Atmospheric
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Discussions

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

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Received and published: 13 October 2014

The authors are grateful to the Editor and Reviewers for the prompt peer-review process. We acknowledge the great attention paid to our work, especially by the Reviewer #1, and useful suggestions. Following these, we have prepared the revised manuscript and included the requested additional plots in the Supplementary Material. Being slightly worried about our communication style, we asked a native English speaker to check the manuscript for language issues once more. Below we address all the comments issued by the Reviewers (*italicised*).

C7938

On the comments of the Reviewer #1

The paper analyzes stratospheric measurements of CO and O3 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 O3 and a mass balance calculation is then used to derive the isotopic composition of the O3 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.

We have the revised manuscript checked by a native English speaker to ensure proper use of English and to remove some uncommon expressions. This has made it easier to follow the train of thought. We would however like to remain our own style of reporting even though this style may seem convoluted and complex.

The other issue is that the analysis chain from beginning to end is not well described, some information/figures 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.

We have amended the structure of Sect. 2 accordingly.

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

wisker 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 O3? Do you need these fences at all? Remove?

We apologise for the quality of graphics that deteriorates in the typeset discussion manuscripts due to scaling; all elements will be clearly visible in the final typeset manuscript, however.

We have improved Fig. 1 according to the suggestions of the Reviewer (please see the new version attached). In particular, more distinct colours are chosen for C2, the [CO] statistics are presented in a separate panel. As for the lower statistical fences, below 400 nmol/mol these fall outside the graph area (also due to the logarithmic scale used), which is, however, irrelevant for the subject of elevated [CO] regarded here. We nonetheless would like to keep the fences it in the figure in order to emphasise how small the variations of [CO] are at $[O_3] > 580$ nmol/mol, where the discrepancy is largest and most obvious. Furthermore, we prefer to leave the definition of the "statistical fences" in the regular text (we reiterate it in the figure caption, however), where it is contextually relevant to the discussion on the outliers in the C1 data.

If you add another panel you may be able to show more WAS data (why only 11, are they representative/ particularly bad?)

The WAS data points are shown mostly to exemplify the sample-mixing processes, *i.e.* how the air sampled for ∼20 min integrates the encountered compositions to

some average with [CO]/[O$_3$] ratios atypical to those observed discretely in the UT/LMS. By chance 11 of these samples have integral [CO] < 80 nmol/mol and [O$_3$] > 300 nmol/mol. Since we discuss the artefact issue in particular, and the compositions at lower [O$_3$] do appear "normal", we do not intend to present these in Fig. 1. The entire WAS CO dataset is presented in Fig. 2. Nevertheless, we add the plot showing the entire C1 *in situ* and WAS [CO] data as a function of [O$_3$] to the Supplementary Material of the paper (Fig. S1).

Fig. 2: You mention several times that the 18O artefact is proportional to O3, or stems exclusively from O3. Can't you add a plot of d18O or d18O artifact versus O3?

We used a colour scale to show correlating enhancements in [O$_3$] and $\delta^{18}O(CO)$ in Fig. 2, pursuing the most efficient presentation of the data. It is unlikely that adding a separate plot (*i.e.*, $\delta^{18}O(CO)$ *vs.* [O$_3$]) will increase the informational content of the manuscript. There are two reasons for that: (i) The average $\delta^{18}O(CO)$ in the WAS tanks is determined by the mix of the air portions with different $\delta^{18}O(CO)$ values, of which those that are more stratospheric are additionally (here – proportional to $[O_3]^2$) are modified by the contamination. Hence the "artefact d18O" (we assume the Reviewer implies the artificial enhancements in the measured WAS $\delta^{18}O(CO)$ value) is not strictly proportional to [O$_3$], but also depends on the average [CO] in the tank (it is being diluted by the tropospheric compositions with lower "artefact" signal). In order to make the $\delta^{18}O(CO)$ *vs.* [O$_3$] plot comprehensible, one needs to add the information of [CO] in each WAS, which will make it a version of Fig. 2 with abscissa and colour exchanged. (ii) Fig. 2 is also a better solution because it allows comparing the C1 data against CB96 in [CO] coordinate, which would not be possible due to very different O$_3$ distributions in these datasets (CB96 have encountered compositions characteristic for "ozone hole" conditions). Nonetheless, we add the requested plot to the Supplementary Material of the paper (Fig. S2). Furthermore, please be aware that Fig. 2 was updated. Due to the error in our graphing software the C1 CO mixing ratios

were lower that the actual values, we apologise for this. Whilst this does not affect our results, the corrected version of Fig. 2 better emphasises the difference between the (mostly) NH CO from C1 and SH CO from CB96.

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

Because Fig. 3 does not present samples, it is not clear to us whether Fig. 2 or 3 is implied by the Reviewer. Fig. 2 shows the entire C1 WAS dataset. Due to the reasons outlined above we cannot separate these WAS samples into strictly stratospheric and tropospheric ones, therefore in Fig. 1 we use $[O_3] > 300$ as a certain condition at which the artefact enhancements in $\delta^{18}O(CO)$ become apparent. Fig. 3 presents the results of the MMA calculation based on the different subsets of C1 WAS samples. This calculation is based on the samples with variable proportions of stratospheric and tropospheric compositions.

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 Cc should definitely be included.

Please see our comment on formulation (A1) below. Furthermore, it is not clear to us what the figure explaining the calculation should contain (we believe the formulation provided in Appendix A is sufficient). However, we add the graph showing the discrepancy between the C1 and C2 [CO] and fitted C_c values as a function of $[O_3]$ in panel (d) in the new version of Fig. 1.

If I understand correctly, these values of Cc are then used for the 2 component mixing model ("approach" not needed in the name).

Yes, this is correct. We add the additional statement in Sect. 3.1 of the revised manuscript to emphasise this. We further refrain from using "approach" w.r.t. the mixing model.

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.

Please see our answer to the comment concerning *P46 L13*.

I cannot follow the kinetic framework equation in App A. I understand that in the end you have a parameterization wrt O3$\hat{2}$, but is the mathematical derivation supposed to be analytical or schematic? It should be explained better.

We put the formulation (A1) (which is a mix of schematic and analytical forms) to keep the Reader aware that in many cases (unlike ours) not only $[O_3]$ may be the decisive factor for the contamination strength. In its schematic form (first line), Eq. (A1) reads "The decomposition of O_3 at the rate of $^{O_3}k_1$ may be followed by secondary reactions with O_3 and/or unknown compound(s) X, which should be inferable through the stoichiometry of the process", *e.g.* κ when O_3 is regarded and/or K for unknown X. The second equation (essentially the RHS of it, $C_c = \lambda_{O_3} k_c [O_3]^\kappa \tau_c$) describes the analytical part of the framework, which quantifies the contamination. As we state, we find the contamination strength being proportional to $[O_3]$ but no other characteristic/parameter in C1 (*i.e.* we cannot infer X and K), therefore the analytical part reduces to that shown at the RHS. Furthermore, the matters of the calculation of C_c are mentioned – that is, "...by discriminating the C1 outliers from respective C2 data" implies that we use the fitting procedure that finds values of C_c as a function of $[O_3]^\kappa$ which, when subtracted from C1 [CO] yield typical C2 [CO] levels the best. The statistics (foremost the lowest red. χ^2 score) yield κ closest to 2 and subsequently the respective $C_c/[O_3]^2$ value.

We find the explanation above has no logical flaws and is derivable from the information given in Appendix A when needed, *e.g.* as an example when a similar problem is tackled. Otherwise, we believe this information overloads the main manuscript. Therefore we – as initially intended, and still would like – present the kinetic framework in the form of an Appendix. We do, however, amend the relevant part of the discussion (*viz.* formulate C_c in the main text, see our answer to the comment concerning *P45 L24* below) and Appendix A (add a statement about the regression analysis, or fitting, of the relevant parameters).

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).

We reformulate it as "higher () pressures imply lower isotope fractionation"

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

In the field of trace gas measurements, particularly of monitoring background carbon monoxide, the achievements of Paul Novelli and his colleagues at NOAA ESRL are recognised internationally and we word this as "famous". The near simultaneous filling of flasks with air was the simplest way to have a practical (be it not complete) check for sample integrity, and this issue is an important part of this paper. "Famous" may be

not to optimal descriptor, but we feel that in the introduction, in this way, the attention of the reader may be influenced in a positive way.

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

Rewritten.

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?

Not at all. The elevations in ^{18}O content of CO in tanks with higher ozone mixing ratios in C1 were spotted earlier, however not thoroughly analysed and thus preliminary speculated by Brenninkmeijer *et al.* (1999) as the effect pertaining only to the CO in tanks, *i.e.* WAS compositions. This has prompted us to resolve the issue in this study, which shows that the effect is more general, *viz.* it concerns the *in situ* measurements as well.

L8: disproportionately is not a good term here

We use "unexpectedly" instead.

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

We change "its concentrations may be higher" → "it is abundant".

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

This statement it redundant indeed.

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?

(pp. 21041−42 are meant?) It is not clear to us how to "describe better" the statistics here – we provide sufficient statistics in distributions shown in Fig. 1; in this paragraph we provide the number of C1 outliers w.r.t. the C2 data. With "numbers quoted" we implied that the statistics presented include the samples in bins with average $[O_3]$ of 420−620 nmol/mol, *i.e.* the total numbers of outliers are the sums of those for the bins above 400 nmol/mol of $[O_3]$. We rewrite this sentence.

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

Yes. One can estimate this from chemical kinetics data (*e.g.*, JPL) and typical CH_4/CO/OH, temperature and pressure distributions with altitude. Our comprehensive calculations with the AC-GCM EMAC model (see Jöckel *et al.*, 2010) yield the average ratio of the CH_4+OH to CO+OH reaction rates of 6−14 in the FT and 8−18 at the C1 flight altitudes (250 hPa), that is double to quadruple than that in the boundary layer (ratios of 3−5, respectively). To compare, the maximum decrease in stratospheric CH_4 mixing ratio in C1 WAS we observed is 10% w.r.t. to the tropospheric values.

L23/24: rewrite more directly

We rewrite this sentence and add additional references (Stevens *et al.*, 1980; Röckmann *et al.*, 1998).

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))

With "unique" we wanted to emphasise that ozone is the initial source of large [18]O enrichments that are transferable to other compounds. We reformulate the sentence and add a relevant reference (Savarino and Morin, 2012).

P45, L12ff: Do you mean that you really reproduce the C2 distribution when you average C1 data over 1200 s? Why would that be? Or do the errors get too large?

No, we mean that the compositions with the $\rho_{O3:CO}$ = $[O_3]$/[CO] ratios similar to those of the suspected (contaminated) C1 data are obtainable from averaging the C2 data only at the intervals of 1200 s and greater. In other words, the WAS samples can bear such $\rho_{O3:CO}$ ratios, but not the *in situ* ones. We reformulate the sentence.

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

We add an in-text formulation for C_c (Sect. 3, new Eq. (1)) and refer the Reader to new Fig. 1 (d). We would like to keep the derivation in Appendix A (please see our reply on the kinetic framework above).

P46 L1: Show better in figure.

This is clarified in Appendix A and is shown in the new version of Fig. 1 (d). We find a few statements (incl. using "contamination signal") somewhat vague in this paragraph, so we reformulate it.

L6: remove and

Removed.

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

In the traditional Keeling plot, it is only possible to infer the admixed source (contamination) signature for the varying component (in our case, C_c) admixed to the initial reservoir of fixed concentration (in our case, different subsets of data with virtually constant C_t, respectively). In essence, we regress the data using $C_a{}^{-1}$ as the independent variable. We neither see any conceptual difference here nor understand which "different type of presentation" is meant. Perhaps, the Reviewer was perplexed by the formulation at p. 21047, l. 2 ($C_c{}^{-1} \rightarrow 0$ implies $C_a{}^{-1} \rightarrow 0$, however)? We add the plots exemplifying the regressions to the Supplementary Material, Fig. S3.

P47, bottom: The 13C discussion is unclear. R2 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.

The regression slope has nothing to do with the Keeling plot. We offer an entirely valid example: Adding molecules with the isotope signature identical to that of the receiving reservoir will produce R^2 of unity and slope of zero.

C7948

We disagree with the statement "*the regressions that you use are delta versus the contamination CO*" (it is a conceptual misunderstanding; see our answer to the previous comment). Finding the δ^{13}C signature of around -47‰ is, as speculated, accidental because the share of the CH_4-derived CO component roughly proportionates with [O_3] in the UT/LMS, hence inevitably with C_c. Such is the case for δ^{18}O, too, however the difference between δ^{18}O(CO) of the *in situ* CO and that from CH_4 oxidation ($-(5-10)$‰ *vs.* ~0‰) is smaller compared to that of δ^{13}C (-30‰ *vs.* -47‰, respectively) and, more importantly, to $+90$‰ of δ^{18}O(O_3). In other words, the δ^{13}C of the contamination source is very close to that of the *in situ* CO and δ^{13}C(CH_4) is very low, therefore we "see" the change in CO photochemical composition, but not the contamination with the MMA.

P48: Rewrite . . .which agrees with other estimates at R2 above 0.75. Not clear at all.

The δ^{18}O regression results at $R^2 > 0.75$ are implied. We change the sentence accordingly.

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

Seasonal changes in δ^{18}O and δ^{13}C of CO are evident in the (more) tropospheric compositions seen by C1, which is the scope of our subsequent communication (in this study we would like to discuss the artefact issue only). Nonetheless, seasonal variations in δ^{18}O(CO) accompanying the well-studied variations in NH [CO] are seen in Figs. 2 and S2 (in Supplementary Material). Much less precise information can be derived on atmospheric mixing processes from the C1 CO data, unfortunately. (We hope to have understood the question correctly.)

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

C7949

It cannot be seen in Fig. 3 which presents the estimates contamination signatures rather than atmospheric δ^{13}C(CO) (besides we also state that the corrected values are not presented). We include the plot of the original and corrected δ^{13}C(CO) C1 data compared to the B96 observations in the Supplementary Material, Fig. S4.

L18-20: rewrite, very hard to follow.

Thank you, we remove this paragraph (it is left over from the previous version of the manuscript by mistake, our apologies). In essence it reiterates the conclusions given in previous paragraph.

P49, L24-end: rewrite, not clear.

Rewritten.

P50 L1: rewrite, not clear

We change "may intervene" → "may affect the $^{18O}\delta_c$ value".

L15: Why "upheld"

We use "supported" instead.

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

No, this is not the main conclusion of our study but rather a valid hypothesis that involves processes that are nearly impossible to tackle using the limited information we possess. After thoroughly studying the extensive literature reviewed by Oyama (2000) we cannot speculate more than given here.

L13 implex ! complex??

We change it to "intricate". S. Gromov admits that his desktop English dictionary (http://www.webster-dictionary.org/definition/Implex) is too old and must be replaced.

P52, L14: mere ! do you mean exclusive?

Yes, corrected to "exclusive".

L15: comparable to what?

Here it means that the contaminating reaction (or exposure) times are similar, which is characteristic for the reaction in the inlet tubing rather that in sample storage tanks. We use "similar" instead.

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.

This is a typing error by us, the C_c (contamination strength) is meant.

Technical:

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

We have changed some long sentences.

Suggest replacing all occurrences of ozone with O3 after introduction on p39, l5

We have replaced all occurrences where appropriate (exceptions are Introduction and Conclusion sections).

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.

It is not clear which page the Reviewer is referring to w.r.t. the sub/superscript notation (perhaps, p. 21048?). We would like to leave the decision on the technical issues at the Editor's discretion.

On the comments of S. Assonov

The authors have observed CO increase in the samples taken in UT/LMS and stored in stainless steel canisters. Elevated CO correlates with elevated ozone and also demonstrates an increase in d18O(CO). Based on that oxidation of hydrocarbons (possibly methane) by ozone in canisters, being catalysed by stainless steel is proposed as the most likely mechanism. Finally the authors discuses that elevated

C7952

CO has (maybe indirectly) recorded d18O signals of ozone in UT/LMS. Notably, the authors write: ". . .the molecular lifetime (the period through which the species' isotope reservoir becomes entirely renewed, as opposed to the "bulk" lifetime) of O3 encountered along the C1 flight routes is estimated on the order of minutes to hours at daylight (H. Riede, MPIC, 2010), thus the isotope composition of the photochemically regenerated O3 resets quickly according to the local conditions." Thus the d18O values observed reflect not the original signature of ozone from the stratosphere but the ozone being photochemically recycled in UT/LMS. This is very interesting scientific finding.

Thank you. However, we are not the first to emphasise the importance of the turnover rate of O_3 for its isotope composition. For instance, Vicars and Savarino (2014) (see also refs. therein) have used the equivalent concept (called "isotopic lifetime") while discussing their measurements of tropospheric O_3 isotope composition. Using our estimates of the molecular lifetime of O_3 along the CARIBIC flight routes we reiterate their conclusions for the UT/LMS, *i.e.* that the isotope composition of O_3 should be determined by the local conditions.

Given that, I would suggest giving some supporting references and/or more detailed info (or discussion) on the reactions involved.

Despite an extensive search, we did not find any plausible mechanism of producing CO with the oxygen content derived from O_3 in the gas-phase chemistry. As we state, we are not aware of carbonaceous compounds that may be present sufficient amounts (tens of nmol/mol) in the UT/LMS, except for CH_4. The latter, however, does not undergo ozonolysis in the gas phase. A more plausible conjecture is the occurrence of heterogeneous reactions on the walls of the inlet/tubing of the C1 sampling system. The information we possess is, however, too limited to be able to scrutinise this hypothesis in detail (see our answer to the third comment below).

C7953

Second, can the authors speculate on the dependence of d18O signals of the recycled ozone on the local conditions in UT/LMS? How large variations could be expected?

This is a valid point which we have implicitly addressed in Table 1. The variations in $\delta^{18}O(O_3)$ listed should mostly follow the seasonal temperature variations, which are within $220-235$ at $[O_3]$ above 300 nmol/mol in C1. The last line in Table 1 presents our "crude" estimate of the expected variations using the laboratory data (8‰). These are comparable to the variations at lower pressures (and same temperatures) and to the uncertainty of our $\delta^{18}O(O_3)$ estimate, however.

Third, is there any information on ozone reactions catalysed by stainless steel?

There is a large volume of literature (most of it covered by Oyama, 2000) devoted to the heterogeneous decomposition of O_3 and its reactions with various hydrocarbons (including CH_4) in the presence of catalysts like MnO_2, Li/MgO, *etc.* CO is often found produced in these reactions. However, these studies are special (in view of typically searching for efficient O_3 scrambling techniques) and difficult to project on the sampling conditions of C1. For instance, we do not know some of the properties of the C1 inlet tubing, *e.g.* the amount of manganese that was likely used to produce some of its stainless steel parts, to make sufficiently precise kinetic estimates. Therefore, catalytic decomposition/reaction of O_3 on the stainless steel parts in C1 is likely, however impossible to quantify.

As a technical comment – I suggest to address the method of d18O(CO) measurements and how the d18O signal of CO is preserved. One can give a few lines supported by references.

The method of $\delta^{18}O(CO)$ measurement used in C1 is the one extensively documented by Brenninkmeijer (1993), therefore we would only like to refer the Reader to this work in the experimental section of the manuscript. If it does not concern the analytical method, it is not entirely clear to us what kind of $\delta^{18}O$ signal preservation is implied by the Reviewer. In case of WAS tanks, the lab tests showed a slow increase in [CO] in with time; in a few tanks that occasionally were stored for a very long time (>10 days, disregarded in the analysis here), the noticeable build-up of CO was not accompanied by the concomitant increase in $\delta^{18}O(CO)$. We attribute this to decomposition of HMNCs/VOCs on the walls of the tanks. As we state in the manuscript (Appendix A), we find no systematic differences between the tanks, neither is there an evidence of isotope exchange processes that may have corrupted the oxygen content of CO.

References

Brenninkmeijer, C. A. M.: Measurement of the abundance of [14]CO in the atmosphere and the ^{13}C/^{12}C and ^{18}O/^{16}O ratio of atmospheric CO with applications in New Zealand and Antarctica, *J. Geophys. Res. Atm.*, **98**, 10595$-$10614, doi: 10.1029/93JD00587, 1993.

Brenninkmeijer, C. A. M., Crutzen, P. J., Fischer, H., Gusten, H., Hans, W., Heinrich, G., Heintzenberg, J., Hermann, M., Immelmann, T., Kersting, D., Maiss, M., Nolle, M., Pitscheider, A., Pohlkamp, H., Scharffe, D., Specht, K., and Wiedensohler, A.: CARIBIC – Civil aircraft for global measurement of trace gases and aerosols in the tropopause region, *J. Atmos. Oceanic Technol.*, **16**, 1373$-$1383, doi: 10.1175/15200426(1999)016<1373:Ccafgm>2.0.Co;2, 1999.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geosci. Model Dev.*, **3**, 717$-$752, doi: 10.5194/gmd37172010, 2010.

Oyama, S. T.: Chemical and Catalytic Properties of Ozone, *Catal. Rev. Sci. Eng.*, **42**, 279−322, doi: 10.1081/cr100100263, 2000.

Röckmann, T., Brenninkmeijer, C. A. M., Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., and Crutzen, P. J.: Massindependent oxygen isotope fractionation in atmospheric CO as a result of the reaction CO+OH, *Science*, **281**, 544−546, doi: 10.1126/science.281.5376.544, 1998.

Savarino, J. and Morin, S.: The N, O, S Isotopes of OxyAnions in Ice Cores and Polar Environments, in: Handbook of Environmental Isotope Geochemistry, edited by: Baskaran, M., Advances in Isotope Geochemistry, Springer Berlin Heidelberg, 835−864, 2012.

Stevens, C. M., Kaplan, L., Gorse, R., Durkee, S., Compton, M., Cohen, S., and Bielling, K.: The Kinetic Isotope Effect for Carbon and Oxygen in the Reaction CO+OH, *Int. J. Chem. Kinet.*, **12**, 935−948, doi: 10.1002/kin.550121205, 1980.

Vicars, W. C. and Savarino, J.: Quantitative constraints on the ^{17}O excess ($\Delta^{17}O$) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitritecoated filter technique, *Geochim. Cosmochim. Acta*, **135**, 270−287, doi: 10.1016/j.gca.2014.03.023, 2014.