

## Reply to reviewer 2:

We thank the reviewer for the relevant comments and remarks which we used to improve the quality of the paper. Nearly all the comments are 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 4476, line 24: delete “realized as”.*** Changed in revised manuscript

***Page 4477, line 18: A little more explanation about the metal-metal collisions is needed- what is colliding? How does a precise fit stop this? Was CH<sub>4</sub> contamination detected without this? Does the TiN coating address the problem?***

Here, colliding means collisions between two metallic bodies. In our case, if the fit between the grater and the lid of the pot is not precise, the grater could move during the shaking and this would involve metal-metal collisions and potentially damage the surface layer of the SS of the lid, which could according to Higaki et al., 2006 lead to CH<sub>4</sub> emissions. TiN is used as coating on the SS grater in order to make the grating surface harder and to protect the SS for potential damage due to the ice grating. The goal of using this coating is then to avoid expected contamination and to increase the lifetime of the grater. This is added in the revised manuscript.

***Page 4478, line 10: T3 presumably traps air including CH<sub>4</sub>?*** Yes! This is added in the revised manuscript.

***Page 4478, line 13:....flushed with He.*** Added in the revised manuscript.

***Page 4479, line 21: delete “used”.*** Deleted in the revised manuscript.

***Page 4479, line 24: how was the 99.999% determined?*** The peak area of the CO<sub>2</sub> peak is 100 times less than the N<sub>2</sub>O peak area, whereas the CO<sub>2</sub> mixing ratio in the initial air is 1000 times higher than for N<sub>2</sub>O. Neglecting possible small differences in ionization efficiency of the two gases, this shows that the CO<sub>2</sub> is removed by 5 orders of magnitude.

***Page 4480, line 1: How much of the remainder is removed by the GC column?*** As described above, the reminder is approximately 1% of the N<sub>2</sub>O peak area for CO<sub>2</sub>. But these peaks are clearly separated.

***CRYOFOCUS.*** This is corrected in the revised manuscript.

***Page 4480, line 8: A description of how the NO<sup>+</sup> fragment determination leads to the position dependent isotopologues would help.*** We use a similar approach as the one described by Brenninkmeijer & Röckmann, 1999. The reference is already in the manuscript.

**Page 4480, line 12: The microtoming- why is this done, how much is removed?**

The microtoming is done in order to clean the ice and to avoid potential contamination from the drilling liquid. The quantity of ice removed depends of the quality of the ice but is generally around 2mm. This is added in the revised manuscript.

**Page 4480, line 1: "is then".** Corrected in the revised manuscript.

**Page 4480, line 15-16: Confusing- 2 evacuation periods are given.** The pot is evacuated at least 90 minutes to reach a pressure of  $10^{-3}$ mb, but generally, we measure one sample per day, so the pot is evacuated overnight. This is clarified in the revised manuscript.

**Page 4480, line 19: Contamination from the system (not from the ice or from the ice grating process)? (presumably that is why the bubble free tests are done).**

Here we mean potential contamination from the grating procedure. This is clarified in the revised manuscript.

**Page 4480, line 21: What was the flow of the He flush used to determine the blank? If it is much faster than the true sample (ie. The residence time much shorter) then it may not reveal any modification of the sample.**

The flow of helium is similar for the tests, the blank, the standard measurements and the ice samples measurements.

**Page 4481, line 8: .by listening, care is taken that the ice sample....**This sentence is changed in the revised manuscript.

**Page 4481, line 15: I wasn't sure what was being determined here. Since the extraction efficiency is unlikely to be 100%, given that there is probably air remaining in many of the 1-2 mm chips, it isn't possible to measure the total amount of air in the sample. Second, the volume (STP) of the air EXTRACTED from the sample is needed to calculate the concentrations of CH<sub>4</sub> and N<sub>2</sub>O- is this what is found from the pressure of the released air?** The pressure of the released air is indeed used with the volume of the system to determine the volume (STP) of air extracted.

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 ice we used for the tests. To calculate the amount of air released, we use the pressure of the air in the pot and the known volume of this part of the system (6150ml). We calculate the mixing ratios using the CH<sub>4</sub> peak area from the chromatogram and the calculated amount of air released from the ice.

$$V_{\text{air in ice sample}} = (V_{\text{system}} * P_{\text{system}}) / P_{\text{atm}}$$

$P_{\text{system}}$  the pressure of the pot after grating,  $V_{\text{system}}$  the volume of this part of the system and  $P_{\text{atm}}$ , the atmospheric pressure (STP).

A sentence of explanation is added in the revised manuscript.

**Page 4482, line 23: Is there evidence that knocking of the ice on the pot damages the oxide layer and leads to CH<sub>4</sub> production? Was it observed or just an expectation? There are several other similar dry extraction ice core techniques in use where ice impacts steel surfaces that apparently do not produce methane. Is it possible that methane produced in this system is due to other origins, such as movement of the grater, when high shake frequencies are used?**

There is no evidence that strong knocking of the ice against the lid and the bottom of the pot leads to CH<sub>4</sub> production, but of course we want to avoid any possible contamination. The idea is similar to the metal-metal collisions mentioned above. For these metal-metal collisions, we actually do now have evidence of CH<sub>4</sub> production. A recently built new pot produced large amounts of methane. It was discovered that the grater did not perfectly fit into the pot and could move back and forth. After this pot was adjusted so that the grater fit perfectly in the pot, the same reproducibility as for the former pot was observed.

One sentence of explication was added in the revised manuscript.

**Page 4482, line 9: How was the 97% efficiency determined?**

The extraction efficiency was determined using the assumption of 10% of air per ice volume and the calculated volume of air in the pot after grating.

One sentence explaining this has been added in the revised manuscript.

**Page 4483, line 11 ...takes a long time....** This has been added in the revised manuscript.

**Page 4483, line 17: reproducible- in terms of amount adsorbed?** Reproducible in term of isotope measurements compared to other adsorbents tested. One sentence is added about this in the revised manuscript.

**Page 4484, line 6: How is it known that the BF ice contains no air? Does it also contain no traces of N<sub>2</sub>O or CH<sub>4</sub>?**

During its preparation, bubble free ice was constantly flushed with helium and no air bubbles were visible. Additional tests were carried out with a wet extraction system, but no CH<sub>4</sub> was measured by the IRMS system.

**Page 4484, line 7: ...they might not be.** Changed in the revised manuscript.

**Page 4484, line 9: As mentioned above, how is the mixing ratio determined- is there a volume/pressure measurement and what is the uncertainty of the calculation?** From the pressure of air released in the known volume, and the peak area in the IRMS, we can determine the mixing ratio of a sample by comparing to the same ratio in a calibrated reference gas. We calculate the mixing ratios using the CH<sub>4</sub> peak area from the chromatogram and the calculated amount of air released from the ice. Given the possibility of air remaining in the flakes on the one hand, and the

measurement of a relatively small amount of air in a large volume on the other hand, the reproducibility is not comparable to state of the art CH<sub>4</sub> analyzers, but it gives a good indication of the mixing ratio in the air.

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

**Page 4484, line 13: no detectable difference- of CH<sub>4</sub> and N<sub>2</sub>O mixing ratios? To what uncertainty?** This means that the difference was in the uncertainty range. This is clarified in the revised manuscript.

**Page 4484, line 26: N<sub>2</sub>O isotope or mixing ratio measurements.** This is corrected in the revised manuscript.

**Page 4485, line 22: trends might be a better word to patterns.** This is corrected in the revised manuscript.

**Page 4487, line 5: This sentence needs a verb.** This is corrected in the revised manuscript.

**Page 4487, line 16: A little information about the ice cores would help- approximate location, elevation.....Could the results for the cores be meaningfully compared with published records, perhaps shedding light on the calibration differences?**

Here, we compare the results of different institutes for the same ice samples, therefore the location and elevation of the ice samples is not important. Moreover, we decided not to compare those results to published data, because those are scarce over this period and do include firn corrections, so a direct comparison is not possible. The goal is not to decide which institute is measuring the “right value”, but to define the differences between the institutes, so we can take these differences into account while comparing our datasets.

**Page 4488, line 9: ...systems are included.** This is corrected in the revised manuscript.

**Page 4489, line 24: use a more precise word for signatures Figure 5 Caption Are the dashed lines best fits or 1:1 lines?** The word “signatures” is replaced by isotopologues in the revised manuscript. The dashed lines in Fig.5 represents the best fit. This information is added in the revised manuscript.