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Interactive comment on "Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign" *by* J. Savarino et al.

Anonymous Referee #2

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The paper entitled "Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign" by J. Savarino and coworkers provides new measurements of the triple oxygen isotopic composition of atmospheric nitrate during the summer (November to January) 2011/12 OPALE campaign at Dome C, Antarctica. The authors present new data on the ^{15}N, ^{17}O, and ^{18}O isotopic composition of atmospheric filter NO_3^-, which is presented along with a data set on the ^{17}O and ^{18}O isotopic composition of atmospheric ozone measured slightly after the campaign over the year 2012. The authors give a detailed account of the gas sampling, analytical techniques and the acquisition of complementary data before they present the oxygen isotope mass balance of NO_3^-. In comparing their December data (a subset of 4 out

of 11 data points) with modeled values, they find a significant difference in $\Delta^{17}O(NO_3^-)$ of the order of 6 to 8 ‰. The possible origin of the discrepancy is then discussed, but despite a very detailed consideration of possible processes (isotope transfer from HONO to NO_3 via OH, heterogeneous hydrolysis of NO_2 and reactive halogen species acting as an efficient isotope transfer pathway from ozone to nitrate), no convincing explanation for the discrepancy could be given. The authors thus conclude that some *unexpected* process contributes to the atmospheric nitrate budget over Dome C.

The paper is mostly very well written with just a few sentences that are unclear and difficult to understand. Despite the model-data comparison and the in-depth analysis provided in the manuscript, there remain five serious questions concerning the approach and the conclusions of the study. First of all, it is not clear why only a subset of data has been chosen for closer interpretation. This seems to be an unnecessary limitation, in particular also because ozone values already needed to be extrapolated from a time series that was started only after the nitrate data had been acquired. Second, systematic biases regarding the measurement of $\Delta^{17}O(NO_3^-)$ and $\Delta^{17}O(O_3)$ are not included in the discussion and there is no baseline modeling which would demonstrate that the isotope mass balance approach would give consistent results (zero discrepancy between measurements and modeling) for the *commonly accepted daytime chemistry of NO_2* (Grenoble or Polarstern data, for example). As pointed out by B. Alexander in the first referee report, it seems that the contrary is the case. This implies that even the *commonly accepted* triple isotope *daytime chemistry of NO_2* is not understood, possibly indicating that $\Delta^{17}O(O_3)$ is too low (see Alexander et al. 2009 and first refree comment) and that $\Delta^{17}O(NO_3^-)$ is therefore underestimated. The current lack of understanding would thus not necessarily be linked to Antarctic isotope chemistry. Third, the 0-D model chemistry used for the isotope mass balance calculation (Table 1) ignores mass independent fractionation in loss processes for OH. While an experimental demonstration is yet lacking, the fact that CO is mass independently fractionated makes the CO + OH reaction a valid candidate for inducing a non-zero $\Delta^{17}O(OH)$. The authors should look up the relevant literature and discuss whether the oberved discrepancy could possibly be explained by that reaction. Fourth, some of the scenarios are not developed sufficiently and it seems that the halogen chemistry case is not presented in a consistent manner. Finally, even if an *unexpected* process is active under Antarctic summer conditions and we thus assume that there is an offset between modeled and measured nitrate isotope data, the study does not go far enough in trying to explain the observed variability of Δ^{17}O(NO_3^-), which likely provides important clues for the interpretation of the data.

Due to the above listed shortcomings, I recommend that major revisions are made before the article can be published in ACP. There are also some stylistic deficiencies which are evident from the items listed in the minor remarks section. It is thus desirable that the manuscript is further revised in terms of style and clarity.

1 Major Remarks

1. The interpretation (see Table 2) seems unnecessarily limited to the December data of the OPALE campaign, which leads to the analysis of 4 data points only. This restriction on 4 out of 11 data points (see Figs. 2 and 3) includes the nitrate concentration peak (Fig. 2), but misses much of the observed variability of Δ^{17}O(NO_3^-). It is unclear why so much observational information remains unusued and why the remaining data does not deserve the interpretation dedicated to the points of the intensive measurement campaign. It has to be expected that including the omitted data increases the discrepancy between modeled and observed data, as October Δ^{17}O(NO_3^-) data are 1 to 3 ‰ higher than the highest December data (see Fig. 2).
2. Measurement and analysis of Δ^{17}O(O_3) and Δ^{17}O(NO_3^-) follow complex experimental procedures (Vicars and Savarino (2014) for O_3. I wonder whether all steps in the analysis are understood well enough and have appropriate uncertainties

associated. It seems that a few permil of systematic bias cannot be ruled out. This could account for the discrepancy between model and measurement. So far, the manuscript lacks to show that the base model (without Antarctic chemistry) provides results that are consistent with available measurements. Another systematic bias could be related to the fact that ozone data have been acquired only after the nitrate measurements had been completed. Since Δ^{17}O(O_3) varies as a function of time, some of the discrepancy might also be due to an inappropriate extrapolation of ozone data.

3. In proposing an unexpected process to occur, the authors suggest that the Arctic oxidation chemistry needs to be extended. The possibility that known chemistry shows an unexpected isotope fractionation is neglected, however. A possible candidate for such a scenario would be the CO + OH reaction, which is the dominant sink of OH (50 %, see Table 1). Any isotope fractionation in that reaction therefore impacts on steady state Δ^{17}O(OH), possibly invalidating Eq. (5). While one would generally not expect a non-zero Δ^{17}O fractionation in any of the loss processes, CO + OH induces a MIF signature in CO (Röckmann *et al.* (1998); Feilberg, Johnson, and Nielsen (2005a,b)) and therefore is a likely candidate for a non-zero value in Δ^{17}O(OH). Usually fractionation effects are small, but associated Δ^{17}O-signatures for CO are on the order of 3 to 4 ‰ at 600 hPa according to Röckmann *et al.* (1998); the measurements of Feilberg, Johnson, and Nielsen (2005a,b) give a slightly higher value. If OH is similarly fractionated, a few per mil effect cannot be excluded, especially because temperatures are different in the Röckmann *et al.* (1998) experiment and in this study. This point must be included.
4. On page 24057 and 24058, the authors discuss the oxidation of NO by halogen monoxides (R7) as a scenario to bypass standard NO_x chemistry and deduce only a very weak perturbation (2 %) of the Leighton ratio. However, it appears that the estimatation underestimates the impact of halogen chemistry or that numbers in the text are inconsistent.

Table 1 states that the main NO_2 source is the O_3 + NO reaction (producing NO_2 at a rate of $27.0 \cdot 10^5$ molecules cm^{-3} s^{-1}). It is also argued that the XO + NO reaction impacts α by 2 % at most. With the oxidation power of XO being 4000 times the oxidation power of ozone, one must conclude that $k(\mathrm{NO} + \mathrm{BrO})[\mathrm{BrO}]/k(\mathrm{NO} + \mathrm{O_3})[\mathrm{O_3}] \simeq 4000\,[\mathrm{BrO}]/[\mathrm{O_3}] \simeq 0.02/3$ (assuming that NO + O_3 contributes 30 % to NO_2 formation). This implies an unrealistic ozone abundance of 1200 nmol mol^{-1} if we take the max. BrO level of 2 pmol mol^{-1} given on page 24058, but even at 10 times lower BrO values, ozone seems to be much higher than what can realistically be expected. We conclude that either the impact on α is larger than 2 % or that a much lower halogen abundance has been assumed in the calculation.

5. The authors focus much on the discrepancy between obserevd and modeled values, but do not sufficiently discuss the observed variability in the data (see also item 1). Within December, observed $\Delta^{17}\mathrm{O}(\mathrm{NO_3^-})$ varies between 27.3 and 29.6 ‰ and the four model scenarios considered in Table 2 give changes in $\Delta^{17}\mathrm{O}(\mathrm{NO_3^-})$ of 0.9, 0.3, 0.9 and 2.1 ‰, respectively, over the same period of time. The last scenario seems to nicely explain the observed changes in $\Delta^{17}\mathrm{O}(\mathrm{NO_3^-})$ by isotope transfer from OH. It thus seems to be possible that the Antarctic oxidation chemistry is quite well understood, but that sytematic biases (which are independent of the Antarctic chemistry) are responsible for an offset between modeled and observed levels of $\Delta^{17}\mathrm{O}(\mathrm{NO_3^-})$. It might be that this interpretation is already somewhere between the lines of the current manuscript, but I could not find it. I thus recommend that Savarino and coworkers clearly point out this possibility in a revised version of their paper.

In the light of these issues, the discussion of the manuscript requires significant extension and the conclusions need corresponding adjustments.

2 Minor remarks

- p. 24043, l. 25 – 27: "The search for ice core proxies related to past change of oxidative properties of the atmosphere is motivated by the need to model simulations of ozone and OH changes over preindustrial-industrial and glacial-interglacial timescales." Please provide a reference for the claim and reword the phrase, which does not make sense immediately. One might question that *simulations need to be modeled*, since a simulation involves modeling by nature. The authors likely want to model or simulate atmospheric concentrations . . .

- p. 24044, l. 23 – 29 & p. 24046, l. 25 – 26 & p. 24051, l. 11: "Here we present . . . between October 2011 and January 2012." & "11 HVAS samples were obtained during the OPALE campaign (from October 2011 to January 2012)." & "OPALE campaign hold in November-January". The exact period of the campaign and the useful data points are unclear. Please use consistent dates and explain which and why only a subset of available data has been interpreted by the model. Later in the text (Table 2) and in Fig. 2 only the data from the intensive measurement period (4 data points) seem to have been used for the interpretation.

- p. 24045, l. 13 – 17: "This was done . . . ". This sentence on aerosols is not at all helpful as it distracts from the main flow. Since I could not find any reference to the mentioned sulfur cycle studies later in the paper, I doubt their relevance for this paper and recommend complete deletion of the sentence.

- p. 24046, l. 12 – 17: "Observed and modeled NO_x production rates are largely capable of explaining the high levels of photochemical activity . . . ". This claim seems to contradict the later mentioned discrepancy of up to a factor of 7 between modeled and observed NO_2 concentrations.

- p. 24049, l. 18 – 19: "…the O_2 or N_2 samples gases …" *sample gases* or *gas samples* ?
- p. 24049, l. 19 – 24: "All analytical steps were simultaneously performed on nitrate …" *simultaneously → identically, equally* ?
- p. 24049, l. 16: What is cryo-focused ?
- p. 24050, l. 4 – 6: "Concurrent chemical measurements conducted at …" → Concurrent chemical measurements were conducted at …
- p. 24050, l. 6 – 7: "…also documented." → A more appropriate word (eg. *registered*) should be used here.
- p. 24050, l. 22 – 25: "…show similar amplitude and phase than …" *similar than → similar to*
- p. 24051, l. 1 – 2: "A time series showing the year-round record of $\Delta^{17}(O_3)_{\text{bulk}}$ at Dome C in 2012 is presented in Fig. 3. $\Delta^{17}(O_3)_{\text{bulk}}$ averaged 24.9 ± 1.9 ‰ over 2012, corresponding …" Delete *over 2012*.
- p. 24051, l. 2: "…, corresponding to" Since the *bulk* values were derived from the *term* values, replace *corresponding to* by *derived from*, or similar.
- p. 24051/24052, l. 26 – 1: "As Dome C in summer is permanently under sunlight, photochemical inter-conversion of NO_x is permanent:" Repetitive use of *permanent*.
- p. 24053, l. 12 – 15: *correspond → corresponds*
- p. 24053, l. 22: "The diurnally mass averaged trend is shown …No trend is observed …". This is somewhat inconsistent. Please correct wording.

- p. 24054, l. 13 – 16: "The degree of isotopic equilibration between OH and $H_2O\ldots".Ifthereisnoequilibration,oneexpectsthedegreeofequilibration\beta = 0$ and if equilibration is complete (degree = 100 %), one expects $\beta = 1$. Eq. (4) defines the complement of what is written in the text.
- p. 24055, l. 20 – 21: "…because of the interplay of HO_x family and the different sources involved in OH formation." Phrase not clear. Usually one writes *interplay between*, but it is not clear how there is an interplay between a family of species (HO_x) and reactions (sources).
- p. 24057, l. 5 – 6: "A possible explanation for the underestimation of $\Delta^{17}O(NO_3^-)$ involves the potential role of halogen chemistry in the troposphere over the Antarctic plateau …" → "A possible explanation for the underestimation of $\Delta^{17}O(NO_3^-)$ involves halogen chemistry in the troposphere over the Antarctic plateau …"
- p. 24057, l. 18 – 20: "For conditions typical of the Antarctic boundary layer …". I doubt that the word "oxidizing power" is mentioned in Atkinson et al., 2007. The oxidizing power of a substance will depend on the chemical mechanism which would need to be detailed. Since it seems that the authors have just calculated a ratio of rate coefficients in order to determine relative oxidation powers, it is probably more appropriate to indicate that by taking rate coefficients from Atkinson et al., 2007, the factor of 4000 has been obtained.
- p. 24058, l. 3: "The interaction of XO in the NO_x cycle …" Revise phrase. The word *interaction* commonly signifies a reciprocal influence. The *interaction of XO* thus is incomplete.
- p. 24058, l. 14: "…specific form of $\alpha \equiv 1/(1+x)$) of which is to low to …" *of which is to low → which is too low*

- p. 24074, Table 1: "Rate of production and sink of OH and mass balance calculation of Δ^{17}O" Data points cover the interval from November 2011 to January 2012.
- p. 24074, Table 1: The concentration of OH misses a factor of 10^5 (or 10^6).
- p. 24076, Fig. 1: ". . . nitrate concentrations observed between October 2011 and January 2012." Data points cover the interval from November 2011 to January 2012.
- p. 24076, Fig. 1: " . . . of the OPALE campaign . . . " Redundant information. Delete *of the OPALE campaign*
- p. 24077, Fig. 2: ". . . nitrate collected between October 2011 and January 2012." Data points cover the interval from November 2011 to January 2012.
- p. 24077, Fig. 2: " . . . of the OPALE campaign . . . " Redundant information. Delete *of the OPALE campaign*
- p. 24078, Fig. 3: *sampling* → *samplings*

References

Feilberg, K. L., Johnson, M. S., and Nielsen, C. J., “Relative rates of reaction of $^{13}C^{16}O, {}^{12}C^{18}O, {}^{12}C^{17}O$ and $^{13}C^{18}O$, with OH and OD radicals,” Phys. Chem. Chem. Phys. **7**, 2318–2323 (2005a).

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