Final Response to Reviewer #1
MS No.: amt-2016-124

We thank the Reviewer#1 for helpful and constructive comments.
Our responses (in blue) follow each comment given by Reviewer#1.

(R1#M1) Major point 1:
CO2-N2O separation. I consider the GC condition shown in the manuscript (4 mL/min and 40C for PoraPLOT Q 25mx0.53mm) is not sufficient for complete separation between CO2 and N2O. Both the flow rate and oven temperature seem a bit high for suitable setting for the CO2-N2O separation. Actually authors declare only 30 sec separation, and Fig5 seems showing touch between tails of the peaks. I guess it makes worse accuracy and precision, particularly for preCO2. Zoom-up chromatogram of m/z 44-46 on preCO2 analysis is required to claim the complete separation. Or, reasons why authors chose such (strange, as I feel) GC condition should be described. Improvement to get further separation will bring more precise analysis and increase the value of this study.

We acknowledge that lower temperatures can result in better separation of N_2O from CO_2. However, the separation that is achieved at 40 °C is clearly sufficient to eliminate the interference to levels that are well beyond our measurement precision. This was shown in Mrozek et al., (2015), where we also provide more details, including a zoom into the chromatogram. We do not think that it is necessary to repeat this in the present manuscript.

(R1#M2) Major point 2:
Contamination. Authors regarded serious contamination in 2 of 10 SAS subsamples and guess a procedure connecting SAS-IRMS system in laboratory as the source of contamination (P11 lines 3-6). In addition, an other SAS subsample was lost due to “accidental instability in He flow”. Because this is the manuscript for successful development of the SAS-IRMS system, it is serious defect and should be solved. Authors should improve the procedure ro avoid the contamination and accident. And results of the test are the revised procedure wll be required in the revised version of manuscript.

The “accidental instability in He flow” that caused loss of one sample was caused by an interruption of the helium supply in the laboratory, which unfortunately happened during the analysis of this sample, but this has nothing to do with the stability of our system. We demonstrate that 7 of the remaining 9 samples were analyzed successfully, and two showed contamination. We think that this may be related to connecting the samples but more statistics may be needed to resolve this issue completely. Nevertheless, we think that our manuscript still proves the successful setup of a system for analysis of $\Delta^{17}O$ in air samples that are provided by the SAS.

(R1#1) P03 lines2-28: These explanation really confused me. A schematic illustration for describing all the instruments and procedure, like a flowchart, seems helpful to understand the whole system from AirCore sampling on the site to IRMS analysis in laboratory.

We include a schematic illustration for describing the overall procedure below:

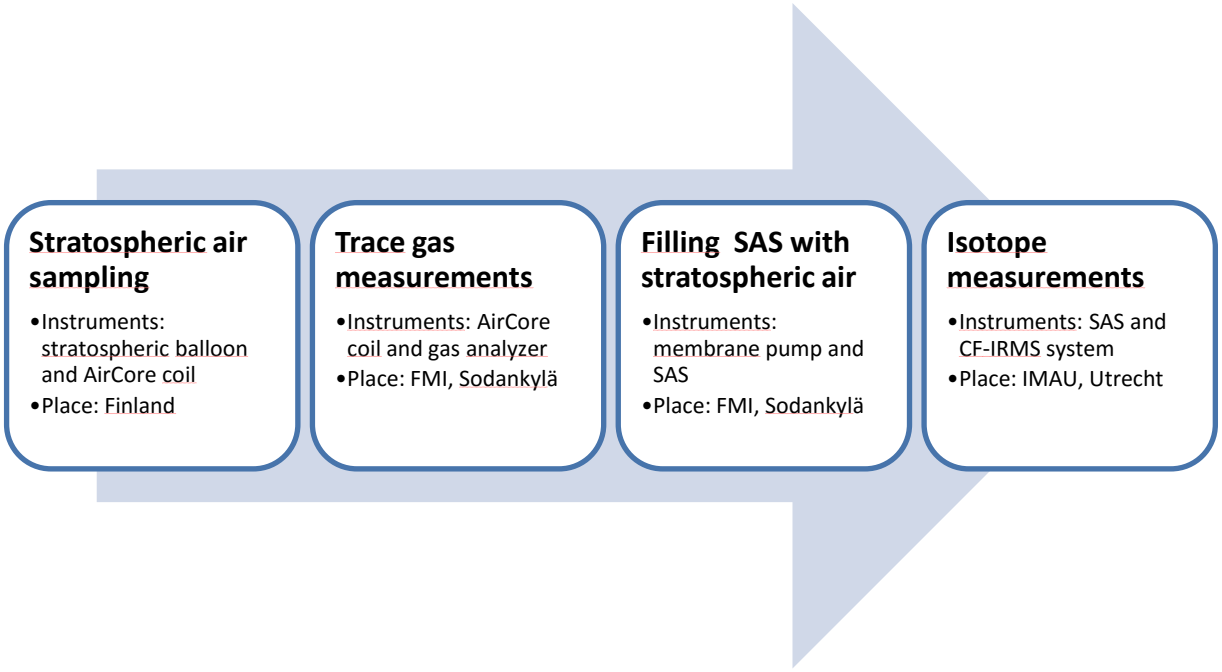

Figure 1. The overall procedure from AirCore sampling on the site to IRMS analysis in laboratory.

(R1#2) page 4, lines14-16: : I feel it is strange. As I read, SAS can get 10 subsamples by each 2m-long tubing. For easy understanding, the description "a 20m-long tubing divided by eleven valves" can be rephrased to "ten 2m-long tubings connected by eleven valves" or like it.

The relevant section was changed to:
The SAS used for the CO_2 isotope measurements in Utrecht is made of ten 2 m long pieces of 1/4 inch diameter stainless steel tubing. The tubings are connected and closed off at the ends by 11 Swagelok valves (part number SS-3CXS4), and bent to form rings. In the following, we refer to the valves as "three-way valves", and the rings as "SAS segments".

(R1#3) page 6, lines13-15: Lines "Under these conditions, the copper metal forms a coating of copper (II) oxide on the surface of the Cu wires according to: Cu+ ½ O2 → CuO" can be deleated

This sentence describes the reaction that creates CuO coating on Cu/Ni wires. We think that this is relevant, since we are describing the procedure to recondition the surface in this section.

(R1#4) page 9, lines17-25: Section 3.2 is important for this study because authors first use CuO/Ni system for oxygen exchanging results of the test should be shown in table or figure.

We added a figure to show that isotope exchange is complete. The relevant section was changed to:

"To quantify the efficiency of oxygen isotope equilibration in the CuO oven we analyzed two samples containing CO_2 with very different isotopic composition. The first one was our RefAir, the second one was a synthetic mixture of $RefCO_2$ diluted to 400 ppm CO_2 in synthetic air. The samples were injected via a stainless tube that is similar to a segment of the SAS, but longer (4 m length 1/4 inch o.d.). First, the reference air was injected multiple times through this tube. Next, we filled the injection tube with the $RefCO_2$ dilution and continued the measurements. Figure 2 presents the results. The isotopic difference between the two CO_2 samples was about 36 ‰ before isotope exchange. After the isotopic exchange reaction both gases were equilibrated to $\delta^{18}O$ = (19.03 ± 0.18) ‰. *From the difference in the oxygen isotopic composition between RefAir and $RefCO_2$ dilution before and after oxygen isotope exchange, the oxygen exchange efficiency in CuO oven was calculated to be >99.5 %. We conclude that the oxygen exchange reaction with CuO/Ni wires at 900 °C is complete."*

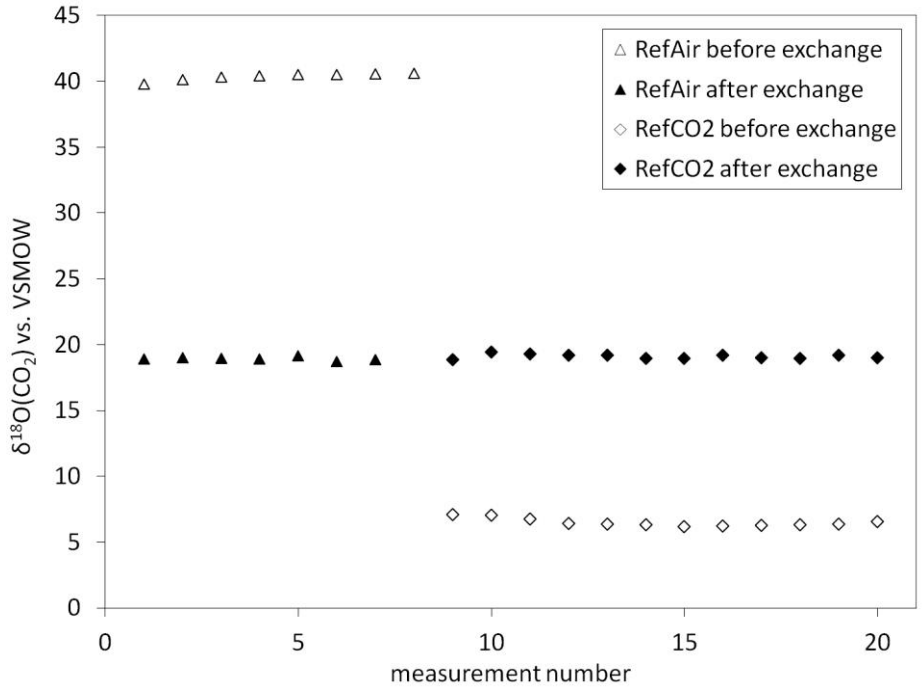

Figure 2. Efficiency of oxygen isotope equilibration in the CuO oven. The $\delta^{18}O(CO_2)$ values of RefAir and a mixture of $RefCO_2$ in synthetic air are shown before and after isotope equilibration. The last point of the RefAir measurement sequence after exchange is missing because the peak of the last run was accidentally not registered.

(R1#5) page 10, line 7: Fig 6?

Yes , correct , "Fig. 7" was changed to "Fig. 6".

(R1#6) page10, lines12-14: Comparison of analytical errors with previous methods actually used for stratospheric air analysis is helpful for readers.

Page 10 lines 12-14 are extended as follows:

"We conclude that repeated measurements on one air sample (up to 54 repetition that corresponds to 2.6 µmol CO_2) can reduce the uncertainty in $\Delta^{17}O(CO_2)$ to 0.2 ‰. More than 54 repetitions on one air sample improves the $\Delta^{17}O(CO_2)$ uncertainty only marginally. This uncertainty is in the same range as previously reported techniques for large samples, most of which did not allow the measurement of very small samples. Bhattacharya and Thiemens (1989), reported an uncertainty of 0.1 ‰ using a BrF_5 -based technique, Brenninkmeijer and Röckmann (1998) obtained 0.2 ‰ with a two-step fluorination method, Assonov and Brenninkmeijer (2001) reported 0.33 ‰ with a CeO_2 exchange method and Mahata et al., 2012 improved this method to an uncertainty of 0.12 ‰. The Kawagucci et al. (2005) method is the only technique that also targeted very small sample sizes (like our system) and they reported an uncertainty of 0.35 ‰.

In our application to the SAS, *for 5 repeated measurements on one stratospheric air sample stored in the SAS* we *expect an uncertainty of 0.57 ‰ for $\Delta^{17}O(CO_2)$ and 0.03 ‰ for both $\delta^{18}O(CO_2)$ and $\delta^{13}C(CO_2)$. This will be compared to the reproducibility of the actual SAS measurements in Sect. 4.2. "*