

Interactive comment on “Reconstruction of the carbon isotopic composition of methane over the last 50 yr based on firn air measurements at 11 polar sites” by C. J. Sapart et al.

Anonymous Referee #2

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The manuscript describes the most elaborate study of $\delta^{13}\text{C}$ of methane from firn air to date. The authors combine records from nine different firn air sites, and use these to derive a record of $\delta^{13}\text{C}$ for both hemispheres. The topic is of importance to both our understanding of the global methane budget, as well as firn air transport processes. The manuscript is well written, and manages to clearly explain the complexities of firn fractionation and how it impacts their ability to reconstruct atmospheric $\delta^{13}\text{C}$.

The rate of change $\delta^{13}\text{C}$ change the authors derive for the recent atmosphere differs considerably (>50%) from earlier estimates. The authors do discuss the discrepancy with earlier estimates from firn and atmospheric measurements, but do not show which

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rate is the correct one. The authors also convincingly show that the large discrepancy between their sites is related to the firn fractionation, and uncertainties in the reconstructed diffusivity profiles. These two things combined leave the reader unnecessarily confused, and in doubt that atmospheric $\delta^{13}\text{C}$ can be reconstructed from firn air in the first place.

Unfortunately I cannot agree with the main conclusions the authors derive from their data and modeling efforts. I believe there is a fundamental error in the methodology, and given all the presented data and model output, I come to a different conclusion. I believe the work should be published in ACP eventually, given the importance of the topic and the amount of data and model work compiled in this study. I am certain this work will make a valuable contribution to our understanding of firn transport, and limitations therein. First a major revision of the work is needed, along the lines detailed below.

My main concern is the implicit assumption in the work that by averaging results at different sites one would obtain a more correct estimate of the true atmospheric variations. This would be correct if the histories reconstructed for the individual sites were consistent with each other – in which case averaging would make the final result more robust against measurement and sampling errors at the individual sites. In this study the authors find huge discrepancies between the single-site reconstructions that sometimes exceed the estimated measurement uncertainties by a factor of 10 or more. This hints at a problem with the reconstruction method, or perhaps calibration issues between the datasets from different labs. Given that the firn fractionation is so problematic, I think the right way to proceed would be to try and understand the firn fractionation better, and to see whether consistent site histories could be obtained using different assumptions about the firn gas transport. We know that the individual reconstructions are unreliable, because they give inconsistent results. By taking the average of two unreliable histories, one does not obtain a reliable history. An erroneous firn correction would probably bias all the individual site reconstructions in a similar manner,

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which cannot be corrected for by averaging between sites. The available atmospheric records (NOAA-ESRL, cape grim archive) are inconsistent with the obtained reconstruction in both hemispheres: in the NH the monitoring data show no downward trend for the last 10 years, and in the SH the isotopic trend in the reconstruction has only half the slope of the direct observations. The atmospheric monitoring data are not subject to the uncertainty of the firn fractionation, and should be considered more reliable. The authors discuss the differences between their reconstruction and previous ones, but do not make any statements about which reconstruction is more reliable. For this reason I think the work as it stands adds more confusion than it resolves.

I would also like to see a more thorough discussion of calibration issues between the different datasets. The authors are trying to resolve small atmospheric trends, and the sites cover different time intervals. Therefore small calibration issues will influence the observed trends. The information given now on calibration issues (Page 9591 lines 21-27) is limited and incomplete. For example, how does the CIC and NOAA-ESRL data relate to IMAU? E.g. in Figure 6a NOAA-ESRL data is introduced, which appears to be isotopically lighter than all the firn data. Most puzzling to me was the following inconsistency: on page 9591 it is claimed that CSIRO and LGGE have no systematic differences, and that IMAU is corrected to be consistent with LGGE (implying IMAU is consistent with CSIRO); yet on page 9602 there is an 0.28 permil offset between IMAU and PSU, while PSU is consistent with CSIRO Cape grim and law dome records (implying IMAU is 0.28 permil offset with CSIRO). It becomes very difficult to see how proper intercalibration is guaranteed. In many places the authors use words such as “possibly” (P9604) and “indirect evidence” (P9603) when discussing the calibration scales. Would it be possible to provide more clarity? Do the SH zero depth firn air samples (i.e. atmospheric measurements) match the reconstructed d13C history and monitoring data?

The technique the authors use is ultimately a statistical one: data from different sites are weighed by their uncertainty, and averaged to constrain the problem. I think some

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statistical tests would therefore be in order to assess the robustness of the final product; in particular bootstrapping and jackknife tests. Looking at the NH reconstruction (Fig. 6a) it appears to me that the NGR dataset is isotopically heavy. How does the reconstruction respond if it is left out? I suspect the downward trend after 2000 would disappear (consistent with the direct NOAA-ESRL data).

I would like to ask the authors to consider, and comment on, the following alternative conclusion from their dataset. I suspect they may have thought of this themselves; I would be very interested in their response.

There are four lines of evidence in the paper that DE08 is the most reliable of all the sites, because the firn fractionation is smallest there: 1. DE08 has very high accumulation, which gives the gases little time to fractionate diffusively, 2. The LGGE-GIPSA and CSIRO models give comparable values for the DE08 firn fractionation (Fig 7), 3. Changes to the diffusivity profile do not influence the calculated fractionation much (Section 5.3), and 4. The DE08 single site reconstruction agrees well with the Cape Grim air archive (Fig 6b). For these reasons I have more confidence in the combined Cape Grim/DE08 firn and ice reconstruction than in the multi-site reconstruction presented in the MS. Would it be possible to use the DE08/cape grim d13C record as a constraint in the diffusivity reconstruction? The authors mention this technique was applied successfully for DML (page 9598, lines 20-28).

The discussion section (section 7) of the MS is basically a summary of the previous pages, and not really a discussion. I suggest merging this section with the previous ones, or with the conclusions.

Other corrections:

Title: I think 11 polar sites is misleading. DI is not used in the reconstruction, and NM and SPO are sampled twice (Should NM 2008 and 2009 be considered different sites?). 8 polar sites would be more appropriate.

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P9589 L14-15: State your actual conclusions in the abstract. What trend do you get, how does the reconstruction compare to other records, etc.

P9592 L3: measurements usually lead to the conclusions that. ... Was this the case for this study?

L17-18: (Martinerie et al 2009): I think Clark et al. JGR 2007 is the more appropriate citation for DI

L24-25: A possible trend. ...our dataset: This is a very important statement. Do the authors mean that the reconstruction after 1993 is unreliable? This has implications for the interpretation of the results. Please elaborate.

P9593 L10-12: The connections between the individual pores and the bubble closure (on the microscopic scale) do determine the transport properties to a great degree. I would say both micro and macro-scale features are important.

L26: Martinerie 2012 is not in the reference list. If the work is still in preparation, remove the citation.

P9594 L1-12: mention in this first paragraph that you use a smoothness requirement for the solution (with link to supplement)

L19: is horizontal diffusion ever negligible? I suspect it occurs at all depths, the model simply does not require/capture it.

P9597 L10 and throughout the MS: Please specify you are referring to Fig 4b (instead of Fig 4). All figures have several panels, so refer to the specific panel.

P9598 L5-8: is it possible that the problem is mathematically under-constrained, and that the differences between NM-08 and NM-09 are in part due to that?

L10: high accumulation sites do not have a thinner diffusive zone. Compare Law Dome DE08 and DSSW20K, where the former high acc site has a longer diffusive zone. Also densification models predict a longer firn column at higher accumulation. From Fig 4

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it is clear that the firn fractionation is mostly sensitive to the diffusivity variations in the lock-in zone. In this zone advection is the dominant transport mechanism; advection does not fractionate, and hence the small sensitivity at DE08.

L26: Replace Fig 4 with Fig 4b

P9599 L20-21: Give a justification for doing this. I suspect using SPO-01 gives better results, but this seems a completely ad-hoc adjustment.

P9600 L10-12: Which reconstruction (green or red) is the better one, and for what reasons? Which one is used in the remainder of the study?

L14: what does "supposedly" mean here?

P9601 L24-25: This is too bad. An IPG estimate would be one of the most interesting things coming out of a reconstruction on both hemispheres. Could it be placed in the supplement (with large uncertainty bars)?

P9602 L5: Discuss the implications of the constant IPG reconstruction, or leave it out.

L16: Leave out "in review" references

L17-19: I disagree. The reconstruction shows a downward trend in the NH which is not there in the atmospheric data. Also, there appears to be an offset of around 0.2 permil. Perhaps it would make sense to show de-seasonalized atmospheric data (moving 1 year average filter) because the firn reconstruction has no seasonality either.

L20-27: It should be mentioned here that the cape grim archive does not suffer from firn fractionation, and is therefore probably more reliable. See my comment above on the calibration scale offset. I am confused, because on P9591 it is stated that IMAU and CSIRO are consistent.

P9603 L9: Also mention here that the difference in slope could be due to the firn fractionation correction that is applied to the data.

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L24: The fact that both models agree well on DE08 also shows that the firn fractionation can be reliably calculated at this site due to the high accumulation rate.

P9604 L2: what does “possibly” mean here? Please be precise with the calibration scales!

P9604 L15-18: This is an important and interesting new observation, which is completely unexpected. Can you explain this effect? Please elaborate.

P9605 L9-11: I would disagree with this statement. As I mentioned earlier I consider DE08 to be a more reliable site for $\delta^{13}\text{C}(\text{CH}_4)$ reconstruction, because it is not affected by the uncertainty in the firn fractionation modeling. More effort should be made to improve the consistency of the single-site reconstructions, e.g. by trying different firn air transport parameterizations, or by using different firn air models.

L16-19: This is an important and interesting conclusion. However, the cape grim record could be used to constrain firn models back to the 1970s.

P9606 L4: 8 sites, or 10 if different sampling campaigns at the same site are counted double.

P9613 and other figures: would it be possible to supply the figures as vector graphics? This should be a simple operation with most graphical editing software, and would considerably improve the readability of the figures. P9614: Why are the SPO-01 errorbars so large suddenly? In Fig 1b they seem comparable to other study sites.

P9618: This is one thing I don’t understand. How is it possible that for 1960-1980 the “best-estimate” reconstruction on both hemispheres is considerably below all the data points? This does not make sense if one tries to minimize the RMS. Is the regularization term of the solution set too high?

Supplement Section 1: the misfit for DI is really remarkable (Fig S1e). Could you comment?

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Supplement Section 3: what are the units of the k^2 term? Is it somehow related to a timescale on which the solution is smooth?

Supplement Section 4: Two methods are described, but which one was used for this study? This is not motivated or even discussed.

Technical / language / spelling:

P9589 L10: firn air transport models (insert “air” or “gas”)

L18: Its atmospheric mixing ratio has rapidly. . . (make ratios singular, insert “has”)

L22: list a few source mechanisms as well (sinks are explicitly mentioned)

P9590 L26-27: replace “results” with “data”

P9593 L5: replace “scenarios” with “histories”

P9595 L20: replace “changes” with “signals”. Add a comma after column

L21: add “a” before $\delta^{13}\text{C}(\text{CH}_4)$ trend

P9596 L3: add “ $\delta^{13}\text{C}$ ” before “atmospheric history”

P9599 L16: remove “sometime”

P9600 L27: replace “convert. . . into temporal isotope values” with “place isotope measurements on a time scale”

P9601 L3: “note” is used twice in sentence.

P9601 L15: add “strongly” in front of “constrained”

P9603 L22: typo, “LGEE” should be “LGGE”

P9604 L2: remove “ice core”

P9604 L18: replace “less” by “fewer”

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P9606 L5: add comma after “inversion”, replace “estimate of” with “calculated” or “modeled”

L6: replace “good” with “well”

P9612: is `z_last` in the caption the same variable as `z_lowest` in the table?

Supplement P3 L18: make plural: two different wayS of excluding. . .

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9587, 2012.