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Comment

## ***Interactive comment on “An estimation of the $^{18}\text{O} / ^{16}\text{O}$ ratio of UT/LMS ozone based on artefact CO in air sampled during CARIBIC flights” by S. Gromov and C. A. M. Brenninkmeijer***

**Anonymous Referee #1**

Received and published: 22 August 2014

The paper analyzes stratospheric measurements of CO and O<sub>3</sub> from two phases of the CARIBIC project and identifies an artefact in the phase 1 measurements. Isotope observations clearly link this to production of CO from O<sub>3</sub> and a mass balance calculation is then used to derive the isotopic composition of the O<sub>3</sub> precursor.

The analysis seems thorough but the paper not easy to follow. This is related to use of complicated language, with numerous uncommon expressions, long sentences and indirect constructions. This disrupts the flow and can get annoying. I needed to read many sentences several times to understand the authors. The other issue is that the analysis chain from beginning to end is not well described, some information/figures

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should be added.

The general structure should be improved. Section 2, experimental, is a mixture of methods and results. For easier reading, include sub-sections to describe C1 WAS, C1 in situ, C2. On P41, L12 start new section “results”. From P42, middle on, you are already deep in discussion, maybe move to discussion section.

Fig 1 is overladen and very hard to read. Is it possible to separate the information in two panels? I suggest using a different base color for the shading. The black box and whisker symbols are very hard to read and totally unreadable on my printout. Also the black small dots do not come out on my printout. The thin and thick black lines are almost indistinguishable. The “statistical fences”, and what they mean, should be described in the caption. At the lower end there is only one fence. In some cases this fence goes outside the data distribution. What happens to the lower fence below 400 nmol/mol O<sub>3</sub>? Do you need these fences at all? Remove? If you add another panel you may be able to show more WAS data (why only 11, are they representative/particularly bad?)

Fig. 2: You mention several times that the 18O artefact is proportional to O<sub>3</sub>, or stems exclusively from O<sub>3</sub>. Can't you add a plot of d18O or d18O artifact versus O<sub>3</sub>?

Fig3: Does this plot now also include samples that are not considered stratospheric?

It is not shown clearly enough how the size of the contamination is quantified. Possibly Appendix 1 should be included in the text and a figure to explain the calculation of C<sub>c</sub> should definitely be included. If I understand correctly, these values of C<sub>c</sub> are then used for the 2 component mixing model (“approach” not needed in the name). Also here, it would be helpful and illustrative to show in a figure one or several examples of fits from which the statistics are ultimately used in Fig 3.

I cannot follow the kinetic framework equation in App A. I understand that in the end you have a parameterization wrt O<sub>3</sub><sup>2</sup>, but is the mathematical derivation supposed to

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be analytical or schematic? It should be explained better.

There is nothing conceptually wrong with this paper, but the presentation should be strongly improved.

Minor points.

P38 L15: ...higher pressures inhibit isotope fractionation... is a strange way of expressing this. A pressure dependence has been clearly demonstrated in the literature (even if at room temp).

L21: Better call is a successful example, not famous. The point that you want to make is that it works.

L23: Such was not the case... rewrite more directly

P39: In L3 you state that Brenninkmeijer et al related the artifact to O3, but in L24 you say that a specific O3 related process has not been reported. Contradiction?

L8: disproportionately is not a good term here

L11: reformulate ... may be higher higher than what?

P40 L26/27: Remove, repeated from L13/14

P40, end – 41 paragraph 1: Describe statistics better. Also: ...numbers quoted are the sums of .... Not clear at all. Which “numbers quoted”? Why the sum?

P41, L18: are you sure it is the p dependency of the rate coefficient, and not simply that CH4 is getting lower?

L23/24: rewrite more directly

L27: Not unique, since O3 transfers the enrichment to others like nitrate (e.g. Savarino et al, ACP 2007 or Morin et al., ACP, 2007))

P45, L12ff: Do you mean that you really reproduce the C2 distribution when you aver-

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age C1 data over 1200 s? Why would that be? Or do the errors get too large?

L24: Include here more information on how Cc is derived, preferably with a figure or an example.

P46 L1: Show better in figure.

L6: remove and

L13: Keeling plot uses a different representation in the plot (versus  $\text{Ca}^{-1}$ ), why do you prefer a different type of presentation (versus  $\text{Cc}^{-1}$ ). Show such a regression (or several) as example.

P47, bottom: The  $^{13}\text{C}$  discussion is unclear.  $R^2$  may not be a good evaluation criterion when the regression slope is close to 0. It is not immediately clear why you find -47 per mill, because the regressions that you use are delta versus the contamination CO, and you are implying that the contamination does not come from methane (rate coeff too slow). So is this coincidence? Is the discussion valid? See also line 5 next page.

P48: Rewrite . . . which agrees with other estimates at  $R^2$  above 0.75. Not clear at all.

L8 f: How can you derive anything on seasonality and mixing from the corrected data?

L14: I do not see a 1 per mill agreement with B96 in Fig 3.

L18-20: rewrite, very hard to follow.

P49, L24-end: rewrite, not clear.

P50 L1: rewrite, not clear

L15: Why “upheld”

P51, L4 ff: This is your main conclusion, comes very late and at much less detail than the discussions of the (unlikely) effects above.

L13 implex → complex??

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P52, L14: mere → do you mean exclusive?

L15: comparable to what?

L17: What is Cs? This appendix needs a figure for explanation on how you derive all the parameters and should probably be included in the main text.

Technical:

Consider seriously splitting several (many) very long sentences in two to improve readability.

Suggest replacing all occurrences of ozone with O<sub>3</sub> after introduction on p39, l5

Notation: use consistent notation, the double superscript plus subscript notation (P46, L1) is not very clear, and not the recommended notation, maybe better be explicit, like in P46, L12.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 21037, 2014.

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