

Reply to the three anonymous reviewers on: **Interactive comment on “A combustion setup to precisely reference $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}\text{C}\text{-CH}_4$ 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 $\delta^2\text{H}$ 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 $\delta^2\text{H}$ measurements. Both points are changed in the revised version of the manuscript.

Response to comments by Anonymous Referee #3

(1) P3502 Section 2.1: a short review is helpful for readers to understand the following sections. It would be even better to have a flow chat for visualizing the components (e.g., purification of biogenic CH_4 , making pure GISp, MISp, calibration of pure CH_4 and producing and measuring GIS and MIS etc.) and the relationship among the components. Those critical values (e.g., 280 μL , 1L, 6L, etc. and the various temperatures) and numbers should be indicated on the chat. Figure 1 may be part of the chat (by its own is not enough).

=> We begin section 2.1 in the revised manuscript with a more introductory sentence and added an additional flow chart figure indicating the relation of all measured gases to the isotope scales. Furthermore, we completed the figure on the setup (now Fig. 3) by adding peripheral components with labels on volumes, temperatures etc. We decided to display physical components of the setup separately from the relation of the gases to the isotope scales and to each other as we feel this separation increases the clarity to the reader.

(2) P3503 line 2: Is CO2 40 339 a referenced pure CO2 gas?

=> Yes, now mentioned in this sentence.

What does it mean “CO2 N48” in Table 1?

=> The specifications N48, N45, labline 5.0 and Alphagaz 1 are company specific information on the purity level of the respective gas. Changed to purity level in the revised manuscript where possible.

It is suggested to have a Table for all the relevant standards (see below) listing their isotopic compositions and indicating the respective traceability path to the primary scales (i.e., VPDB-CO₂ in $\delta^{13}\text{C}$, VSMOW-2 and SLAP-2 in $\delta^{18}\text{O}$ and δD respectively). Those should include the follows:

- RM-8563
- CO₂ - 40 339
- DC'02
- NM'09
- -15

=> We added the isotope values to Table 1 suggested by reviewer #1.

(3) P3503 lines 24 – 26: it is stated that two quartz glass tubes are routed through one tube furnace. I am wondering how to control the different temperature at each individual quartz tubes as shown in Fig 2a (850°C vs. 600°C).

=> The two quartz tubes are used at the same temperature in two consecutive steps: the oven is first heated to 850°C for the combustion. The oven temperature is afterwards reduced to 600°C for the reduction. Now explained in more detail in the revised manuscript.

(4) P3504 lines 5-8: the 250mL should be marked on the figure (Fig 2a). Is the tear shaped bottle be able to be disconnected from the system for pipetting the sample into a vial? If yes, why is it not shown on Fig.2a?

=> All points considered in the revised version of the manuscript.

(5) P3504 line 19: It is suggested replacing “1l” with “1L” and throughout the whole text.

=> The journal requires small letters for the units.

(6) P3505 lines 2-4: It is suggested to mark the pathway for the cryo-transfer in Fig.2. Should H₂O-trap be merged first or CO₂ -trap be merged first? How to prevent H₂O from being trapped in CO₂-trap (at -198°C) during the alternations of submerging? Again, a clear flow chat suggested in (1) will clarify those questions.

=> The points are addressed in section 2.2 of the revised manuscript. Cryo-transfers and gas flow within the system are explained in more detail; therefore we did not mark it in the figure on the setup.

(7) P3505 line 9-10: The verification of the quantitative combustion of CH₄ should be described and discussed in more details. Fig 3 and its caption are not well understood. It seems that three scans of mass abundances were overlapped in Fig.3A, which is not clearly mentioned in the caption.

=> Both, the figure and the figure caption are revised in the manuscript. We followed the suggestions of reviewer # 1 to avoid the baseline overlap of the three lines and introduced an offset on the y-axis. This improves the clarity of the figure.

How long does it take for one cryo-transfer cycle?

=> It takes about 10 minutes and is now mentioned in section 2.2 of the revised manuscript.

(8) P3506 line 1: how to transfer the H₂O from the tear shaped bottle into the 1ml glass vial?

=> This is now mentioned in section 2.2 of the revised manuscript

(9) P3506 lines 23-24: it is suggested to re-phrase the sentence as “ we mix the fossil CH₄ with the Biogenic CH₄ and barometrically controlled the mixing ratio between the two.”

=> rephrased in the revised manuscript

(10) P3507 lines 1-14: it is suggested including the procedure of making CH₄ free air (N₂/O₂), as a component, in the flow chat suggested in (1).

=> The components used for the N₂/O₂ purification are now shown in Figure 3. As mentioned above, we found the separation of physical setup components and methodological relations to increase the clarity.

(11) P3507 line 18: It is suggested replacing “6l” with “6L” and throughout the whole text.

=> The journal requires small letters for the units.

(12) P3507 line 21: I am wondering why at a pressure of 1 bar, the CH₄-free air flow was re-routed through the aliquot instead of at the vacuum pressure from the beginning.

=> Now explained in section 2.4 of the revised manuscript

(13) P 3507 line 27: I am wondering what the maximum pressure is after the filling.

=> 2.8 bar, described in section 2.4 of the revised manuscript

(14) P3509 lines 11-19: The offset implies that the isotopic fractionation in mixing (with N₂/O₂) procedure could not be totally ruled out, as other procedures you mentioned. It is suggested to list GIS and MIS values (i.e., the means and the corresponding standard deviations) measured by GC-IRMS, which are the data before offset corrections, then to derive a relative difference between GIS and MIS, which should be equal to the corresponding relative difference between GIS_p and MIS_p measured by off-line if the whole approach introduces the same degree of isotopic fractionation for both GIS and MIS. Otherwise, the method may not provide with you a consistent air-CH₄ isotope reference for a period of long time (e.g., decadal time), which is required by serving the WMO-GAW atmospheric measurement network.

=> The suggested data are indirectly shown in Table 2. Table 2 lists the results for MIS_p and GIS_p along with the “daily system error” of the GC-IRMS setup. The sum of the respective data represents the mean of the measurements for MIS and GIS, e.g. $-42.21 + (-0.29) = -42.5$ ‰ for GIS and $-47.25 + (-0.34) = -47.59$ ‰ for MIS. The difference of both uncorrected mean values is 5.09 ‰, the difference between MIS_p and GIS_p is 5.04 ‰. The mean of the unprocessed MIS and GIS data therefore agree within the uncertainty of 0.04 ‰ which we stated for the offline combustion method and assume for GIS and MIS. Even though this agreement is very convincing, it contains a random component and is therefore not a reliable measure for fractionation effects during the reference gas mixing. This is because the raw results vary with the potential day to day variability of the “daily system error”, where the latter can exceed the uncertainty of MIS_p and GIS_p by an order of magnitude. For example, the measurements of NEEM versus MIS could inhere a much smaller “daily system error” than NEEM versus GIS if both were measured on different days. If this offset was due to fractionation in the mixing of the isotope reference gases, the processed results of NEEM would disagree. Due to the nature of the “daily system offset”, we cannot compare measurements that were done on different days without measurements of an additional gas as mediator. As for the manuscript, the co-measured NEEM gas is corrected for this offset in both cases and shows the results that agree well within the uncertainty. This concludes the mixing of isotope reference gases does not produce significant isotope fractionation. The suggestion to compare the raw results of GIS and MIS is a very good point if both gas mixtures were measured against each other during the same day and were thus superimposed by the same “daily system error”.

I am wondering how many 6L flasks of GIS and MIS were prepared in total for this work. You should derive an uncertainty of GIS and MIS from those independently prepared flasks, including both preparing and measuring processes. It is likely that the current errors listed in Table 2 are only measurement errors from the GC-IRMS.

=> The errors in Table 2 are the propagated standard errors of the mean from sample and standard measurements as well as the uncertainty of MIS_p and GIS_p (explained in section 3). The measurements were done on one mixture each, thus uncertainty that is introduced by the mixing procedure is not included. Unfortunately, we cannot provide additional data on this matter at this point, but in the manuscript we highlight the importance of this issue when it comes to the production and distribution of such standards to other laboratories.

(15) P3514 line1 in Table 1: what is N45?

=> As mentioned above, changed in the revised version of the manuscript.

(16) P3518 Fig 3b: What is the definition of the normalized $\delta^{13}\text{CH}_4$ offset? The legends in Fig. 3 are not clear. It is suggested to replace black line with red line

=> The normalized offset refers to the difference between expected and measured value. In the revised manuscript, the “normalized $\delta^{13}\text{CH}_4$ ” will be changed to Δ , similar to Merritt et al. (1995a). We changed the presentation of the data in the figure to improve clarity. We therefore suggest keeping the colours of the lines, as the simultaneous use of red and green in a plot of close lines can introduce additional ambiguities.