Author’s response to reviewers comments on:

“An automated setup to measure paleoatmospheric δ^{13}C-CH_4, δ^{15}N-N_2O and δ^{18}O-N_2O in one ice core sample”

P. Sperlich[1,2], C. Buizert[1,3], T.M. Jenk[1,4], C. J. Sapart[5], M. Prokopiou[5], T. Röckmann[5], T. Blunier[1]

1: Centre for Ice and Climate (CIC), Niels Bohr Institute, University of Copenhagen, Denmark
2 now at: Max-Planck-Institute for Biogeochemistry (MPI-BGC), Jena, Germany
3 now at: College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, USA
4 now at: Paul Scherrer Institute, Villigen, Switzerland
5: Institute for Marine and Atmospheric Research in Utrecht (IMAU), University of Utrecht, The Netherlands

We would like to thank both referees’ for their helpful and constructive comments. We find that the suggestions of both reviewers have helped improving the manuscript considerably and appreciate the initiated discussion. All comments by both reviewers were carefully discussed and most of the suggested changes are considered in the new manuscript. While referee # 1 (J. Schmitt) found the manuscript as “well structured and written”, referee # 2 (J. Rudolph) exclusively suggested changes to the structure and the way the manuscript was written. However, both referees’ agree in the point that the manuscript is too long. The new manuscript is shortened in the main section but now longer in the discussion of the intercomparison offset. Furthermore, referee # 1 suggested minor changes regarding the content and way of presentation, which we followed in almost all cases.

Comments to referee #1: J. Schmitt

[...] The only suggestion in that direction would be to provide a few sentences on the integration and background properties for N_2O.

Suggestion accepted

The comparison with δ^{13}C-CH_4 measurements performed at IMAU on almost parallel ice core samples from the NEEM core shows interesting and a bit worrying results and I propose to change the way the comparison is presented (see detailed comments).

Please find our response at your detailed comments

While 5 out of 6 samples agree very well, there is one depth interval, where an easy explanation could not be offered so far, but the authors point to impurity content as a possible reason for the difference between the two methods. A careful design of comparison measurements using different extraction methods and different ice cores from the same hemisphere is needed to allow identify the causes for this discrepancy among records which should be essentially the same.

We absolutely agree. A dedicated comparison campaign is needed to solve this problem.

Page: 2184

line 1: not to forget also the atmospheric mixing ratio itself

Suggestion accepted

line 26: For a comparison with other labs the term accuracy is not really defined. I would say that two labs agree or not.

Suggestion accepted

line 27: I agree that it is common practice and important to claim that a new technique produces data that agrees well with previous data. But what if the new data (your data) is better in terms of accuracy? You are in the comfortable position to own a device at CIC (Sperlich et al. AMT 2012 (combustion setup) which can produce CH_4 standards and the combusted CH_4-derived CO_2 can be measured with dual inlet against international standards. In principle you can check the accuracy of your own results. Further, you checked your system if it is affected by an interference with Kr and you showed that your system is not affected. On the other hand, several published δ^{13}C-CH_4 data sets suffer from an unaccounted interference with krypton with its magnitude often larger than your measurement precision. With this in mind, your statement that your data is in "good agreement with previously published data" basically means that the latter is also good and the

applied lab offset and Kr-correction was done successfully. My suggestion is to make two individual sentences: One were you state your own reproducibility of the ice core measurements. And the second, where you state how your data compares to others (I would term it general agreement, as one of the 6 NEEM sample intervals differed markedly and a long paragraph was written about that)

Suggestion accepted

Page: 2185

line 1: I am not sure if I would term CH_4 a long-lived gas (N_2O of course), because it's lifetime is shorter than 10 years. You could just omit long-lived, or state the life-time for both gases.

We acknowledge this classification doesn't represent an unambiguous distinction for short- from long-lived GHG. Since the lifetime of CH_4 and N_2O differ by more than one order of magnitude it might seem doubtful to classify both as long-lived. Therefore, we add the IPCC report 2007 (Solomon et al., 2007) as reference. Solomon et al. (2007) distinguish between long-lived GHG with decadal to centennial lifetime (CH_4, CO_2 and N_2O) versus short-lived GHG (e.g. SO_2, CO) with a lifetime in the order of days to weeks. One characteristic of the short-lived GHG is their high spatial variability in recent atmospheric mixing ratios due to their short lifetime, which does not apply as much for CH_4 as it does for CO.

Even though the lifetime statement is not absolutely crucial for this manuscript, we would like to keep it and to apply the established classification made by IPCC. We hope the added reference and this explanation will satisfy the reviewer.

line 2: typo: analysis

Suggestion accepted

line 5: You should add that the reconstruction of the palaeo-atmospheric CH_4 and N_2O mixing ratios offers much more than the knowledge of the radiative budget and the atmospheric side in general. Especially CH_4 serves as a proxy to reconstruct terrestrial/marine processes like the extent of wetlands, or the stability of methane clathrates or other CH_4 sources.

Suggestion accepted

line 11-13: I would move the aspect of biogeochemical processes directly after line 5, see comment there.

We tried the reviewers' suggestion but went back to the original. The paragraph is intended to have some sort of a time line. It very briefly discusses the relevance and findings of GHG analysis in glacial ice core samples, leads via the development of atmospheric mixing ratios during the industrialization to the arguments why this work is important in the light of future atmospheric variability. The temporal line of this review would be disturbed, therefore, we decided to leave the order of sentences. We made this time line more clear in the paragraph of the new manuscript and hope to convince the reviewer this solution has a clear structure.

line 15: integrated?

Suggestion accepted

line 26: a point is missing

Suggestion accepted

line 26: add at STP (standard temperature and pressure) conditions

Suggestion accepted and considered throughout the manuscript

Page: 2186

line 1: delete of

Suggestion accepted

line 7-8: The sentence is not immediately clear. Is your scheme with all 3 items (permanent oxidation, post-combustion cryo-trap and second GC) similar to Melton et al. 2011, or only the second GC?

We clarified this in the new manuscript. Our system comprises all 3 items, also indicated in Figure 1.

also remove the () around the citation

Suggestion accepted

line 15: clearly CO_2 and N_2O are isobaric species, but for the reader CH_4 and N_2O would be clearer omitting the conversion of CH_4 to CO_2 to have the isobaric species to N_2O

Clarified in the manuscript

line 20: you can shorten a bit by deleting "that are important ." We suggest the presented system as a useful tool to provide high-precision isotopic analysis of palaeo-atmospheric CH_4 and N_2O.

Suggestion accepted

__Page: 2187__

line 5: shorten to: flushed by helium

Suggestion accepted

line 16: placed?

Suggestion accepted

__Page: 2188__

line 1: a high variability in $\delta^{13}C\text{-}CH_4$.

Shortening accepted, sentence subject to more changes

line 5-6: perhaps you could draw T2 a bit more detailed since it is not really clear to me how to glass wool and SST mesh is oriented in the trap

Suggestion accepted

line 6: is this the maximum capacity of the trap?

The maximum is ~1.5 L, now mentioned in text.

line 8: format -1

Suggestion accepted

line 11: better: extraction flow (50 mlmin-1 He)

Suggestion accepted

line 15: I am not sure if I understand the argument with the heated tubing. I guess the idea is to increase the efficiency of the gas transport from the melt pot to T1 and T2. While it is true that at higher temperature the pressure rises, but at the same time the viscosity of the gas increases. Further, the pressure gradient from the melt pot to the hot tubing is reversed thus reducing the flux to T1. But obviously you have positive test results about that to justify the effort of heating and insulating the tubing and valves.

This is now written more clearly and moved to another position in the text. The heating of the extraction line does not significantly impact the air sample transport but it helps removing water from the extraction line into the water traps during and after analysis.

line 15: ...can be trapped more efficiently..

Sentence subject to more changes

line 17: omit the 50 ml...and just say: into the extraction flow, because you defined it above for this purpose

Suggestion accepted and applied throughout manuscript

line 21: see comment line 17

Suggestion accepted

Page: 2189

line 4: add most, since some N_2 and O_2 usually remain on the traps together with CH_4

Suggestion accepted

line 13: reorder: holds Ascarite () to remove CO_2 and $Mg(ClO_4)_2$ to remove H_2O

Suggestion accepted

line 21: two-position

Suggestion accepted

line 23: you could also give these flows a name as you did for the extraction flow

Suggestion accepted, transfer flow (10 mL/min) and analytical flow (1 mL/min)

Page: 2190

line 7: chromatographic?

Suggestion accepted

line 23: just curious: was this actually tested? Do you have proof that CO_2 flakes escape?

It was not tested and is possibly unlikely to be observed by eye because mobilized CO_2 particles would sublimate in the warm line components before the vent. However, when we froze out large quantities of CO_2 (120 mL STP) in the referencing setup (Sperlich et al., 2012), we observed flaky CO_2 that moved down the surface of the glass trap. This was just by gravitational force in a static system without air flow. We applied the Ni wire and found very stable CH_4-induced CO_2 peak sizes.

Besides that, the wording is a bit unclear:...prevent CO_2 particles from being blown out..

Suggestion accepted

Page: 2191

line1 and the entire procedure: check tenses? usually present is used for describing the procedure

Suggestion accepted

line 2: rewrite: To increase heat conduction...T1 is pressurized..

Suggestion accepted

line 7: by removing

Suggestion accepted

line 8: any attached sawdust was removed..

Suggestion accepted

line 10: to prevent contamination

Suggestion accepted

line 12: this is a lot, so for a 500 g sample you melt for the extraction you actually use 700 g "raw ice"?

We remove 3-5mm which means our decontamination is similar to the procedures described in other publications. However, a quantification of the removed ice mass wasn't given in any of the other publications. Note, that the stated 30 % also include the ice that we removed due to cracks or impurities. Here is a brief summary how other authors quantify/discuss the decontamination for similar measurements:

Schaefer and Whiticar (2007) cut off 2-3 mm, same method used by Melton et al (2011),

Sowers et al. (2005) remove ~5mm,

Etheridge (1996) trimmed off 5-20 mm,

Sapart et al. (2011) cut off ~2mm after using the band saw to cut the sample in shape,

Behrens et al. (2008)remove about 15 %,

Bock et al. (2010) did not quantify how much is removed,

Bernard et al. (2006) did not mention decontamination of their ice core samples at all.

line 12: I am aware that volcanic tephra layers are cut out, but I have never heard that gas-people remove dust layers and soot layers (does the NEEM core really has visible soot layers?). It would be really interesting to measure these cut-out dust layers for the isotopes.

Some of our samples contained visible impurities. A correlation between impurities and CH_4 artefacts has very recently been described (Rhodes et al., 2013). The cut out sections are stored at CIC for future analysis. However, since they are from different time intervals, the true atmospheric background of that time has to be known and because of the inherent atmospheric variability, measuring all sections together as bulk will be of limited information.

<u>Page: 2192</u>

line 1: is the water trap close to the pump shown on Fig. 1? I could not find it?

now shown in figure 1

line 1: With this method we avoid frequent opening..

Suggestion accepted

line 16: (and a many places elsewhere) to get rid of a few unnecessary words, you can delete the word isotope and just write reference gas, it is clear to the reader that you reference the isotopes

Suggestion accepted

line 24: Is it pumped to the pump symbol on the left side of the melt pot?

Yes

what kind of pump do you use?

Now specified in the method section (turbo pump, Pfeiffer).

line 25: actually the ice water (0°C) bath warms the sample which is colder as it was in the freezer before at -15°C and due to pumping on it the ice cools further. So actually you warm the ice to achieve more sublimation on the surfaces and help clean the sample.

That is very true for the ice sample. Please note, we wrote that we cool the melt-vessel to prevent the ice from melting. Not cooled, atmospheric water vapour will freeze on the melt-vessel until it quickly warms to temperatures above freezing. The ice sample will also warm during this step, much depending on shape and size of the ice sample. Until the melting is started, the evacuated sample will be attached to the system for ~1 hour (30min evacuation + ~30min during analysis of previous sample). The ice water is needed to prevent the ice from melting during this time.

Page: 2193

line 17: you could mention somewhere in this paragraph that it is the pressure at P2 (it is clear, but it makes it faster to get).

Suggestion accepted

By the way, do you use P1 during the extraction to monitor the temperature and pressure evolution during melting?

We monitor the pressure during melting using P2 (p_{max} = 15 mbar, pressure max. during melting ~6mbar). We use P1 to measure the pressure of the evacuated melt-vessel to make sure the melt-vessel is leak-tight. We do not open the valve to P1 to prevent “dead-ends” in the extraction line.

line 20: I am wondering how you adjusted your procedure for the variability in melting duration. Sample size varies from 200 to 500 g, and I guess that the larger samples take longer to melt.

Samples of all sizes are evacuated for the same amount of time. When the melting is started, we simultaneously start the extraction of the deliberated air. As soon as the sample is completely melted, the pressure decreases exponentially to approach 0. For ice core samples of all sizes, the measurement routine that follows the melt-extraction is started at the moment the pressure falls below 0.11 mbar. That way, all samples are extracted to a similar pressure. The melting time does vary with sample size but even more with the way the melting sample rods “fall” into the melt water as they shrink, which is less predictable.

line 24: often some portion of O_2 and N_2 still remain in this fraction so you could write with residual O_2 and N_2.. ...which becomes separated later by GC and post combustion trap

Suggestion accepted

line 24: there is several occasions with Krypton in the text were it should read krypton.

Suggestion accepted

Page: 2194

line 7: yes, CO and CO_2 are required to be separated before the trap, but Kr should pass the trap, and N_2O is well separated by the GC

Suggestion accepted

line 14: delete in

Sentence removed

line 21-22: It is also possible that Umezawa et al. 2009 had a problem with krypton instead of a formation of N_2O from N_2 and O_2. But if it was krypton it is strange that the contaminant peak eluted before CH_4. In case of CO it would fit better. see Umezawa et al. 2009: "On the other hand, the trap T2 also adsorbed a portion of major air constituents such as N_2 and O_2. We confirmed that the air constituents adsorbed onto the trap T2 adversely affected the overall precision of the $\delta^{13}C$ measurement: they produced an unknown peak with masses 44, 45, and 46 several tens of seconds before the retention time of the CH_4-derived CO_2. The unknown peak interferes with the $\delta^{13}C$-measurement mainly with masses 45 and 46 because of its long tailing that heightened the IRMS baseline. Hereafter, this unknown peak is called ''the contaminant peak.'' To cope with both complete adsorption of CH4 and minimum adsorption of air constituents on the trap T2, we selected 130°C as the best temperature for attaining high-precision measurements."

Kr does not elute before CH_4. We therefore assume the problem described by Umezawa et al. (2009) is due to N_2 and O_2, which would match the chromatography and the fact N_2 and O_2 have a stronger impact on m/z 45 and 46 due to the formation of N_2O and NO_2. However, we removed this section to shorten the new manuscript.

Page: 2196

line 20: Theoretically, Kr should not be trapped at all at LN temperature. I wonder if you can estimate the fraction of trapped Kr from the total fraction of Kr. Do you have a measurement were you have the Kr not separated by T5? In our system in Bern the typical Kr signal measured at m/z43 (major cup tuned to m/z 43 instead of m/z 44) of an atmospheric sample is around 70 mV (Fig.3a, Schmitt et al. 2013). Looking at your Fig. 4 I see a Kr m/z 43 signal of smaller than 0.1 mV. From that I would assume that the trapped Kr is smaller than 1/700 of the total Kr.

We have to normalize the Kr peak for the amount of injected air as well. Kr freezes at -150°C, therefore some of it should freeze out in the capillary trap at -196°C. Though, I wouldn't want to quantify how much as we didn't inject the Kr peak directly.

Page: 2197

line 25: could you add more information here, because this is novel and others could learn from your experience. e.g., why did you hold the catalyst at 60°C? Have you tested also lower/higher temperatures? There are studies showing that Aurolite oxidizes CH_4 as well if temperatures are higher (i.e. 200°C). Reversely, is the CO conversion too slow at room temperature? Does the Aurolite catalyst needs to be replaced after a certain time? Would be nice to have some more info about your experience since this is the first application of this new catalyst. At the strem chemical website, there are three different kinds of Aurolite catalysts offered using different carrier material for the gold. Besides TiO_2, which you selected , there is also Al_2O_3 and ZnO. Have your tried also the others?

Our first experiments using Aurolite at 60°C indicated quantitative CO conversion and satisfied our requirements. Therefore, we did not make further experiments e.g. on different temperatures, column lengths or support material. All other points are answered/considered in the new version of the manuscript.

Page: 2199

line 24: and to complement the already long list of individual blank contribution you should add that N_2O (perhaps also CH_4) can also be produced in the water AFTER the sample was extracted. The melt water contains a lot of inorganic nitrogen (NO_3^-, NH_4^+) and is certainly not sterile, so microbial activity can add to the N_2O which is then extracted in the blank run. This N_2O (after extraction production N_2O) could likely explain your relatively high blank of 3%.

Suggestion accepted. However, we have no experience on that and can therefore not quantify this effect.

Page: 2200

line 5 to 12: while it is true that N_2O is more soluble that CH_4, your extraction efficiency should be better than 97% for N_2O as you continuously extract the gases while you melt in vacuum. So solubility is not a good explanation, my guess is N_2O which is produced in the water, see comment before.

See point above

line 20: yes, vacuum extraction is better than stripping.

Comment appreciated

Page: 2201

line 5-6: the meaning of this sentence is not clear to me, please rewrite it.

Suggestion accepted.

Page: 2202

line: delete molecules

Sentence deleted

line 18: I would not call this "equilibration time" 2 min is too short to reach equilibrium. Just say: after 2min.

Suggestion accepted.

line 19: history???

deleted

line 26: gases

Suggestion accepted.

Page: 2203

line 8: has not been

Suggestion accepted.

Page: 2204

line 1: would be shorter to say: GIS measurements are bracketing the ice core sample.

Suggestion accepted.

line 6:   ...end of the measurement day

Suggestion accepted.

Page: 2205

line 19-22: this sentence is rather long and difficult to read, please make two sentences.

Suggestion accepted.

Page: 2206

line 18: please make a distinction between the original data published in Sapart et al. 2012b and the data which are used here, i.e. corrected for Kr effect. e.g., you could name them IMAU Kr-corrected. I know this makes everything longer but helps the reader to see this difference.

Suggestion accepted, the IMAU data set which is corrected for the krypton effect is referred to as $\mathrm{IMAU}_{\mathrm{Kr}}$.

It would also be helpful to state how large the Kr correction is for the individual samples. As the Kr correction scales with CH_4 mixing ratio, you could also give the min and max correction value.

Suggestion accepted.

line 22: for non-ice core people a difference of 24 years sounds a lot. You could bring this into perspective by stating the width of the age distribution. Then it becomes clear that these samples have almost the same air included.

Suggestion accepted

line 25: From the pure text, it is not clear if you mean a disagreement among CIC and IMAU or only among the 4 CIC samples. In the figure it is clear that you mean that all 4 CIC samples are very similar, but deviate from IMAU by 1 permil. It would also be helpful for the reader to say the direction of this disagreement. e.g., with the IMAU sample about 1 permil heavier (or the other way around if you like)

Suggestion accepted

Page: 2207

line 4: gravel are very large particles ranging from mm to several cm. I think you mean much smaller particles? Or are there really visible particles like in an ash layer? Further, the precise meaning of the sentence is not clear to me. Did someone actually see small gravel in the sample which was measured at IMAU or is this a possibility?

Suggestion accepted. Visible inclusions were cut out at CIC while observed particles were recorded but not removed at IMAU.

line 25: I agree, at the moment you can only speculate about these effects until this time interval is revisited again with another method and/or other ice core. One puzzling thing about your particle theory is that the Sapart et al. 2012b data set looks precise and smooth and there is no indication of scatter or erratic effects due to particle effects or whatever. At the 946 AD position there is a broad maximum (referred (2) in Fig. 1 of Sapart et al. 2012b). It is hard to assume that this special sample at 946 AD is an outlier of 1 permil in Sapart et al, because of this smooth peak. If this were the case then the entire (2) peak has to be questioned. On the other hand, your 4 samples agree so well, that it is also very unlikely that they all represent outliers due to a certain in-situ process. Given the high temporal variability of particles in the ice it is unlikely that your 4 samples have all the same level of in-situ production from particles. So I fully agree that this is a puzzling situation. Since your disagreement for this particular age is large (comparable to the entire variability of $\delta^{13}C\text{-}CH_4$ between 1 AD and 1500 AD) and well settled, I suggest to make this observation visible also in terms of a time series in a modified Fig. 8. My suggestion is to plot the NEEM $\delta^{13}C\text{-}CH_4$ time series of Sapart et al. 2012b (Kr corrected version) and your results together on an age AD x-axis like in Sapart et al. (it would be elegant if you could provide also a secondary x-axis on top of the figure showing roughly the depth range for these sample). For 5 age intervals your samples will perfectly lie on the Sapart data, but for 946 AD there is 1 permil difference. With that figure you convey your original message (perfect agreement, but one "outlier") AND the reader can think about the different possibilities, i.e. which process or which method could have produced the outlier.

We acknowledge that displaying the full data sets over time would give additional information to judge the agreement/disagreement in the context of the variability of the signal over time. Before initial submission and during this review, we discussed this point extensively within the author group. We decided on the direct comparison of CIC versus $IMAU_{Kr}$ data because this comparison alone is sufficient for the discussion of measurement agreements. Even though we provide a hypothesis what might be related to the observed offset, the true reason for this offset remains unresolved. This disagreement has been intensively investigated and a measurement campaign dedicated to investigate this problem is currently being planned. This work will require more time and exceeds the scope of this technical paper. Therefore we feel strongly about not presenting our data in this way. We hope this argument will convince reviewer # 1 that the presented comparison is a sufficient solution for this manuscript.

Page: 2209

line1: typo, measurement control

Suggestion accepted

Page: 2215

Table 1: please align the CH_4 ppb and $\delta^{15}N$ and $\delta^{18}O$ columns on the right side to prevent scrambled columns

Suggestion accepted

Page: 2220

Fig. 3 top: I wonder if the last N_2O std-on off peak is too close to the N_2O sample peak. Usually a long-lasting slope is involved with such a large pre-peak and could influence the background region before the N_2O sample peak. It would also be helpful to show how you dealt with the background for the N_2O sample peak in a separate figure zooming into the N_2O peak region (perhaps in an inlay figure)

Suggestion accepted. Please note that the on-off peaks only seem “large” in comparison to the “small” glacial ice core sample N_2O peak. The on-off peak intensity of about 500 mV is accounts for 1% of the maximum intensity of 50 V of the Delta V Plus IRMS. The isotope determination of smaller on-off peaks would be less precise.

Figure 3 and caption:

Top panel: For me the arrow with "CO_2 trace" was very confusing at the beginning (I thought these peaks were CO_2 peaks). To indicate, that these peaks are all N_2O you could write N_2O std on off peaks in the top panel and CO_2 ..in the bottom panel.

Arrow is removed, N_2O and CO_2 is specified in the axis labels

I would remove the arrow with the text CO_2 trace and put this information into the text (like: CO_2 elutes about 60 s before the N_2O sample and is usually covered by the N_2O rectangular peak, except when the Ascarite is exhausted then I guess that you see a CO_2 peak within the rectangular N_2O peak?

Suggestion accepted

Page: 2221

caption 4: I would not call this a krypton-effect, because you tuned the IRMS precisely to m/z 43 thus to a m/z where Kr has a regular mass contribution. I would use kr-effect in those occasions, where a signal is measured at a m/z where one is surprised to see it like m/z 44 or m/z 45

Suggestion accepted

Page: 2222

caption Fig. 5: you could extend the regression line towards zero in order to show that both lines have their origin in zero/zero

Suggestion accepted

Page: 2223

figure caption Fig. 6: the shaded area is not visible in a print-out, and hardly on the screen. Please apply a bit more grey tone.

Suggestion accepted

comments to referee #2: J. Rudolph

[...] I think that there are some parts of the paper where redundant or unnecessary explanations can be avoided or condensed. There are also parts that should be reorganized to make the paper more readable. A problem that, in my opinion, adds length and makes the paper sometimes difficult to read is an unusual structure. Chapter 2 is called "Experimental set-up". However, it already contains significant description of procedures. It also contains several statements explaining the purpose or intention of a specific step in the procedures or part of the set-up. In some cases the explanations are based on results that are only presented in a very general way. These statements are out of place in a method description and the reader will not know to which extent the stated purpose has been achieved, unless the subject is evaluated in the results and discussion section. In some cases those statements connecting method description with explanations also lack clarity.

In the new manuscript, we followed the suggestion of referee # 2 and re-structured the manuscript. The new "method" section only comprises technical descriptions followed by explanations of the analytical procedures. Lengthy explanations (e.g. CO-oxidizer, krypton effect, etc.) are removed from this section. Next, a "results and discussion" section follows that now contains the discussion of our findings, some of which have been part of the previous "Experimental set-up" section.

"The good performance of the.."

we removed this part

"that make a minimum path length through the glass beads of _50 mm"

we removed this part

"Intensive extraction tests using several charcoal adsorbents in T2 showed additional CH4 contribution and a high variability in isotopic analysis in our setup. We found that the speed of adsorption can significantly be increased with larger cross-sections of the adsorbing trap"

We agree that this section is not typical for a method chapter. However, we feel that both points on adsorbent material and trap diameter might be important for those readers, who plan constructing a similar device to extract trace gases from air samples. Because charcoal adsorbents are used by several laboratories measuring CH4 isotopes in air samples, we spend a lot of experiment time and trusted the material in the first place. If we had known of a publication that was critical of charcoal adsorbents, we might have been more critical as well. We could provide experimental evidence on the effect of an increased trap diameter. However, discussing both points in detail would furthermore lengthen the manuscript and we feel that addressing these points briefly in the method section is a good compromise. In the new manuscript, we are more specific and identify the used charcoals and quantify the effect of the increased trap diameter.

“to increase the water vapour pressure so any ice core sample derived water can be more efficiently trapped in T1“

we removed this part

“thereby minimizing the manual valve operation and analysis time.”

we removed this part

”to enable CH4 and N2O mixing ratio analysis from the total amount of air analysed and the trace gas peak areas in the IRMS analysis [...]”

this part is shortened

”The dimensions of this trap combine a relatively long contact-time [...]”

we removed this part

The other subchapters of “experimental set-up” contain similar statements. They should be removed from the method description. In cases where the authors consider the subject to be highly relevant for the performance of the methodology, it should be part of the discussion section using experimental results, theoretical considerations or information from literature to demonstrate to which extent the desired purpose is achieved.

we followed this suggestion

Several of the subchapters are a description of procedure and not so much an experimental set-up. This makes the separation between this chapter and other chapters that describe procedures or tests somewhat arbitrary. Chapter 3 (System performance) also contains a mixture of material that I would expect either in a method section, or results and discussion. Chapter 4 also is mainly description of method, it is very short and consists of only one paragraph. Chapters 2-4 should be combined under in a “Method sections” and information referring to results and arguments about the rational for specifics of the set-up should be moved to the results and discussion section.

we followed this suggestion

The conclusions contain a significant summary component. Change the heading to “Summary and conclusions”.

we followed this suggestion

References

Behrens, M., Schmitt, J., Richter, K. U., Bock, M., Richter, U. C., Levin, I., and Fischer, H.: A gas chromatography/combustion/isotope ratio mass spectrometry system for high-precision delta c-13 measurements of atmospheric methane extracted from ice core samples, Rapid Communications in Mass Spectrometry, 22, 3261-3269, 10.1002/rcm.3720, 2008.

Bernard, S., Rockmann, T. R., Kaiser, J., Barnola, J. M., Fischer, H., Blunier, T., and Chappellaz, J.: Constraints on n2o budget changes since pre-industrial time from new firn air and ice core isotope measurements, Atmos. Chem. Phys., 6, 493-503, 2006.

Bock, M., Schmitt, J., Behrens, M., Möller, L., Schneider, R., Sapart, C., and Fischer, H.: A gas chromatography/pyrolysis/isotope ratio mass spectrometry system for high-precision delta d measurements of atmospheric methane extracted from ice cores, Rapid Communications in Mass Spectrometry, 24, 621-633, 10.1002/rcm.4429, 2010.

Etheridge, D. M., Steele, L. P., Langenfelds, R. L., Francey, R. J., Barnola, J. M., and Morgan, V. I.: Natural and anthropogenic changes in atmospheric co2 over the last 1000 years from air in antarctic ice and firn, Journal of Geophysical Research-Atmospheres, 101, 4115-4128, 1996.

Melton, J. R., Whiticar, M. J., and Eby, P.: Stable carbon isotope ratio analyses on trace methane from ice samples, Chemical Geology, 288, 88-96, 10.1016/j.chemgeo.2011.03.003, 2011.

Rhodes, R. H., Faïn, X., Stowasser, C., Blunier, T., Chappellaz, J., McConnell, J., Romanini, D., Mitchell, L. E., and Brook, E. J.: Continuous methane measurements from a late holocene greenland ice core: Atmospheric and in-situ signals, Earth and Planetary Science Letters, 368, 9-19, 10.1016/j.epsl.2013.02.034, 2013.

Sapart, C. J., van der Veen, C., Vigano, I., Brass, M., van de Wal, R. S. W., Bock, M., Fischer, H., Sowers, T., Buizert, C., Sperlich, P., Blunier, T., Behrens, M., Schmitt, J., Seth, B., and Röckmann, T.: Simultaneous stable isotope analysis of methane and nitrous oxide on ice core samples, Atmos. Meas. Tech., 4, 2607-2618, 10.5194/amt-4-2607-2011, 2011.

Schaefer, H., and Whiticar, M. J.: Measurement of stable carbon isotope ratios of methane in ice samples, Organic Geochemistry, 38, 216-226, 10.1016/j.orggeochem.2006.10.006, 2007.

Solomon, S., Qin, D., Manning, M., Alley, R. B., Berntsen, T., Bindoff, N. L., Chen, Z., Chidthaisong, A., Gregory, J. M., Hegerl, G. C., Heimann, M., Hewitson, B., Hoskins, B. J., Joos, F., Jouzel, J., Kattsov, V., Lohmann, U., Matsuno, T., Molina, M. J., Nicholls, N., Overpeck, J., Raga, G., Ramaswamy, V., Ren, J., Rusticucci, M., Somerville, R., Stocker, T. F., Whetton, P., Wood, R. A., and Wratt, D.: *Climate change 2007: The physical science basis. Contribution of working group i to the fourth assessment report of the intergovernmental panel on climate change*, 2007.

Sowers, T., Bernard, S., Aballain, O., Chappellaz, J., Barnola, J. M., and Marik, T.: Records of the delta c-13 of atmospheric ch4 over the last 2 centuries as recorded in antarctic snow and ice, Global Biogeochemical Cycles, 19, 10.1029/2004gb002408, 2005.

Sperlich, P., Guillevic, M., Buizert, C., Jenk, T. M., Sapart, C. J., Schaefer, H., Popp, T. J., and Blunier, T.: A combustion setup to precisely reference delta c-13 and delta h-2 isotope ratios of pure ch4 to produce isotope reference gases of delta c-13-ch4 in synthetic air, Atmos. Meas. Tech., 5, 2227-2236, 10.5194/amt-5-2227-2012, 2012.

Umezawa, T., Aoki, S., Nakazawa, T., and Morimoto, S.: A high-precision measurement system for carbon and hydrogen isotopic ratios of atmospheric methane and its application to air samples collected in the western pacific region, J. Meteorol. Soc. Jpn., 87, 365-379, 10.2151/jmsj.87.365, 2009.

Walther, G., Cervera-Gontard, L., Quaade, U. J., and Horch, S.: Low temperature methane oxidation on differently supported 2 nm au nanoparticles, Gold Bull., 42, 13-19, 10.1007/BF03214901, 2009.