Answers to comments by Todd Sowers (referee 3) on article “Improving accuracy and precision of ice core δD(CH4) analyses using methane pre- and hydrogen post- pyrolysis trapping and subsequent chromatographic separation” by M. Bock et al.

Comments by Todd Sowers (R3) are reproduced in normal font, our answers appear *italic (A)*.

Dear Todd, thank you very much for the positive review. We are happy to improve the manuscript following your suggestions as follows:

R3: Pg 11285, L3: slope threshold is not a universal term. I understand but common reader will need clarification.

A: We shortly explain and cite Ricci et al. (1994): “Often the integration limits are determined based on the derivative of the beam time series according to thresholds of the slope (e.g. Ricci et al., 1994).”

R3: Pg 11287, L5-12: The absolute VSMOW calibration. This section is unclear. I suggest your remind us how CIC and MPI get to VSMOW. There should be a way to assess uncertainty in the Bern dD scale for CH4 by adding uncertainties in the original calibration to VSMOW to the uncertainties in the Alert/Air Controlle calibration.

A: No round robin has been performed due to the lack of international reference material for CH4 isotopes and needs to be undertaken in the future, however, bilateral measurements performed at 5 institutions in Europe, give additional confidence that our values exhibit a deviation from the VSMOW scale not larger than 3.5 ‰ (W. Brand, I. Levin, T. Röckmann, P. Sperlich, personal communication 2013 and 2014, Sperlich et al., 2012). At the Centre for Ice and Climate at the Niels Bohr Institute of the University of Copenhagen (CIC), Denmark, Sperlich et al. (2012) used 3 water references, which have been calibrated against VSMOW-2 and VSLAP-2, to calibrate water samples generated by methane combustion with a precision of 0.7 ‰. At the Max Planck Institute in Jena, Germany (MPI), the latter results have been reproduced and a publication is currently in preparation on this CH4 referencing project.
Two air tanks filled in Jena at the same day have been measured for δD(CH4) by MPI and the lab in Utrecht (Institute for Marine and Atmospheric research Utrecht, Utrecht University, The Netherlands (IMAU)). Precision for IMAU was 4.0 ‰ and resulted in a +3.0 ‰ difference wrt MPI Jena.
IMAU and our lab compare well, as is demonstrated in our previous papers (Bock et al. 2010, Sapart et al. 2011), the discussion version of this paper (Bock et al. 2013) and in our updated manuscript (please see Table A2 in the answer to referee 2 for new data produced with updated system)
C. Veidt measured our Alert sample in Heidelberg (IUP) and provided an uncertainty range of 1.0 permil (Veidt, personal communication 2014). Error propagation incorporating our measurements in Bern (Bock et al., 2010a) of

Alert (1σ = 2.7 ‰) and Air Controle (1σ = 2.0 ‰) leads to an estimated error of our anchor in dD(CH4) of 3.5 ‰.
In summary, we think that these two-sided lab links demonstrate a coherent scale for our results (Climate and Environmental Physics, University of Bern, Bern, Switzerland) and IUP, IMAU, CIC and MPI within the error limits.

We write in the paper:

"Our reference used to calibrate all samples is "Air Controlé", a recent clean air tank (CH4 concentration = [CH4] = 1971 ± 7 ppb) for medical purposes (bottle 541659, filled February 2007 in Basel, Switzerland, Carbagas). "Air Controlé" was cross-referenced to −93.6 ‰ with respect to Vienna Standard Mean Ocean Water (wrt VSMOW) using bottled air from Alert station "Alert 2002/11" (Bock et al., 2010a; Poss, 2003; Marik, 1998), previously measured at the Institute of Environmental Physics (IUP, Heidelberg University, Germany). At the IUP two scales for dD(CH4) co-exist, one is based on mass spectrometric measurements of water derived H2 (named MAT) and one is based on methane-in-air gases measured using a tunable diode laser system (named TDLAS). The anchors are IAEA (International Atomic Energy Agency) water standards VSMOW and VSLAP (Vienna Standard Light Antarctic Precipitation) for MAT and CH4 in air standards, the latter originally calibrated by the Bundesanstalt fuer Geowissenschaften und Rohstoffe (BGR) Hannover, Germany for TDLAS (Bergamaschi et al. 1994, 2000). The two scales agree within 1.0permil (MAT > TDLAS), which is within their precisions of 2.4permil and 1.0permil for MAT and TDLAS, respectively. dD(CH4) for "Alert" was measured in Heidelberg twice using each method and was calibrated with respect to the mean of both scales (-82.2permil +/- 1permil, Veidt, personal communication, 2014).
In our previous report (Bock et al., 2010a) we presented 4 air samples (Dome 6, Dome 13, Groningen Air, NAT-332 air) in the δD(CH4) interval [−70 ‰, −110 ‰] with good agreement compared to Bräunlich et al., (2001) and younger measurements performed by the Institute for Marine and Atmospheric research Utrecht (IMAU) (Sapart et al. 2011), who so far use the same TDLAS scale as IUP. Two of these air samples (at the margins of the dD(CH4) interval) have been re-measured with our improved set-up (Table 1), again with good agreement.
Note that a new independent scale for dD(CH4) is currently being established at MPI for Biogeochemistry, Jena. Accordingly, stringent round robin tests for methane isotopes will be possible to further check the agreement of different dD(CH4) scales in the future.
In summary we are confident that our measurements are close to the VSMOW scale (to about 3.5 permil), however, we note and will show later in this section that effects due to differences in matrix and/or concentration of samples and references can hamper highly accurate results, while deviations are difficult to pinpoint for individual laboratories and inter laboratory comparison exercises."

R3: Pg 11287, L17: Please add depth interval to age interval . 181-191mbs corresponding to gas ages between X and Y.

A: The requested information is now given in the new section "Exemplary results" as well as the updated Table 2: "No B34 specific gas age scale has been established, however, due to its vicinity to EDML, we make use of the Antarctic Ice Core Chronology (AICC) 2012 (Veres et al., 2013) to derive gas age estimates: On the EDML scale the depth range 181-191 mbs corresponds to an age of the occluded air of 1401-1532 a BP (Table 2 (not in this answer)). Using the firn model of Spahni et al. 2003 we calculated the age distribution for EDML in the Holocene: The most abundant gas ages are 33 years and the width at half maximum is 67 years."

R3: Pg 11287, last paragraph: The variability in dD over this 10m depth interval is very interesting. Another way to think about this is whether the rate of dD change over time is unrealistic. How much time represents 190-191m? I'd guess it is short such that the ddD/dt is enormous. Compare with anthropogenic signal to make the case. Any thoughts about why the ddD/dt is so large? Could we be talking about in-situ production (Rhodes et al. 2013)? If this core was used for d13CH4 development/standardization, one would suspect similar excess variability if the root of the problem is in-situ production. Hopefully not….

A: Thanks for the comment. We elaborate a bit more in the new section "Exemplary results" and the Rhodes et al. 2013 paper is cited. Unfortunately we do not have d13CH4 data in comparable resolution. New text:

"Given the width of the age distribution the variations in δD(CH4) observed for for polar ice samples (B34) seem to be large. However, while some replicates (samples from exactly the same depths) indicate good reproducibility, there are also depth ranges with higher scatter making it difficult to decipher the contribution from measurement uncertainty and variability potentially inherent in ice core samples. Taking the measurements at face value, we observe changes in δD(CH4) of ca. 8 ‰ over approximately 30 years (from 183 to 185 m depth, ca. 0.3‰/a). Braeunlich et al. (2001) find rates of dδD(CH4)/dt which are even higher for the last century (±2 ‰/a), which are however influenced by strong anthropogenic emissions. Concerning the smaller scale changes within the meter 191 the observed variation within 0.3 m amounts to 7.3 ‰ when taking the averages of the two highest and three lowest replicates. The latter translates to 1.7‰/a, which appears rather high for being of atmospheric origin. However it can not be decided at this time if in-situ production of CH4 is biasing our values (Rhodes et al., 2013). Our results call for measurements which cover only a few cm depth for the total suite of methane, namely CH4 mixing ratio, δD(CH4) and δ13CH4, performed on the same sample depth with high precision."

Pg 11288, first paragraph: This paragraph seems a bit out of place and I'd argue superfluous in the context of accuracy. As we don't know the real interpolar dD gradient, this paragraph point more to the biogeochemistry of atmospheric CH4 than to the accuracy of the new technique. I vote to remove the entire paragraph and include in next paper dealing with the interpolar gradient.

A: In order not to confuse readers, who are not familiar with the idea of dD(CH4) differences between north and south, we feel a comment on the interpolar difference in dD(CH4) is necessary as 2 different numbers for similar time intervals are given in Table 1. In line with referee 2 we move the section to the new section "Exemplary results" but shorten it considerably. New text:

"Mean values for WAIS (Antarctica) and B30 (Greenland) from similar (pre industrial) time periods (around 410 and 670 a BP, respectively) are −73.0 ‰ and −91.5 ‰. This difference of 18.5 ‰ with a combined error of 1.9 ‰ (the square root of the sum of the squared standard deviations of samples and reference measurements) can be largely explained by the expected inter polar difference in δD(CH4). It is beyond the scope of this article to discuss the biogeochemical implications of this finding, but we note that it is in line with earlier work (Sowers, 2010; Quay et al., 1999).

Pg 11290, L11: Replace "as in Bock" with "compared to Bock"

A: Thanks, changed accordingly.

Table 2: Can you add gas ages here?

A: Yes, we add the gas ages in a new additional column.

Figure 6, text box insert, first line should be using only pre pyrolysis trapping.

A: This is a mis-understanding: Between 2010 and 2012 we measured using only the post pyrolysis trap (= trapping H2 after pyrolysis step). Only in 2013 we added an additional trap before the oven (= trapping CH4 in the pre pyrolysis trap). The legend of Fig. 6 is correct. In the final version it will be extended by measurements of 2014 using the latest developments (please see answer to referee 2).

R3: Finally, I read the comments from Reveiwer 1 on this manuscript. I think that changing the notation from dD to d2H will cause confusion for those of us who think about dD of CH4. While correct IUPAC notation is sometimes preferred, I believe there will be more confusion using the d2H notation than dD. If we had to remember the chemical formula for Freon-11 and write it every time we used it, the world would be awash in chemical formulas that our politicians would never understand. There is a place for non-IUPAC terminology in literature. Keep the dD notation.

A: We support the view by Todd Sowers, but leave the decision to the editor (please note also comment by referee 1).

Added References:

Bergamaschi, P.; Bräunlich, M.; Marik, T. & Brenninkmeijer, C. A. M. Measurements of the carbon and hydrogen isotopes of atmospheric methane at Izaña, Tenerife: Seasonal cycles and synoptic-scale variations Journal of Geophysical Research: Atmospheres, 2000, 105, 14531-14546

Bergamaschi, P.; Schupp, M. & Harris, G. W. High-precision direct measurements of 13CH4/12CH4 and 12CH3D/12CH4 ratios in atmospheric methane sources by means of a long-path tunable diode laser absorption spectrometer, Appl. Opt., OSA, 1994, 33, 7704-7716

Marik, T., Atmospheric d13C and dD Measurements to Balance the Global Methane Budget, University of Heidelberg, 1998

Veres, D., Bazin, L., Landais, A., Lemieux-Dudon, B., Parrenin, F., Martinerie, P., Toy«e Mahamadou Kele, H., Capron, E., Chappellaz, J., Rasmussen, S., Severi, M., Svensson, A., Vinther, B., and Wolff, E.: The Antarctic ice core chronology (AICC2012): an optimized multi-parameter and multi-site dating approach for the last 120 thousand years, Climate of the Past, 2013.

*Ricci, M. P.; Merritt, D. A.; Freeman, K. H. & Hayes, J. Acquisition and processing of data for isotope-ratio-monitoring mass spectrometry Organic Geochemistry, Compound-Specific Isotope Analysis in Biogeochemistry and Petroleum Research, **1994**, 21, 561-571*

Spahni, R., J. Schwander, J. Flückiger, B. Stauffer, J. Chappellaz, and D. Raynaud (2003), The attenuation of fast atmospheric CH_4 *variations recorded in polar ice cores, Geophys. Res. Lett., 30, 1571, doi:10.1029/2003GL017093, 11.*