

This manuscript by Sperlich et al. reports on a new online method to determine $\delta^{13}\text{C-CH}_4$, $\delta^{15}\text{N-N}_2\text{O}$ and $\delta^{18}\text{O-N}_2\text{O}$ on a single ice core sample using only one mass spectrometer. The last decade has seen several publications dealing with new methods to measure $\delta^{13}\text{C-CH}_4$ and also methods to determine the isotopic composition of N_2O on ice core samples. Yet the new method of Sperlich et al. is not just a collection of well-established technologies which were combined and optimized, instead, this paper presents several new approaches and technical solutions to old problems of this field (e.g. novel CO oxidation with gold catalyst, clever design of T3, vacuum-melt extraction instead of He purging, and more). For these achievements, I want to congratulate the authors of this paper. Besides these technical aspects this publication has a strong focus on referencing protocols and intercomparison exercises as well which become more and more important since data of several labs has to be combined. The paper is well structured and written very detailed which allows the reader to follow each step in the analysis. This detailed description, however, makes this paper long. I thought about possibilities to shorten it, but considering the complexity of the technique, I made only a few minor suggestions to delete some words. Regarding language, the readability of the paper could be improved by native speaker editing; I did not make too many comments. The paper has a bias towards the CH_4 part, but since the paper is already comprehensive, I am fine that the N_2O part is not that detailed. The only suggestion in that direction would be to provide a few sentences on the integration and background properties for N_2O . From my experience with N_2O isotope analysis, precision and accuracy of $\delta^{15}\text{N}$ and especially $\delta^{18}\text{O}$ is very sensitive to the background before the N_2O peak and how this background is treated (sloping background or constant background, duration and distance to the peak start). Additionally, I suspect that the large rectangular N_2O peak before the N_2O sample peak could produce a slope which is difficult to handle and provides opportunities for improvement. Little is mentioned about these issues. Does this mean that the background situation for N_2O is perfect, so it is insensitive to your choice? Given that the shot noise contribution explains only 20-30% of the total reproducibility for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, it could be worthwhile to invest time in this direction. In contrast, for $\delta^{13}\text{C-CH}_4$ the shot noise contribution explains already half the variance, indicating that the system is well optimised for $\delta^{13}\text{C-CH}_4$ and hard to improve further. The comparison with $\delta^{13}\text{C-CH}_4$ 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). 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. For that reason, a method like this described here by Sperlich et al. is a step forward, because these differences among records can only be resolved, if the method is precise and uncompromised by interferences, and at the same time, well automated to allow a rapid sample throughput.

Overall, this manuscript meets the criteria to be published in Atmospheric Measurement Techniques with only minor changes.

Please find below a list with detailed comments, questions and suggestions:

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line 1:

not to forget also the atmospheric mixing ratio itself

line 26:

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

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 CH₄ standards and the combusted CH₄-derived CO₂ 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 $\delta^{13}\text{C}$ -CH₄ 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 where 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)

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line 1:

I am not sure if I would term CH₄ a long-lived gas (N₂O of course), because its lifetime is shorter than 10 years. You could just omit long-lived, or state the life-time for both gases.

line 2:

typo: analysis

line 5:

You should add that the reconstruction of the palaeo-atmospheric CH₄ and N₂O mixing ratios offers much more than the knowledge of the radiative budget and the atmospheric side in general. Especially CH₄ serves as a proxy to reconstruct terrestrial/marine processes like the extent of wetlands, or the stability of methane clathrates or other CH₄ sources.

line 11-13:

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

line 15:

integrated?

line 26:

a point is missing

line 26:

add at STP (standard temperature and pressure) conditions

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line 1:

delete of

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? also remove the () around the citation

line 15:

clearly CO₂ and N₂O are isobaric species, but for the reader CH₄ and N₂O would be clearer omitting the conversion of CH₄ to CO₂ to have the isobaric species to N₂O

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 CH₄ and N₂O.

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line 5:

shorten to: flushed by helium

line 16:

placed?

Page: 2188

line 1:

a high variability in $\delta^{13}\text{C-CH}_4$.

line 5-6:

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

line 6:

is this the maximum capacity of the trap?

line 8:

format -1

line 11:

better: extraction flow (50 mlmin⁻¹ He)

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.

line 15:

...can be trapped more efficiently..

line 17:

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

line 21:

see comment line 17

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line 4:

add most, since some N₂ and O₂ usually remain on the traps together with CH₄

line 13:

reorder: holds Ascarite () to remove CO₂ and Mg(ClO₄)₂ to remove H₂O

line 21:

two-position

line 23:

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

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line 7:

chromatographic?

line 23:

just curious: was this actually tested? Do you have proof that CO₂ flakes escape?

Besides that, the wording is a bit unclear:...prevent CO₂ particles from being blown out..

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line 1 and the entire procedure:

check tenses? usually present is used for describing the procedure

line 2:

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

line 7:

by removing

line 8:

any attached sawdust was removed..

line 10:

to prevent contamination

line 12:

this is a lot, so for a 500 g sample you melt for the extraction you actually use 700 g “raw ice”?

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.

Page: 2192

line 1:

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

line 1:

With this method we avoid frequent opening..

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

line 24:

Is it pumped to the pump symbol on the left side of the melt pot? what kind of pump do you use?

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.

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

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.

line 24:

often some portion of O₂ and N₂ still remain in this fraction so you could write with residual O₂ and N₂..
...which becomes separated later by GC and post combustion trap

line 24:

there is several occasions with **K**rypton in the text were it should read **k**rypton.

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line 7:

yes, CO and CO₂ are required to be separated before the trap, but Kr should pass the trap, and N₂O is well separated by the GC

line 14:

delete in

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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ -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 CH_4 and minimum adsorption of air constituents on the trap T2, we selected 130°C as the best temperature for attaining high-precision measurements."

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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.

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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?

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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%.

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line 5 to 12:

while it is true that N_2O is more soluble than 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.

line 20:

yes, vacuum extraction is better than stripping.

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line 5-6:

the meaning of this sentence is not clear to me, please rewrite it.

Page: 2202

line:

delete molecules

line 18:

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

line 19:

history???

line 26:

gases

Page: 2203

line 8:

has not been

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line 1:

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

line 6:

...end of the measurement day

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line 19-22:

this sentence is rather long and difficult to read, please make two sentences.

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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. It would also be helpful to state how large the Kr correction is for the individual samples. As the Kr correction scales with CH₄ mixing ratio, you could also give the min and max correction value.

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.

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)

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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?

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 $\delta^{13}\text{C-CH}_4$ 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 $\delta^{13}\text{C-CH}_4$ 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.

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line:

typo, measurement control

Page: 2215

Table 1:

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

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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 N₂O sample peak in a separate figure zooming into the N₂O peak region (perhaps in an inlay figure)

Figure 3 and caption:

Top panel: For me the arrow with "CO₂ trace" was very confusing at the beginning (I thought these peaks were CO₂ peaks). To indicate, that these peaks are all N₂O you could write N₂O std on off peaks in the top panel and CO₂ ..in the bottom panel. I would remove the arrow with the text CO₂ trace and put this information into the text (like: CO₂ elutes about 60 s before the N₂O sample and is usually covered by the N₂O rectangular peak, except when the Ascarite is exhausted then I guess that you see a CO₂ peak within the rectangular N₂O peak?

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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

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caption Fig. 5:

you could extend the regression line towards zero in order to show that both lines have their origin in zero/zero

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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.