2</sub> and pCH<sub>4</sub> compared to times without? An illustrative example of the flawed argument is the time period before D-O 17, as shown in Fig. 9. Fig 7 shows that the pCO<sub>2</sub> rise starts already 64 ka BP, which means that pCH<sub>4</sub> stayed flat for another 3ka. Yet the authors use the event as support for a co-evolution of pCO<sub>2</sub> and pCH<sub>4</sub>. This is not a robust test of the hypothesis; for a convincing argument one needs to demonstrate a pattern that is

**generally valid and a plausible explanation for exceptions. This passage is a real weakness in the paper and should be either rectified or taken out.**

*We disagree that this whole argument was based on selective use of evidence. Maybe Fig. 9 was misleading, but in fact we showed 7 out of a total of 8 time windows from 70 to 15 kyr, which show a strong CO<sub>2</sub> flank related to AIM variations. So while we still think that there is an influence of CO<sub>2</sub> on the CH<sub>4</sub> baseline during MIS2-3 (as discussed on pages 4676-4677), we realise that this discussions on baselines is disconnected from the main topics of the paper and thus removed the whole section 4.3.*

**Section 4.4.: as mentioned before, parts of this discussion are relevant for explaining variability in  $\mu$ .**

*See comment above.*

**Page 4680, lines 19-22: it would be helpful to explain the direction of these changes and how that aligns with the observed CH<sub>4</sub> variability.**

*Based on the suggestion of the first reviewer, Eric Wolff, this paragraph has been deleted.*

**Fig. 1: I find it very hard to distinguish between old and new data in the current colour scheme. It may also be helpful to plot the data from individual existing studies separately in order to show potential biases (or demonstrate that the applied corrections are correct).**

*The diamonds of the old data have now black lines and dark grey fill. So it is easier to distinguish between old and new data. It demonstrates that the applied corrections are correct. The time intervals of the individual studies are quite distinct (see table 1), so one colour is enough to separate them.*

**Fig. 3: this is an important figure for the discussion of trends over time, specifically concerning insolation or potential CO<sub>2</sub> driven changes. It would be very useful to provide visual guidance on the ages of the data points. One suggestion would be to use a colour scheme for the plotted points that reflects their age (so that one could easily see if, e.g., warmer colours group in one sector).**

*We divided the total age range from 120 to 10 kyr into 11 bins of 10 kyr each and attributed a grayscale beginning with 10 to 20 kyrBP in white and ending with 110 to 120 kyrBP in black. Since the variations in  $\mu$  are primarily determined by insolation (as indicated in Fig. 7), we are not able to identify groups of the same colour at one spot. However, we agree that Fig. 3 benefits from this additional information.*

**Fig. 7: it would be helpful to include the NGRIP temperature reconstruction here. I have also argued above that the time markers for D-O warmings should be placed on the spring insolation curve rather than the summer one.**

*The temperature amplitudes of the DO events will be available in the new figure included for the revised version. We prefer not to show NGRIP temperature in Fig. 7, since this figure already has too much information in it. The time markers for DO warmings are now placed on the insolation curve at 30°N of 6 June, as explained in a comment above.*

**Fig. 8: as explained above, I recommend omitting this figure.**

*Done.*

**Fig. 9: as detailed above, I don't see a place for this figure. However, if the authors can make a convincing argument why it should be used, please note that the different x and y-axis scales in the bottom row make it impossible to see the alleged similarity of changes.**

*Fig. 9 has been removed.*

**Page 4667, lines 2-4: please check grammar of this sentence.**

*Done. 'For CH<sub>4</sub>, we consider an increase as significant if...'*