

Author's response to Referee #1: Aydin, Murat

report 28 Mar 2023

Report #2

The manuscript has been substantially revised and does not need major revisions. Still, I want to clarify a few important points regarding the uncertainty estimates for the isotope data and have a couple of recommendations that I consider minor. I will state once more that measurements of dual isotopic signatures of xsCH₄ is a significant advancement in the current state of knowledge on this topic.

The point I made in the first review regarding the bias in linear fits (Figs. 8 and 9) with low N was with regards to the bias in the uncertainty estimates of the fit, not bias in the fit itself. For example, the del13CH₄ intercept for NGRIP bag 3453 is reported as -46.2 +- 1.5 permil (Fig. 8a). The +-1.5 permil uncertainty estimate is highly uncertain and expected to be biased regardless of the analytical regression method one uses (least squares vs. orthogonal) because N=3. I do not mind displaying the uncertainties for the individual intercept estimates on the figures simply because this is the common convention and the authors do not use these estimates during the subsequent data analyses anyway. Unfortunately, the uncertainty estimates for the weighted mean calculations are also uncertain for the same reason. That is, there are only four intercepts that are being averaged for del13C, which is akin to estimating a standard deviation from four measurements. If I'm not wrong, you use a different method for the delD data shown in Fig. 9 and calculate a weighted average of the two individual uncertainty estimates for the intercepts. This is ad hoc and somewhat unusual but OK to do in this case since there are two data points otherwise, although you should probably note this in the caption.

In any case, my main point here is that the true uncertainties in the weighted average values of del13CH₄ and delD based on Figs. 8a and 9 are probably larger than the reported values. As a result, I have more confidence in the uncertainty estimate for the 2nd extraction results than the uncertainty estimates for the Keeling plots. I acknowledge that the 2nd extraction measurements are more difficult to make due to small sample sizes and the uncertainties in individual measurement are higher. However, this shortcoming is counterbalanced by the ability to determine the overall uncertainty more precisely by averaging a larger number of data points. This actually provides stronger justification to conclude that 1st and 2nd extraction results cannot be differentiated from each other with the existing data and that the delD measurements do not contradict the previous estimate by Lee et al. (2020). However, I will suggest showing the 2nd extraction results (from Fig. 8b) in Fig. 11. I would also display the estimate by Lee et al. (2020) in the same figure. I believe this would provide a more comprehensive review of all currently available information in Fig. 11. I am

comfortable with the related discussions and conclusions remaining as is, including favoring the Keeling method results for isotopic signatures in the discussions. The authors also favor the ROS explanation over the adsorption/desorption mechanism. I agree with them that the theoretical and literature-based considerations of the possible mechanisms render a chemical mechanism more likely.

There must be a misunderstanding. We use the same method to estimate the weighted average of the dD-CH₄ and d¹³C-CH₄ signature and its uncertainty. The weighted mean and its weighted standard deviation are both weighted according to the number of samples measured per bag. This is explained on the text in line 578 ff. (no changes in the text here).

We agree with the referee that the sample number is small and therefore also the uncertainty estimate has its own error. However, we stress that the y-intercepts all agree within their calculated uncertainty. In response to the referee's comment, we added the following text to reflect this.

Line 582-589: new text

.... With the small number of samples that go into the determination of the y-intercept and its error in the Keeling plot for each individual bag, the estimates of the y-intercepts and their error have to be regarded statistically uncertain. However, comparing the results for the individual bags, they all agree within each within the estimated errors. In order to get a more representative value for the isotopic signature of excess CH₄ and its error, we calculate a weighted average for all bags for the y-intercept and its error. Nevertheless, this weighted error may still not be entirely representative because of the small sample number and the true error may likely be somewhat higher.

Line 652-655: new text

... As stated above, with the small number of samples that go into the determination of the y-intercept and its error in the Keeling plot for each bag, the estimates of the y-intercepts and their error have to be regarded statistically uncertain.

New Fig. 11a: values for NGRIP samples from the 2nd extraction were added. The estimate by Lee et al. (2020) cannot be added to this figure, as they only estimated the dD-CH₄ signature but not the d¹³C-CH₄ value.

The uncertainties in isotopic signatures from both the 1st and 2nd extractions can be reduced by more measurements of the same nature in the future. Such work may reveal that the del¹³C signature from 1st and 2nd extractions are in fact different, implying a more complex situation that involves more than one production mechanism. As a final suggestion, it may be worth dropping a brief note somewhere in the text acknowledging this possibility (for example a sentence or two in section 3) so the door remains slightly ajar for unexpected results from future data sets.

Of course, our discussion and interpretation would benefit from a more certain statistics with more data points. However, we refrain from adding such a statement as you proposed for the following reasons: if we consider the possibility that more measurements could show completely different results would imply that we do not trust in our results. We refer again to the new text added (see above) which stresses that all the results agree with each other within their calculated uncertainties.

Nevertheless, we do not close the door for new insights in the future regarding the best isotopic signatures nor for our interpretation. We do not determine one mechanism responsible for excess alkanes, but we explain what we favor or consider as likely in light of our results. If there will be more (and possibly unexpected) results in the future and thus more lines of evidence, we will review the discussion about potential mechanisms again.

Line 642: Negative sign missing. It should be -341.
corrected