<u>Final Response to Reviewer #2</u> MS No.: amt-2014-151

We thank the Reviewer#2 for the helpful comments.

Our responses (in blue) follow each comment given by Reviewer#2. Please note, Reviewer#2 in his comments uses line numbers of the manuscript. In our response, for consistency with the answers to Reviewer#1, we use the page and line numbers of the ATMD document.

1. Abstract: The abstract needs to explicitly state that this method is suitable for stratospheric CO2. Although I'm sure one could also measure tropospheric CO2 with this method, the precision for the 17O-excess is not good enough to be meaningful for the small values in the troposphere.

It would also be good to explicitly state in the abstract and again in the manuscript (such as section 4 and Figure 9) what the observed 17O-excess values are for stratospheric CO2 so the reader can immediately assess whether or not the stated precision is adequate for examining actual variability in the stratosphere.

The abstract adjusted, P6824, line 4:

This paper presents an analytical system for analysis of all singly-substituted isotopologues (${}^{12}C^{16}O^{17}O$, ${}^{12}C^{16}O^{18}O$, ${}^{13}C^{16}O^{16}O$) in nanomolar quantities of CO₂ extracted from stratospheric air samples.

P6824, lines 20-23 extended to:

The precision for RECONCILE data is 0.03 ‰ (1 σ) for δ^{13} C, 0.07 ‰ (1 σ) for δ^{18} O and 0.55 ‰ (1 σ) for δ^{17} O for sample of 10 measurements. This is sufficient to examine stratospheric enrichments, which at altitude 33 km go up to 12 ‰ for δ^{17} O and up to 8 ‰ for δ^{18} O with respect to tropospheric CO₂: δ^{17} O ≈ 21 ‰ VSMOW, δ^{18} O ≈ 41 ‰ VSMOW (Lämmerzahl et al., 2002). The samples measured with our analytical technique agree with available data for stratospheric CO₂.

The section 4 extended, P6840, line 20 should be read:

In Fig. 9, we show the oxygen isotopic composition of three stratospheric air samples together with already published data. At 18 km the observed ¹⁷O excess values for stratospheric CO₂ go up to 7 ‰ for δ^{17} O and up to 3 ‰ for δ^{18} O with respect to tropospheric CO₂ (δ^{17} O ≈ 21 ‰ VSMOW, δ^{18} O ≈ 41 ‰ VSMOW).

2. It is not explicitly clear what a "repeated analysis means". Since this is continuous flow and not dual inlet, I assume that the authors mean that they take multiple aliquots of the same sample. Later (line 426; P6841, line 16) the authors use the term "multiple measurements". Again this could be made more clear with the phrase "multiple aliquots of the same sample".

As the term "repeated analysis" is not explicitly clear we change Abstract (P6824, line 14) for: Multiple measurements on an air sample reduce the measurement uncertainty.

For clarification we explain the term "multiple measurements" in <u>P6832</u>, line 6-9. P6832, line 6-9 should be written as:

A single measurement of an unmodified aliquot and a CO_2 aliquot after isotope exchange takes 15 minutes. The short analysis time and a low sample usage allow injecting multiple aliquots of the same sample into the analytical system, giving possibility of multiple measurements on each sample. In 2.5 h of analysis, we can repeat measurement on each air sample ten times and improve the analytical precision statistically, see section 3.4

d) P6841, line 16 extended to:

Although the standard deviation of a single run is higher than for already established methods that use CeO_2 (Assonov and Brenninkmeijer, 2001; Hofmann and Pack, 2010; Mahata et al., 2012) it can be decreased statistically with injecting multiple aliquots of the same sample.

3. The authors report their sample quantities as volumes, but this is meaningless without information on the pressure of the sample containers. Information on the pressure is not given until the second to last line of the manuscript. I wondered right away in the abstract (line 22; P6824, line 11) how much air, or CO2, a certain volume represents, as I am not familiar with the collection methods of stratospheric CO2.

Also, when comparing with previous work (line 87; P6826, line 87), the authors state the sample quantity as the number of nanomoles of CO2. It's hard to know how this amount compares to what is measured in the present paper. I would prefer nmoles throughout, but perhaps this is my own bias. Either way, it is best to be consistent with units throughout the paper. If the authors choose to stick with volumes, also provide information on the pressure.

The temperature and pressure is stated in the abstract. P6824, line 10 specifies that a single measurement of the ¹⁷O excess requires two injections of 1 mL of air with a CO_2 mole fraction of 390 µmol mol⁻¹, temperature of 293 K and 1 bar pressure (corresponding to 16 nmol CO_2 each).

In the setup described here, we need to provide air sample at overpressure of 1.4 bar because of the mass flow controller (MFC injection). This means that the total amount of air must be larger then what we use for analysis, but how much depends on the sample container size. Note, after automated sample injection unit, the pressure in the analytical system corresponds to ambient pressure, and for sample of ten measurements only 30 ml of the sample air (corresponding to 48 nmol of CO_2) is used.

Following suggestion of Reviewer #2 an additional axis to Figure 7 was add to show CO_2 sample amount in nmol. The modified Figure 7 is presented below.



4. Line 411; P6840, line 26: What is an "in-depth analysis ion"?

The quoted line is misspelled. The correct sentence is: An in-depth analysis on the new data set will be published in a separate paper.

The corrected abstract

This paper presents an analytical system for analysis of all single substituted isotopologues (¹²C¹⁶O¹⁷O, ¹²C¹⁶O¹⁸O, ¹³C¹⁶O¹⁶O) in nanomolar quantities of CO₂ extracted from stratospheric air samples. CO2 is separated from bulk air by gas chromatography and CO_2 isotope ratio measurements (ion masses 45/44 and 46/44) are performed using isotope ratio mass spectrometry (IRMS). The ¹⁷O excess (Δ (¹⁷O)) is derived from isotope measurements on two different CO₂ aliquots: unmodified CO₂ and CO_2 after complete oxygen isotope exchange with cerium oxide (CeO₂) at 700 °C. Thus, a single measurement of the ¹⁷O excess requires two injections of 1 mL of air with a CO_2 mole fraction of 390 $\mu mol\ mol^{-1}$ at 293 K and 1 bar pressure (corresponding to 16 nmol CO_2 each). The required sample air size (including flushing) is 2.7 mL of air. A single analysis (one pair of injections) takes 15 minutes. The analytical system is fully automated for unattended measurements over several days. The standard deviation of the ¹⁷O excess analysis is 1.7 ‰. Multiple measurements on an air sample reduce the measurement uncertainty, as expected for the statistical standard error. Thus, the uncertainty for a group of ten measurements is 0.58 % for Δ (¹⁷O) in 2.5 h analysis. 270 repeat analyses of one air sample decrease the standard error to 0.20 ‰. The instrument performance was demonstrated by measuring CO₂ on stratospheric air samples obtained during the EU project RECONCILE with the high-altitude aircraft Geophysica. The precision for RECONCILE data is 0.03 ‰ (1 σ) for δ^{13} C, 0.07 ‰ (1 σ) for δ^{18} O and 0.55 ‰ (1 σ) for δ^{17} O for sample of 10 measurements. This is sufficient to examine stratospheric enrichments, which at altitude 33 km go up to 12 % for δ^{17} O and up to 8 % for δ^{18} O with respect to tropospheric CO₂: δ^{17} O $\approx 21\%$ VSMOW, δ^{18} O $\approx 41\%$ VSMOW (Lämmerzahl et al., 2002). The samples measured with our analytical technique agree with available data for stratospheric CO₂.