

Reply to reviewer 1:

We thank the reviewer for the relevant comments and remarks which we used to improve the quality of the paper. Nearly all the comments were included in the revised version of the manuscript. Here below is our detailed answer point by point:

Specific comments from the reviewer are in **Bold *Italic***:

Page 4477, line 3-6:

What is the normal ice weight required for CH₄ and N₂O stable isotope analysis for ice core air? The ice weight required for isotope measurements depends of course of the amount of gas in the ice sample. For Holocene samples, the amount of ice required is about 0.3-0.7kg (Behrens et al., 2008, Mischler et al., 2009) for $\delta^{13}\text{C}$, 0.5kg for Bock et al., 2010 and 1-1.6kg (Mischler et al., 2009) for δD and about 1kg for N₂O isotopes (Sowers et al., 2002 & Bernard et al., 2006). One sentence is added at the end of the introduction in the revised manuscript.

What is the rough temporal resolution for 200-800g ice? That depends of the depth of the ice sample, of the length of the sample, of the location and of the accumulation rate of the drilling site. Therefore, it is very difficult to estimate the temporal resolution. However, for a sample of Greenland Holocene ice, of 200-800g, the temporal resolution will roughly be 10-20 years. Nevertheless, it is important to note that every bubble represents roughly 50 years average of atmospheric composition. This is added in the revised manuscript.

Page 4478, line 6-8: What is the shape of T1, T2, and T3? Coil trap or U-tube trap? Are they stainless steel or glass? What is diameter and length? It is better to mention them here. T1, T2 and T3 are U-shape glass traps. Those traps are originally described at Page 4483, line 15-20 of our manuscript, but following the reviewer advised this has been moved to part 2.1 in the revised manuscript.

Page 4478, line 17: The reference “Brass and Rockmann, 2010” should be the final revised AMT paper instead of the discussion paper. Thanks for noticing the mistake. This has been corrected in the revised manuscript.

Page 4478, line 20-21: What is the carrier gas used? UHP helium? The carrier gas used is helium BIP 5.7 from Air products. This is added in the revised manuscript.

Page 4478, line 23: What kind of cold bath is used to keep -132degC?

Page 4478, line 24-25: “the cooling is stopped” to “the cold bath is removed and the cooling is stopped”. The cooling/heating systems of the PRECON and CRYOFOCUS of our CH₄ IRMS system are extensively described by Brass & Röckmann, 2010, therefore we did not explain it in detail in this manuscript. To make it clearer, one sentence is added to the revised manuscript referring to Brass & Röckmann, 2010.

Page 4478, line 25: What is the temperature for warming up? Room temperature? The heating is done by step, first to -75degC when CH₄ is released to the CRYOFOCUS, then to 60degC to release the impurities to the vent. This is also explained in details in Brass & Röckmann, 2010, therefore we don't explain it in details in this manuscript.

Page 4479, line 2: "focussed" to "focused": Thanks for noticing the mistake. This has been corrected in the revised manuscript.

Page 4479, line 15: Does this mean the ice sample size will double for simultaneous analysis of both δD and $\delta^{13}C$ of CH₄? It is technically not possible to measure both $\delta^{13}C$ and δD simultaneously, so for one ice sample, we measure or $\delta^{13}C$ + N₂O isotopes or δD + N₂O isotopes. In practice, if we have an ice sample of 1kg, we will use 1/3 for $\delta^{13}C$ and 2/3 for δD and N₂O isotopes.

Page 4479, line 21: Rockmann et al., 2003b presented N₂O isotope measurements based on >125mL air sample with ambient N₂O concentration. The analytical uncertainty is 0.1‰ and 0.2‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. But 200-800g ice core provides much less amount of N₂O. What is the analytical uncertainty for your auto-mated system based on similar amount of N₂O as that from 200-800g ice sample? The uncertainties are shown in Fig.3. The standard deviation of zone B represents the analytical uncertainties for similar amount of N₂O than 500-700g of ice samples with 220-270ppb of N₂O.

Page 4479, line 23: How pure is your helium? We use helium BIP 5.7 from Air products. This is added in the revised manuscript.

Page 4480, line 12: How much ice is removed by microtome? 1-2 mm thickness? The amount of ice removed depends of the quality of the ice sample. But generally, about 2 mm of ice is removed. This number is added in the revised manuscript.

Page 4480, line 16-17: What is the final pressure after pumping for 90 min? The vacuum reached 10⁻³mb. This number is added in the revised manuscript.

Page 4480, line 21: "blank is also carried out" to "blank measurement is also carried out". This is corrected in the revised manuscript.

Page 4480, line 22: Why do you use different procedure for blank run from real ice core sample run? When you run blank measurement, you should mimic the same procedure as real ice core sample, e.g. keep T2 and T3 cold first and then remove cold baths and warm them up. One important issue here is that for a real blank run, a bubble free (BF) ice should be placed in the grating cylinder inside the SS pot. After evacuation, UHP helium is loaded in and the same procedure described in section 3.3 should be followed.

The goal of our blank measurement is to verify that no CH₄ stays in T3 in order to ensure that all the air adsorbed has been transferred to the IRMS system. We used bubble free ice only in the test stage and the goal of testing the system with bubble free ice was to verify that no CH₄ was formed during the grating.

Making bubble free ice is complicated and time consuming and making large amount of this ice as for routine analysis is not possible. Moreover, measuring bubble free ice after our ice sample would not add any information, because what we need to test is if all the air has been transferred from the pot to T3. This has been tested in adding a defined amount of reference air to the pot (where the leftover of ice remained) and in extracting this air as a real ice sample in order to verify that no extra CH₄ remained in the pot. This has been clarified in the revised manuscript.

Page 4481, line 8: How to prevent the ice from knocking against the walls?

If we start the grating very slowly, the ice is moving slowly in the grater and we can clearly hear that no knocking occurs. The shaking frequency can be controlled manually and is slowly increased as shown in Fig.2.

Page 4481, line 10: Ethanol-liquid nitrogen mixture cannot hold -80_C for a long time. If you want a cold bath to remove water vapor, you can use ethanol-dry ice mixture.

We are using ethanol-liquid nitrogen mixture in place of ethanol-dry ice mixture for practical reasons. The temperature of the mixture is verified several times during the extraction process and the mixture is renewed for each extraction.

Page 4481, line 13-16: How accurate is the MKS Baratron pressure gauge? Could you clarify how you exactly calculate the amount of air in the ice and the gas mixing ratio?

The MKS Baratron pressure gauge has an accuracy of 0.05mb.

To estimate the extraction efficiency, we use the assumption that 10% of the ice volume is air which is the average total air content for the test ice we used. To calculate the amount of air released, we use the pressure that builds up in the pot and the attached lines of this part of the system and the volume of this part of the system. We calculate the mixing ratios using the CH₄ peak area from the chromatogram and the calculated amount of air released from the ice.

A sentence is added in the revised manuscript about the calculation of the mixing ratios.

Page 4483, line 9: how do you determine how much air is extracted from ice?

We calculate it using the pressure of air in the pot (P_{system}) after grating and the volume of this part of the system (V_{system}). $V_{\text{air in ice sample}} = (V_{\text{system}} * P_{\text{system}}) / P_{\text{atm}}$. A sentence of explanation is added in the revised manuscript.

Page 4483, line 16: Does the mesh size of the Haysep D affect the trapping efficiency? How do you determine the optimal mesh size of 80/100?

We tested several mesh sizes and with smaller mesh size, it took much longer to adsorb the air, but also to release it from the Haysep. This is due to the fact that a

relatively large amount of Haysep D is packed and smaller mesh size are less porous so does not allow an efficient desorption of the air. A sentence is added in the revised manuscript to clarify this.

Page 4484, line 4: Is the container sealed when you make BF ice? How do you take BF ice out from the plastic tube? Is the BF ice clear?

The container is sealed and the ice is simply retrieved in cutting the plastic tube with scissors. The BF is completely transparent.

Page 4484, line 5: Before the BF ice is grated, do you also first cut with band saw and then clean with microtome?

The bubble free ice samples were handled exactly the same way than real ice samples, so cut with the same band saw and microtomed. This is added in the revised manuscript.

Page 4484, line 6-7: Why is BF ice softer than deep ice core ice? Are you sure about this?

The bubble free ice softer than a deep ice core, because it was not made under pressure. Therefore, a bubble free ice sample was completely grated after 10 minutes while a deep ice core ice sample was completely grated after 20 minutes only.

Page 4484, line 9: Why didn't you run BF ice with reference with IRMS instead of GCFID? To ascertain your system is working for isotope analysis, you should run BF ice with different reference gases in IRMS (the same procedure for real ice core sample, use one piece of BF ice for each run) and obtain the isotopic ratios and find out the accuracy and precision of isotope analysis from these tests (not mixing ratio only). The consistent mixing ratio does not guarantee consistent isotopic ratios. Your design of tests with BF ice is way too simplistic. Section 3.3 should be a very important part in this paper.

The analyses of bubble free ice were carried out with both GC-FID and IRMS system and both showed no significant contamination. As mentioned above, bubble free ice is difficult to make and therefore cannot be used routinely. More details about the tests with BF ice are added in the revised manuscript.

Page 4484, line 18: Can you clarify how you run the reproducibility tests with leftover grated ice samples? Is the leftover grated ice the ice left in the SS pot after a real ice core sample run? Do you mean you mix the reference gas with the leftover grated ice? Shouldn't the reproducibility tests be based on BF ice instead of the leftover grated ice? Because you can mimic the process of real ice core run with BF ice and reference gas including the cutting, microtoming, and grating. A BF ice sample should be used only once and then discarded. Multiple BF ice samples are needed to get precisions. Please refer to the above comment.

The goal of the reproducibility tests with leftover ice was to verify that no air from the ice sample was left in the pot after adsorption. A defined amount of reference air was introduced in the pot, then adsorbed and analyzed following the same

procedure as for a real ice core samples. After this it was verified that the average isotope values and the standard deviation of those tests were similar to the average and standard deviation of standard measurements carried out before the ice core sample analysis. Analyzing bubble free ice would not add any information there, because it would not allow to make sure than no CH₄ was left in the pot after measurement. This is clarified in the revised manuscript.

Page 4484, line 26-27: How do you determine 200-350 g ice is enough for high precision for CH₄ isotope analysis? And how do you get the precision? Do you run leftover grated ice with reference gas to get the standard deviations? This “high precision” is an arbitrary word. Have you done some calculation and figured out the required precision for providing useful information on the methane budget in the paleoatmosphere based on existing methane ice core records?

In recent publications (Mischler et al., 2009, Bock et al., 2010 and Sowers et al., 2010) the precision reached was 0.3‰ for $\delta^{13}\text{C}$ and about 4‰ for δD , which allowed detection of atmospheric trends. We defined the precision of our measurements by measuring 5 times the same ice sample and by calculating the standard deviation of those measurements. High precision means here that the precision of our measurement reach or is better than the precision of already published datasets. One sentence is added in the revised manuscript to clarify what we mean by “high precision”!

Page 4485, line 3: Similar as the above comment, how do you determine 600 g ice is enough for N₂O isotope analysis? And how do you get the precision? Do you run leftover grated ice with reference gas to get the standard deviations? Have you done some calculation and figured out the required precision for providing useful information on the N₂O budget in the paleoatmosphere based on existing N₂O ice core records?

To date, the 2 published datasets for N₂O isotopologues reported uncertainties of 0.27‰ for $\delta^{15}\text{N}$ and 0.42‰ for $\delta^{18}\text{O}$ (Sowers et al., 2002) and about 0.5‰ for $\delta^{15}\text{N}$, 0.7‰ for $\delta^{18}\text{O}$ and 1-1.5‰ for the position dependent $\delta^{15}\text{N}$ signatures (Bernard et al., 2006). Both studies used relatively large amount of ice (>1kg) to reach this precision. Our goal here is to reach or improve this precision in decreasing significantly the amount of ice needed. However, it is difficult to determine what is the optimum precision/amount of ice balance, because it is difficult to estimate what is the expected range of natural variability in N₂O isotopologues in the past. Nevertheless, regarding the precision of atmospheric measurements and previous ice samples analysis, we believe that the error we reach for 600g of ice will allow to identify significant variations in the past N₂O budget.

Page 4486, line 7-8: Why do you need a better precision at zone B? What is the precision you really need for the ice core samples? Please refer to the above comment.

Please see comment above.

Page 4486, line 13: “the reproducibility remains good” is an arbitrary statement. How do you define “good”? How do you know the reproducibility in zone A is large enough to provide useful information on the methane budget in the paleoatmosphere based on existing methane ice core records?

For general comment, please see comment above. The sentence “the reproducibility remains good” has been changed in the revised manuscript in order to be less arbitrary!

Page 4488, line 5: Can you give the numbers of the differences and the combined error?

The combined error is added in the revised manuscript.

Page 4497, Table 2: Why is the ice weight and gas amount rough numbers? Didn't you weight the ice before you grated ice? And you mention you calculate the amount of air in the ice. So the gas amount should be a certain number. It is better to show numbers with errors instead of rough numbers.

Thanks for this comment. It is indeed more appropriate to refer to errors instead of rough numbers. This is corrected in the revised manuscript.

Page 4498, Table 3: Can you provide the exact number of measurements for each sample type?

The exact number of measurements is not reported, because this differs per isotope signature. Therefore, the minimum number of measurements is presented.