Reply to the three anonymous reviewers on: **Interactive comment on “A combustion setup to precisely reference δ^{13}C and δ^{2}H isotope ratios of pure CH_4 to produce isotope reference gases of δ^{13}C-CH_4 in synthetic air” by P. Sperlich et al.**

We would like to thank the three anonymous reviewers for their positive feedback and the constructive comments. We greatly appreciate the improvement of the manuscript. We considered all comments and either changed the manuscript accordingly, replied to them in the following or both.

Before answering the reviewer’s comments point by point, we feel the need to mention that

- the presented method was developed to serve the need of our laboratory for well referenced CH_4 including pure CH_4 as well as CH_4 in atmospheric mixtures. Despite the appreciated effort of the Centre for Ice and Climate (CIC) to support the development of the presented method, the CIC cannot produce, provide and maintain those air standards for other laboratories in future. However, the method we present can serve this purpose.
- we prepared supplementary information that describe 1) the determination of the purity level of the biogenic CH_4 and 2) the analytical control and a sensitivity test on potential blank contamination of the offline combustion system.
- we would like to add Trevor Popp to the co-author list for his work on δ^{2}H measurements.
- we found a small error in the determination of the uncertainties in Table 2, resulting from a copy-paste error in the underlying Excel file. This changes the uncertainty stated for the values determined for NEEM from 0.05 to 0.06 ‰ for GIS, and from 0.08 to 0.06 ‰ for MIS. The “daily system error” of NEEM$_{MIS}$ changes from 0.07 to 0.06 ‰.
- we erroneously referred to the TC/EA-IRMS as GC-IRMS in the description of the δ^{2}H measurements. Both points are changed in the revised version of the manuscript.

Response to comments by Anonymous Referee #1

P 3501 L14: Replace “rare over the abundant isotope” by “heavy over the light isotope” (this is the IUPAC convention, see Coplen, RCM 2012)
=> Changed in the revised manuscript.

P 3502 L7: Reference ‘Brand 2011’ missing
=> There might be a misunderstanding? We referred to the reference “Brand, W.A.: GAW Report No. 194, 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurements Techniques, Jena, Germany, 7–10 September 2009, 2011. 3502” which is part of the reference list.

P 3503 L8: The abbreviation GISP is a bit unfortunate, can be mixed up with GISP
=> We came across this discussion, too, but found the indexed “$_p$” to sufficiently clarify. Moreover, nowhere in the manuscript do we refer to the GISP ice core.

P 3503 L11: “..see Fig.1 and section 2.2”
=> Changed in the revised manuscript.

P 3503 L19: “..the results for two external. . .”
=> Changed to “…the results that two external laboratories found for NEEM…”

P 3505 L9: Comment: So, the yield is the criterion for accuracy. Any other sources of error (eg increasing blank) detected?
=> We decided for yield as main criterion because it is sensitive to critical processes parameters such as number of cryo-transfers, oxygen availability and temperature. We improved the description that 25 cryo-transfer cycles were suffienient to completely oxidize all injected samples, regardless of sample size and oven temperature variability. Furthermore, we describe the monitoring of laboratory-air leakage into the sample as well as a sensitivity test for laboratory-air leakage in the supplementary information.

P 3506 L17: Comment: this is not shown in Fig 2b
=> Changed in the revised manuscript.

P 3506 L21: Comment: How did you measure the purity of the biogenic CH4? Please provide a quantitative figure (Any residual organic compound would show up in the final delta value).
=> We add a detailed explanation as supplementary information to the paper in order to answer this critical point in depth.

P 3508 L2: Comment: Both gases (MIS and GIS) do not have CO2 or N2O at atmospheric levels. This might become important during on-line trapping and separation when NEEM air is analyzed.
=> This is true and highlights the importance to complement “real-atmosphere” standards containing more than one trace gases with such a synthetic standard comprising of the target gas in an air matrix. Measuring both types of standards in GC-IRMS systems with the same accuracy allows the conclusion that interferences have no significant impact.

P 3508 L3: Comment: You either need to describe the analytical system in more detail, or provide a reference for further details.
=> We provided more details on the GC-IRMS and data processing method and give a reference to a paper that describes a similar GC-IRMS system. A manuscript on our GC-IRMS system will be in preparation soon.

P 3508 L7: This is certainly not compatible with the IT principle. The CO2 square peaks go through a different history, including the capillary, and can serve only as a mediator between complete air aliquots used as samples used reference.
=> We might have chosen an unfortunate wording and changed the manuscript to prevent any doubts concerning this point. It was not our intention to refer to the referencing of air samples versus pure CO_2 as IT-principle.

P 3508 L12: Comment: Please describe correction procedure. Moreover, the primary scale anchor seems to be NEEM, not MIS or GIS, right? But NEEM has not been calibrated independently by DI-IRMS. What is the anchor value? Please clarify.
=> We used GIS and MIS to anchor NEEM to the VPDB scale. We rephrased this part in the manuscript to clarify this point.

P 3509 L2: Comment: What does this offset consist of? Laser system calib versus calibration using uranium reduction / ms measurements?
=> This offset only affected the last batch of our measurements and is not based on the laser system which produced very good data on the same day. Despite our investigations, the reason for this offset could not be identified. Technical problems occurred with the auto-sampler and the first attempt to measure our samples had to be terminated. This resulted in a longer than usual time which the otherwise refrigerated samples were exposed to room temperatures in the laboratory. We speculate that this caused evaporation in the sample vial which might have caused the isotope offset of our samples. The rather small volume of our sample might be the reason that these samples were affected while the standards that were measured at the same day were not.

P 3509 L20: Comment: This is almost too good to be true. Do you expect this to be typical?
=> This agreement is indeed surprisingly good. Results shown in Sapart et al. (2012) represent more typical agreement between several laboratories on different air mixture (firn air) in the order of 0.14 ‰.

P 3510 L18: Comment: I think this should simply be a more 2-H enriched source gas? ’Heavyly fractionated implies a process for producing such gas, which is not the only option.
=> Changed in the revised manuscript.

P 3514 Table 1: Please add the isotope reference values used for the respective materials

in this study
=> Changed in the revised manuscript.

P 3517 Fig. 2: cleaning equipment for bio-CH4 missing
=> Changed in the revised manuscript.

P 3518 Fig. 3: - The upper plot would be easier to digest as a 3-d plot (with 3 traces) - Caption line 3: replace "CH4 and CO2 fractionate in the source, but" with "CH4+ and CO2+ decompose in the ion source; but..." (Comment: It is not correct to say that the gases fractionate in the source. They do, but the processes are much more complex when it comes to unimolecular decomposition of ions in the ion source following electron impact.) - Caption line 10: Why is the offset negative?

=> 1) We tested several versions of 3-d plots as suggested. However, we found that this made it more difficult to assess the alignment of the three curves and therefore returned to a 2-d plot but introduced an artificial offset to separate the three baselines. Figure 3 is now a lot clearer and more informative.
=> 2) We changed to "CH4+ and CO2+ decompose in the ion source…" as suggested
=> 3) The character of the observed offsets due to incomplete combustion matches the trend that Merritt et al. (1995a) described for the combustion of CH_4 with different combustion temperatures. We observed a negative trend in the $\delta^{13}C$ offsets when the incompleteness of combustion was small (Figure 3) which is due to a faster reaction of lighter isotopes in an incomplete combustion. However, the trend reached a turning point and changed towards positive offsets when the incompleteness of combustion exceeded a certain level, which is most likely due to fragmentation effects in the ion source as described by Zeng et al. (1994). We decided to show the applicability of our method to detect incomplete combustion in detail on a logarithmic scale, therefore excluding the large variability from Figure 3.