We thank the reviewers for their in-depth review, comments and suggestions to improve the manuscript. We hope that in the following we alleviate all their critical questions;

The following codes are use through our reply:
Blue : authors' response
Blue-Italic: text added to the MS

Anonymous Referee

1 Major Remarks

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 $\Delta^{17}O(NO^{-}_{3})$. 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 $\Delta^{17}O(NO^{-}_{3})$ data are 1 to 3‰ higher than the highest December data (see Fig. 2).

The reason is simple. OPALE campaign during which all ancillary data were available (NOx, HOx, NOy XO) was limited to Dec 2011 – Jan 2012. As shown in figure 1, only four collected nitrate samples overlap the OPALE campaign. Outside this period, there is simply no HOx, NOx, NOy XO concentration available. We found that even using known concentration of these family species, the isotope mass balance present enough uncertainties. Modeling $\Delta^{17}O$ of nitrate outside the OPALE period will require extrapolation of concentration for very reactive species leading to a very poor constrained chemistry and therefore isotope balance. Regarding ozone, the good implementation of the ozone collection was not established before 2012. Therefore we concluded that would have been too speculative to extrapolate the isotopic mass balance outside the OPALE campaign.

Measurement and analysis of $\Delta^{17}O(O_3)$ and $\Delta^{17}O(NO^{-}_{3})$ follow complex experimental procedures (Vicars and Savarino (2014) for O_3.

No really, actually. Coating filters has been used for decades as passive or active samplings. Any chemical analyzer is much more complicated that our method in my view. This method is also radically simpler that the previous method (liquid helium condensation) used to monitor O3 isotope in atmosphere. Procedure in isotope chemistry should not be compared to chemical procedures. They are looking completely different aspects of the matter.

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 chem- istry) 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 $\Delta^{17}O(O_3)$ varies as a function of time, some of the discrepancy might also be due to an inappropriate extrapolation of ozone data.

We agree with the reviewer and have now taken into account this remark in the revised version of the MS as this comment overlaps one comment of reviewer1. Reviewer can refer to our reply to B. Alexander's comment. In short, yes it is always possible that a systematic error (the most difficult to find) exists. However, our measurements using the coating filter match other methods that used a completely different approach. It is unlikely that these different methods will present the same systematic error. Therefore is no reason to believe that such error exists. In fact, the approach of using the O_3 isotopic composition as the adjustment variable is no better justified. On the other hand, the past decades, research in atmospheric chemistry has revealed our poor knowledge of certain aspect of the atmospheric reactor, in particular the NOx chemistry (daytime production of HONO unexplained, strong impact of halogen chemistry on NOx, role of $ClNO_2$, etc). Even during OPALE, the NO2/NO ratio is incompatible with the known NOx chemistry (extended Leighton cycle + NOx sink), with concentration of NO_2 7 times higher than the photochemical steady state (Frey et al., 2015). Therefore we think it is legitimate to question the NOx chemistry more than the O_3 isotope composition, which has been shown to vary little in the lower troposphere in agreement with its poor sensitivity to temperature and pressure.

Frey, M. M., Roscoe, H. K., Kukui, A., Savarino, J., France, J. L., King, M. D., Legrand, M., and Preunkert, S.: Atmospheric nitrogen oxides (NO and NO2) at Dome C, East Antarctica, during the OPALE campaign, Atmos. Chem. Phys., 15, 7859-7875, 10.5194/acp-15-7859-2015, 2015.

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 $\Delta^{17}O(OH)$, possibly invalidating Eq. (5). While one would generally not expect a non-zero $\Delta^{17}O$ 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 $\Delta^{17}O(OH)$. Usually fractionation effects are small, but associated $\Delta^{17}O$-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.

We agree with the reviewer's view on unexpected isotope fractionation during the chain oxidation of the NOx. This is now explicitly mentioned in the revised version (see reply to B. Alexander). Concerning the CO+OH, the fact that CO gets a positive $\Delta^{17}O$ during this reaction doesn't necessarily imply that OH will carry ones. O2+O is the only other chemical reaction producing non zero $\Delta^{17}O$ and studies have shown that it is during the stabilization of activated complex O_3^* to O_3 that non-zero $\Delta^{17}O$ is generated. If same applied to CO+OH, then $HCO_2^* \rightarrow CO_2 + H$ should be the step generating $\Delta^{17}O$. Unless there is a O-atom scrambling within the HCO_2^*, there is no reason to believe that OH will carry a non-zero $\Delta^{17}O$ and if it was the case, mass balance will impose a negative value. Nevertheless, because many unknown remain about the $\Delta^{17}O$ value of OH, the following sentence is now added in the revised version.

-Line 21 P24061 *"It is also possible that OH could display a strange $\Delta^{17}O$ considering that the reaction CO + OH produces a positive $\Delta^{17}O$ in the remaining CO {Feilberg at al., 2005;Röckmann et al., 1998)"*

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 $k(NO + BrO)[BrO]/k(NO + O_3)[O_3] \simeq 4000\ [BrO]/[O_3] \simeq 0.02/3$ (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.

When we write that 1 pptv of XO has the same oxidation power than 4 ppb of O_3 it means that $k(NO + BrO)[BrO]/k(NO + O_3)[O_3] \simeq 1$ and not 4000. It can easily be seen in kinetic database that the ratio of the kinetic rate $k(NO + BrO)/k(NO + O_3) \simeq 4000$. The oxidative power (or in other words oxidation potential) applies to kinetic rates, not to production rates. It is a potential and thus should be independent of the concentration. So we confirm that at XO concentrations found at Dome C, XO has a very limited impact on alpha, especially as alpha includes also NO+HO_2 reaction.

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 $\Delta^{17}O(NO^-_3)$ varies between 27.3 and 29.6 ‰ and the four model scenarios considered in Table 2 give changes in $\Delta^{17}O(NO^-_3)$ 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 $\Delta^{17}O(NO^-_3)$ 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 $\Delta^{17}O(NO^-_3)$. 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.

We disagree that Antarctic oxidation chemistry is quite well understood. OPALE, ANTCI, ISCAT and other studies, on chemistry ground, have ample demonstrated that the chemistry over polar ice sheets is not completely understood. For instance, $ClNO_2$ has never been measured. HONO concentration is not well constrained. The role HO_2NO_2 is not very clear and the ratio of NO_2/NO is way too high. Therefore, our affirmation that the chemistry is not well understood is at first demonstrated by concentration measurements, not by the isotopic mass balance. The fact that ^{17}Oexcess cannot be explained by the most basic NOx chemistry just reinforces this opinion. As explained above, there is always a possibility that a systematic error is the cause of the discrepancy between observation and model for the isotope but we think that it is the conjunction of the NOx chemistry and the isotopic mass balance that let us think that something unknown is at play. Turning the question in the other way, it will be very puzzling to claim that because the isotopic mass balance is closed, NOy chemistry is well understood when the basic of the basic, the NO_2/NO ratio, is difficult to understand. Regarding the variability, this is indeed an interesting observation and thus we have added a specific sentence to mention this observation:

Line 22, P24061 *"On the other hand, Table 2 shows that the variability of $\Delta^{17}O$ (but not the absolute values) is correctly caught by the model when α is constrained by the observations and $\Delta^{17}O$(OH) by the observed HONO concentrations. This observation would favor the view that the chemistry and associated $\Delta^{17}O$ transfer are well understood and a systematic error is probably at the origin of the discrepancy of the absolute values. However, this conclusion will be in contradiction with NO_x-HO_x chemistry observations showing that in fact such chemistry is not very well understood (Frey et al., 2015;Legrand et al., 2014;Slusher et al., 2010)."*

As a general perspective, the following sentences were added in the conclusion.

"Systematic errors and/or bad isotopic transfer functions for $\Delta^{17}O$ are not completely excluded for explaining the discrepancy between observed and modeled data and we encourage laboratory experiments to reduce these uncertainties. However, given the fact that unexplained NO_x chemistry has been revealed by other means, we are in favor of a missing chemistry to explain the mismatch observed."

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 . . .

Now the sentence read as:

"The search for ice core proxies to reconstruct past change of oxidative properties of the atmosphere is motivated by the need to simulate ozone and OH changes over preindustrial-industrial and glacial-interglacial timescales (Thompson, 1992;Wang and Jacob, 1999; Murray et al., 2014)."

- p.24044,l.23–29&p.24046,l.25–26&p. 24051,l.11: "Herewepresent ...between October 2011 and January 2012." & "11 HVAS samples were ob- tained during the OPALE campaign (from October 2011 to January 2012)." & "OPALE campaign hold in November-January". The exact period of the cam- paign 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.

Period is now consistent through the MS. October was actually mentioned because one data what collected during end of October but it makes more sense to define the period as November 2011 January 2012

- 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.

Done

- 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.

The sentence refers to NOx emission; not NOx concentration. Previous studies have shown that snow photolysis of nitrate and emission fluxes are responsible for the high oxidative capacity over inland polar ice sheet (i.e. high OH concentration, O3 production, two observations that were impossible to imagine until NO was measured for the first time). This doesn't mean that NO_2/NO ratio, or NO_2 or OH concentration are quantitatively understood and/or modeled.

- p. 24049, l. 18 – 19: "...the O_2 or N_2 samples gases ..." *sample gases* or *gas samples* ?

replace by *gas samples*

- p. 24049, l. 19 – 24: "All analytical steps were simultaneously performed on nitrate . . . " *simultaneously → identically, equally* ?

replace by *identically*

- p. 24049, l. 16: What is cryo-focused ?

It is a term very common in isotope geochemistry to describe the condensation and focusing of a gas sample on a small cold section of a line by the mean of liquid nitrogen or liquid helium, depending on the vapor pressure of the considered gas.

p. 24050, l. 4 – 6: "Concurrent chemical measurements conducted at ..." → Concurrent chemical measurements were conducted at . . .

done

p. 24050, l. 6 – 7: ". . . also documented." → A more appropriate word (eg. *registered*) should be used here.

Replace by *recorded.*

p. 24050, l. 22 – 25: ". . . show similar amplitude and phase than . . . " *similar than → similar to*

done

- p. 24051, l. 1 – 2: "A time series showing the year-round record of $\Delta^{17}(O_3)_{bulk}$ at Dome C in 2012 is presented in Fig. 3. $\Delta^{17}(O_3)_{bulk}$ averaged 24.9 ± 1.9 ‰ over 2012, corresponding . . . " Delete *over 2012*.

done

- p. 24051, l. 2: ". . . , corresponding to" Since the *bulk* values were derived from the *term* values, replace *corresponding to* by *derived from*, or similar.

done

- 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*.

Replace permanent by *continue*

- p. 24053, l. 12 – 15: *correspond* → *corresponds*

done

- p. 24053, l. 22: "The diurnally mass averaged trend is shown ...No trend is observed . . . ". This is somewhat inconsistent. Please correct wording.

Replace by "*The diurnally mass average of $\Delta^{17}O(NO_2)$ calculated…*"

- p. 24054, l. 13 – 16: "The degree of isotopic equilibration between OH and H_2O . . . ".If there is no equilibration, one expects the degree of equilibration $\beta = 0$ and if equilibration is complete (degree = 100 %), one expects $\beta = 1$. Eq. (4) defines the complement of what is written in the text.

As it is set (EQ4), if there is no equilibration, k[H2O] << L and beta = 1 as stated in the paper.

- 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).

Replace by "*The value of $\Delta^{17}O(OH)$prod. is more difficult to assess because of the interplay between HO and HO_2, and the different sources involved in OH formation.*"

- 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 . . . "

done

- 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.

Replace *oxidizing capacity* by *chemical activity.* We think the concentration of the species is more expressive than the kinetic rates as what is measured in the atmosphere is concentrations. This avoids piling numbers up with different meanings and units.

- 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.

Replace *interaction* by *involvement*

- 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*

done

- p. 24074, Table 1: "Rate of production and sink of OH and mass balance calculation of $\Delta^{17}O$" Data points cover the interval from November 2011 to January 2012.

Table 1 is given as a example of how isotopic mass balances are calculated. Since the caption seems to be confusing we change it for «*Example of mass balance calculation of $\Delta^{17}O$ for Dec.19th, 2011 3:45 pm conditions* »

- p. 24074, Table 1: The concentration of OH misses a factor of 10^5 (or 10^6).

done

- p. 24076, Fig. 1: ". . . nitrate concentrations observed between October 2011 and January 2012." Data points cover the interval from November 2011 to January 2012.

done

- p.24076,Fig.1:"...of the OPALE campaign..."Redundant information. Delete *of the OPALE campaign*

done

- p. 24077, Fig. 2: ". . . nitrate collected between October 2011 and January 2012." Data points cover the interval from November 2011 to January 2012.

done

- p.24077,Fig.2:"...of the OPALE campaign..."Redundant information. Delete *of the OPALE campaign*

done

- p. 24078, Fig. 3: *sampling → samplings* done

Again we thank the reviewers for their interesting comments.