Reply to the three anonymous reviewers on: **Interactive comment on "A combustion setup to precisely reference $\delta^{13}C$ and $\delta^{2}H$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}C$-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 $\delta^{2}H$ 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 $\delta^{2}H$ measurements. Both points are changed in the revised version of the manuscript.

Response to comments by Anonymous Referee #2

How long is the total time to prepare a CO2 and H2O for offline analysis?
=> It takes a full day for one sample, now mentioned in the revised manuscript.

P3505 – Lines 4-10. The concept of cryo-transfer cycles is not clear. How long is each cycle? Why are 25 needed to get 100 % yield. Does this not imply that the copper oxide combustion efficiency is low? Would the number of cycles required be lower if the combustion temperature was increased?
=> We revised the respective section in the manuscript. The auto-ignition temperature of CH_4 is about 600°C. We therefore assume that the combustion efficiency is primarily limited by the oxygen availability that again depends on temperature. Increasing temperatures for increased oxygen availability reduces the life-time of the reactor; we increased the number of cryo-transfers during the first tests and found good reproducibility after 25 cryo-transfers.

P3506 – Line 1 – What do you mean by a 1 ml glass vial? Is this a breakseal?
=> 0.7 ml glass vial, specified in the revised manuscript. It is not a breakseal, but has a septum for use in a standard autosampler with syringe.

P3506– Line 2 – How long does re-oxidation take?
=> About 10 minutes, now mentioned in section 2.2 of the manuscript

P3506 – Line 6 – What are the instrument precisions? Are these the errors shown in Table 2?
=> For the δ^2H, Table 2 shows the pooled standard deviations taking all samples into account that were combusted using the offline-combustion method. We added a reference that provides further information on the performance of both systems.

P3507 – Line 8 – This should read 'two traps in series removed H2O from the air flow'
=> Changed in the revised manuscript.

P3507 – Line 25 – These errors suggest that MIS and GIS aliquots have to be prepared separately each time. Is it not possible to make up a cylinder of MIS or GIS for regular analysis?
=> The section in the manuscript is re-phrased. The error bars are large because the analytical system is not tuned for high precision measurements of CH_4 mixing ratios. The described setup enables to produce synthetic isotope reference gases in larger tanks with pressures of up to 60 bar.

P3508 – Line 6 – reference gas peaks are rarely square but thay are always flat-topped unlike the sample peaks.
=> Changed in the revised manuscript.

P3508 – Lines 9-12 - This discussion implies that both mass specs must give the same d13C value for pure CO2. Has the same pure CO2 gas been measured directly by injection into both mass specs?
=> Yes, both IRMS systems CO_2-40339 has been used as isotope reference gas with an assigned δ^{13}C value versus VPDB.

P3508 – Line 25 – Table 2 shows that multiple analyses of the samples have been made so why is the precision identical for every standard measured?
=> We decided to show the pooled standard deviation to better reflect the typical precision of the complete system, based on a rather small number of sample measurements. Therefore, we give the same number as precision for all samples prepared with the offline combustion system.

P3509 – Line 14 – Please name the IT-principle in full, not just the abbreviation.
=> Changed in the revised manuscript.

P3509 – Line 16 – how constant is the daily offset? Is there any evidence of drift during the day.
=> Mentioned in the revised manuscript, section 3.

P3510 – Lines 17-18 – Producing reference gases at various mixing ratios and within a 17 ‰ range is clearly demonstrated. What needs to be clearly stated are the volumes of reference gas that can be offered. Can 30 litre cylinders be filled to 200 bars for example? Some extraction methods require large volumes (2-5 L) for extraction and standards need to be measured on a regular basis. Offering the fossil and biogenic standards diluted in zero air would also be useful for the atmospheric community.
=> This important point is answered in the conclusions of the revised manuscript and in the beginning of the answers to the reviewers. The mixing of isotope reference gases is limited by the maximum pressure of the Silcocans we used (2.8bar). If large tanks were used, the maximum pressure would be limited by the maximum pressure of the components in the gas manifold (60 bar).

P3510 – Line 22 – You could finish by mentioning the next steps to produce a useful product for the community.
=> Considered in the revised manuscript.

Table 2 – Is the 4.4 ‰ offset defined using the same reference gas as on the GCIRMS?
=> The offset is defined by measurements using IRMS and the laser instrument on combustion products of the same source gas as well as the offset between results from the laser instrument and the expected value of one of the gas mixtures according to a mass balance calculation.

Table 2 – How can the precision be the same for all standards when multiple analyses have been made on each?
=> Please find information in the answer to your comment on P3508 - Line 25

Figure 2 – It is not clear where the 1 ml H2O vial is attached. Is the whole of the CO2 trap removed and taken to the mass spec for analysis? It should be made clear where the collection vials are located and at what point they are disconnected.
=> This is now described in the method section and indicated in Figure 2 of the revised manuscript