Author Response to Referee #2

We thank Referee #2 for the helpful comment. Please find our responses below.

General Comments: My main concern after reading this manuscript is that it does not do more to quantify to what extent the triple oxygen isotopic compositions of sulfate and nitrate can be used as a measure of atmospheric oxidation capacity. Dumont d'Urville (DDU) should represent a well known case where the many contributing factors could be examined by applying statistics and modeling. I am convinced that the analytical method is sound, the samples come from a unique and potentially very important location, and a nice time series is delivered. It is not clear whether the goal is to establish the technique of using a combined oxygen triple isotope analysis in O3, NO3- and SO4– as an important proxy, or to use these measurements to tell us something new and interesting about the earth system (in which case what?).

We thank Referee #2 for this general but fundamental comment and we think that in some way this agrees with the comment of Referee #1 concerning the definition of the oxidation capacity of the atmosphere (OCA in short). We are fully aware of the limitation of the $\Delta^{17}O$ tracer. By essence, $\Delta^{17}O$ is an integrator of the different oxidation pathways and thus give a broad view of the relative importance of the involved oxidants. By no means its value is a measure of the oxidation capacity, first because $\Delta^{17}O$ is not a measure of the total oxidant concentration (it is a measure of the relative importance of different oxidation pathway), and second as mentioned by Referee #1, the oxidation capacity itself is not very well defined. So we should abandon the idea that from $\Delta^{17}O$, we can extract the OCA. $\Delta^{17}O$ should be seen as a way of constraining the oxidation scheme of a model by different mean than concentration measurements alone. And there are few examples now in the literature where $\Delta^{17}O$ has proven to be meaningful with respect to concentration analysis (e.g. Morin et al. (2008) and Savarino et al. (2013) with the bromine nitrate formation, McCabe et al. (2006) with the metal catalyzed sulfate formation, Alexander et al. (2012) and Chen et al. (2016) with the sulfate formation by halogen oxidation, etc.). Therefore, combining the measurement of $\Delta^{17}O$ values of SO_4^{2-}, NO_3^- and O_3 has three main objectives.

1- Producing a set of data that can be used to constrain chemistry/transport model scheme, and because production schemes of nitrate and sulfate are interconnected through oxidant, the two species provide more constrain that each taken separately.

2- Demonstrating that the seasonality of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ is a direct consequence of the oxidation scheme and not the seasonality of $\Delta^{17}O(O_3)$ (This is the first time the seasonality of $\Delta^{17}O(O_3)$ is confronted with $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$. It has always been assumed before).

3- Revealing any features that can help to decipher the oxidation mechanisms of the precursors at this specific location.

As demonstrated by Legrand et al. (2009, 2016) DDU is in fact a very difficult case to treat because the chemical state of its atmosphere depends strongly on the export of oxidants and precursors from the plateau during katabatic winds. Even halogen chemistry is very different than other coastal sites. Considered with a sampling resolution of a week, we don't think that modeling the DDU data is an easy task and would certainly require a specific study, if not a specific model. So in short and to respond directly to the referee's comment, the goal of our paper is to document the $\Delta^{17}O$ variability over space and time. In summary section, we have added that future study using atmospheric chemistry and transport model is required.

Taking into account the throughout comment by Referee #2 as well as the comments by Referee #1 concerning the unclearness of hypothesis in this study, we have re-written our introduction in a way that we think now better emphasize the interest of measuring these isotopic tracers. We hope our new introduction answer the referee comments and questions.

Specific comments: The abstract starts with a big promise: 'Reconstruction of the oxidative capacity of the atmosphere is of great importance...Triple oxygen isotopic compositions.. in the Antarctic ice cores have shown potential as stable proxies because they reflect the oxidation chemistry involved in their formation processes.'

A useful proxy must have a good correlation with the thing we can't measure directly. In this case the authors propose that the triple oxygen isotope anomalies in nitrate and sulfate are a useful proxy for the oxidative capacity of the atmosphere. This is a great goal because potentially, sulfate and nitrate in ice cores (or from other places, sediments, fern..) could be used to deduce past oxidative capacity. My concern is that the authors have not defined what it is exactly they are trying to determine based on their oxygen isotope measurements, and, they have not demonstrated that there is a correlation between the measurements and whatever that is, and therefore, they cannot claim that the triple

oxygen isotope anomalies in NO3- and SO4-- are useful proxies.

First, the authors should define what they mean by oxidative capacity. The oxidative capacity is not an exactly defined property as it could mean oxidation by O2, O3, OH, HO2, RO2, H2O2, O(1D), O(3P), NO3, Cl, BrO and so on. Oxidative capacity is sometimes taken to mean OH, but oxidation is a general process, not a specific one. The use of D17O would seem to be a better measure of relative exposure to ozone than [OH], since OH in the troposphere does not carry the D17O signal. The authors note (R2), oxidation by OH, will not transfer any of the anomaly from ozone to sulfate, and reactions R3, R4 and R5 transfer variable amounts of the ozone anomaly to sulfate. Because of the many pathways of SO2 oxidation it is difficult or impossible to find the relative contributions of the four proposed formation mechanisms based on one observable. In any case, since R2-R4 are all oxidation reactions converting S(IV) to S(VI), they all qualify as components of the atmosphere's oxidation capacity. The authors should be more exact about what it is that they propose to do with the measurements.

Second, the discussion contains a lot of speculation about what may or may not cause the patterns shown in Figure 2. No firm conclusions are ever made from this discussion, and clearly, if you cannot show what causes the signal that is measured, there is no hope to use that same signal, measured at a different location, to make conclusions about its origin. There is a bit of a 'chicken vs egg' element to the discussion in which the data are assumed to be important and then used to justify assertions in the abstract about the O3/ROx and hypohalous acid mechanisms, and I would like the authors to be more clear in the logical progression: first show that this is a useful proxy (i.e. correlated to some observable e.g. [O3] or [OH]), and then as a second step, if possible, use the proxy to make a prediction or conclusion about the atmosphere.

After some thoughts and discussions with the co-authors, we fully agree with the referee's comment and decide to rephrase the motivation of our study. First DDU cannot be used as a place to establish any ice core proxy. The coastal chemistry and transport is very different than inland sites. To establish a proxy, more than a strong correlation, a mechanism invariant in time and space is needed, and clearly the correlation between O_3 and $\Delta^{17}O$ at DDU should not be seen as a proxy of ozone and used to interpret ice cores. We know that such correlation is only fortuitous and results mainly from phenomena others than a simple cause-consequence effect induced by a change in ozone concentration (e.g. transport, radiations, aerosol burden, acidity all influence $\Delta^{17}O$). However, DDU with strong seasonal contrasts and proximity with the ocean source is an interesting place to study Δ^{17}O with the goal to understand the different mechanisms at play. For instance, we show that Δ^{17}O(O_3) does not change with season despite contrasted environmental conditions during the year. One direct consequence, actually applicable to ice cores is that any variation of Δ^{17}O of sulfate and nitrate in ice core is solely a consequence of the oxidation mechanisms and mixing. Rephrased, the objective of our study is more to confront the theory behind Δ^{17}O (i.e. the transfer of the Δ^{17}O of ozone to other compounds) than directly producing an oxidation proxy for ice core. It should be bare in mind that the ^{17}O transfer theory relies mainly on hypothesis not validated by any observation (see e.g. Morin et al. 2011) and continuous observation are thus necessary. However, Δ^{17}O of ozone, as well as testing the theory indirectly benefit to the ice core study. In order to dissipate this misunderstanding, our text has been modified to better focus on the general understanding of the Δ^{17}O as a tool to probe the chemistry of the atmosphere than producing an ice core proxy.

Equation (2) is used to determine non sea salt sulfate. The amount of sea salt sulfate is approximated by multiplying the sodium concentration by a factor ’k’ which is the mass ratio of sulfate to sodium in sea water (0.25), and this is subtracted from total sulfate, leaving non sea salt sulfate. The ratio of the concentration of sulfate to sodium in sea water is well known, 0.25, but a value of ’0.13 plus or minus 0.04’ is used for samples collected from May to October to account for ’sea salt fractionation processes that affect the Antarctic region in winter when temperatures drop below -8oC’. First, please rewrite to clarify that this is a chemical and not an isotopic fractionation.

We modified the expression as suggested by Referee #2, to emphasize that sea salt fractionation is a fractionation in chemical component and different from an isotope fractionation (p.6, l.30). It is due to the formation of the mirabilite, a Na_2SO_4 crystal phase that precipitates at −8°C and thus depleting the seawater in SO_4^{2-} relative to Na^+.

Second, how was the error of plus or minus 0.04 propagated in the calculation? I do not see error bars in the corrected valued in Figure 2.

In Supplementary material, we added the error of [nss-SO_4^{2-}] propagated from the uncertainty in concentration measurement by IC (i.e., 5%) and standard deviation (1σ) of filter blank values, and *k* value (0.13 ± 0.04 in winter). The error propagated to Δ^{17}O(nss-SO_4^{2-}) values are shown in

Figure 2, by red vertical line with each circle.

Through this correction, the standard deviation filter blank was newly added into consideration for the uncertainty analysis. Due to this correction, the uncertainty for $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values was also slightly changed, which is now applied to Figure 2. Also the explanation for the uncertainty analysis was modified (p.5, l.7-12 and p.6, l.31 - p.7, l.2).

Third, the paper by Jourdain and Legrand (2002) states that the summer sulfate to sodium ratio exceeds the seawater value due to biogenic sulfate, ornithogenic sulfate (DDU is famous for having many penguins) and heterogeneous uptake of SO2. Why wasn't a similar correction applied to summer sulfate?

In our study, $\Delta^{17}O(SO_4^{2-})$ measurement was performed only on the submicron (fine) particles, as sulfate in the supermicron (coarse) mode particles consists of more than 80% of $ss\text{-}SO_4^{2-}$, and will results in a large uncertainty in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ if this fraction was used. As discussed by Jourdain and Legrand (2002), the ornithogenic soil input affects mainly this supermicron (coarse) size particles. Thus, the penguin's emissions are not considered to impact our data. This is specifically mentioned in section 2.2.2 in the previous manuscript. However to better emphasize this, we have modified the order of sentences and separated the paragraph dealing with this (p.7, l.3-5).

Fourth, the winter chemical fractionation is believed to be due to the precipitation of mirabilite when seawater freezes, and is thus dependent on the location of sea ice relative to DDU. Have there been any changes in sea ice and sea surface temperatures around DDU over the last 15 years that would have influenced the fractionation?

Finally, if the correction is an empirical value taking into account sea ice, biogenic sulfate, penguin activity, heterogeneous chemistry and sea surface temperature, is the resulting value truly representative of just sea salt aerosol?

The *k* value of 0.13 ± 0.04 is derived from the examination of the $[SO_4^{2-}]/[Na^+]$ ratio of aerosol present in supermicron modes at DDU (Jourdain and Legrand, 2002) from May to October. Also for our dataset of the $[SO_4^{2-}]/[Na^+]$ ratio of submicron mode particle, we obtained k value of 0.13 by the same calculation with Jourdain and Legrand (2002). (Note that for this calculation, we removed data of 18/07/11 because of anomalously high sulfate loading as discussed in the manuscript, and data of 18/10/11 and 24/10/11 because they are included in the latter half of October.)

Thus indeed, this factor is completely empirical and probably average few processes. However, it was done by Jourdain and Legrand (2002) over two winters when the population of penguins has long ago vanished (there is still a Emperor colony but its number unit has no comparison with the 10 000 Adélie penguins present in summer), the station recovered its thick snow blanket and biogenic emissions completely ended. Furthermore, since a physical separation is necessary to generate depleted sulfate aerosols, the precipitation can only happen on the sea ice. In winter the temperature drop well below −8°C each year, and the sea-ice area is rather similar from one to another year. We have therefore assumed that the value of 0.13 is typical and can be applied for any year.

As discussed, the D17O(SO4–) anomaly results from a combination of four mechanisms. The D17O(NO3-) anomaly depends on D17O of NO2, and of the oxidation mechanism. The authors discuss that NO2 formed from NO + O3 will contain a terminal oxygen atom from ozone, and these carry the D17O anomaly, resulting in preferential transfer to the NO2. First, what is known about photolysis? It plays a role in the equilibrium between NO, NO2 and O3, but does it produce an isotope anomaly?

A study of the NO_2 photo-dissociation dynamic (Jost et al, 2005) has not been able to demonstrate the MIF nature of this photo-dissociation. Thus, NO_2 photolysis is believed to be a reaction without a detectable oxygen isotope anomaly, and the NO products preserve $\Delta^{17}O$ values of NO_2 from a statistical point of view.

Second, in Section 4.1.2 I would have appreciated an estimate of the D17O value in nitrate for each of the mechanisms discussed.

We added Table 1 to show both $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values for each reaction and added the reaction schemes of nitrate formation at section 4.1.2 (p.11, l.4-25). The $\Delta^{17}O(NO_3^-)$ values shown in Table 1 were estimated by Morin et al. (2011), using photochemical box model with photochemical steady state approximation. Since $\Delta^{17}O(SO_4^{2-})$ values are also summarized in Table 1, we also modified section 4.1.1 (p.10, l.11-28), $\Delta^{17}O$ values of sulfate, to avoid the repetition and the lack of information. Additionally, to make the explanation clearer, we summarized the principle of $\Delta^{17}O$ estimations in section 4.1 (p.10, l.2-9).

Third, would the authors estimate how much of NO3- is produced via NO2 + OH + M –> HNO3 + M, and how much by the dark reaction NO2 + O3 –> NO3, NO3 + RH –> HNO3.

We added one paragraph in section 4.2 (p.13, l.7-26) to mention about the relative contribution of oxidation pathways, estimated from observed $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values. For sulfate, the relative contribution of only $SO_3^{2-} + O_3$ oxidation can be calculated. For nitrate, the relative contribution of oxidation pathways can be estimated only for summer samples, because in winter, the main nitrate source is believed to result mainly from the deposition of polar stratospheric clouds (Santacesaria et al, 2001; Savarino et al, 2007), which is not representative of oxidation chemistry occurring in the boundary layer of DDU. Therefore, only for summer sample, the relative contribution of NO_2 + OH pathway was estimated. For further constraints on the relative contribution of other oxidation pathways, a coupled stratosphere/troposphere CTM will be necessary, which is clearly beyond the scope of this paper.

Consider adding reaction schemes or figures to describe the S(IV) –> S(VI) and N(IV) –> N(V) conversions and the propagation of ozone in these mechanisms.

We added Table 1 to describe $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values produced via each oxidation pathways.

Many mechanisms are discussed, but it would be useful to have a statistical link between the data shown in Figure 2 and other data, for example, the output of a chemical model or a transport model (back trajectories, sea surface/ice conditions, etc), or measurements of [O3] and so on. This would clearly show whether these measurements are a good proxy for the oxidation capacity. Many atmospheric measurements have been made at the DDU station, and it seems that it ought to be possible to look for statistical correlations between the data in Figure 2 and station measurements (ozone, sunlight, humidity, NOx, modeled radical concentrations, temperature, wind speed and direction) – this data would be the key to establishing what the D17O proxies means.

As shown in figure 4, we compared the $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values to $[O_3]$. We also found correlations between $\Delta^{17}O$ values and the time of air-mass under sunlight, which was calculated using back trajectory and daytime data, exhibiting the correlation coefficients of 0.51 and 0.65 for sulfate and nitrate, respectively. However, seasonal variation in [O_3] is known to be mainly controlled by its photochemical destruction, and indeed, sunlight data was correlated to [O_3] with R^2 value of 0.68. Therefore, we used the comparison with [O_3]. One sentence was added at the beginning of section 4.3 to describe the reason why ozone mixing ratio was used.

Although we compared the $\Delta^{17}O$ values with other parameters, such as temperature and humidity, we couldn't find better correlation than $\Delta^{17}O$ values vs. [O_3]. There is no annual observation neither model estimation of [OH] or [NO_X] (OPALE experiment, which included HOx, NOx and other reactive species quantifications was unfortunately conducted in 2010/2011, a year ahead of our time coverage), limiting us to compare our data to the other oxidant than O_3. As correctly pointed out by Referee #2, there is a need to use a chemistry/transport model to estimate $\Delta^{17}O$ values for further quantitative analyses. However, because of the unique chemical state depending on the transportation of oxidants and precursors from the plateau as well as surrounding ocean (Legrand et al., 2009, 2016), modeling of the DDU data is not an easy task and would certainly require a specific study. In this study, we provide the dataset to constrain the model, and demonstrate one of the assumption for estimates of $\Delta^{17}O$ values by modeling. We consider that this is one big step on the way for prognosticating the oxidation chemistry using $\Delta^{17}O$ values.

The authors conclude that the seasonal changes in D17O in sulfate and nitrate are not due to seasonal trends in D17O in ozone; presumably the trend is due rather to different relative contributions by ozone oxidation to the oxygen in the sulfate and nitrate.

It seems difficult to figure out where sulfate and nitrate come from (sea salt, many atmospheric chemistry mechanisms, transported by katabatic wind from the stratosphere or entrained upper troposphere or wind from the sea), and without the knowledge of how the material formed, how is it possible to determine the amount of ozone or OH that was present along the trajectory? And, if all that additional knowledge was necessary to determine the oxidation capacity along the path, this would seem to severely limit the power of this proxy. Ideally the DDU measurements would be an easy ideal test case to establish the proxy, a well studied site where all of the contributing factors can be qualtified. But, if the oxygen isotope anomaly cannot even be understood here, what hope

is there for these measurements at less well studied sites, and at times in the past when there is uncertainty about basic things like extent of sea ice, air flow patterns, atmospheric chemistry, etc.

As mentioned before we totally agree with the reviewer with his critic concerning the building of a new proxy from $\Delta^{17}O$ of sulfate and nitrate. It is still too early to for that. The main difficulty resides in the fact that the different oxidants (O_3, OH, XO) have very different chemical lifetimes among them and with respect to sulfate and nitrate, disconnecting the causal effect especially in winter. Moreover, the one-week integration of the aerosol collection does not help, neither. Therefore, measurement at one site is certainly not sufficient to establish any causal effect between $\Delta^{17}O$ and oxidant concentrations. More observations around the global are necessary. In the revised version, the idea of a proxy is now abandoned for the profit of more general concerns, which is the understanding of the $\Delta^{17}O$ build up. We think that a major result of our study is to show that the seasonal trend of $\Delta^{17}O$ sulfate and nitrate has nothing to do with the seasonal trend of $\Delta^{17}O$ ozone, which is a new and important result for the interpretation of the $\Delta^{17}O$ sulfate and nitrate. This result demonstrates that all the variability of $\Delta^{17}O$ of sulfate and nitrate is somehow embedded in the oxidation schemes of NO_X and SO_2. As a last thought, it may in fact be impossible to establish an oxidant proxy from $\Delta^{17}O$ of nitrate and sulfate because fundamentally sulfate and nitrate are antagonist with respect of the oxidation capacity of the atmosphere, there are too short lifetime to be integrators of a large part of the atmosphere but at the same time too long lifetime to transcribe the local oxidative state of the atmosphere.

Technical Comments:

2,3 it is not clear from the grammar if ’its’ refers to ’The reconstruction of changes in the past oxidative capacity’ or ’climate change’

2,4 assuming that past oxidative capacity is what is meant, then I don’t understand the inclusion of HCFCs in the list as these are a modern anthropogenic trace gas whose lifetime is only determined by the modern oxidative capacity, no comparison to preindustrial atmospheric chemistry can be made.

Since we modified our introduction, the indicated parts were removed.

2,18 please double check definition or ROx, which would seem to indicate organic odd oxygen species (organic oxy and peroxy radicals). Is it standard to include OH and H2O2?

As suggested by Referee #2, we changed the 'RO_X' into 'HO_X, RO_X, and H_2O_2' throughout the manuscript.

8,2 check 'summer,.as *has often been reported previously'

We corrected to 'summer, as has often been reported previously' (p.8, l.28-29).

14, 2-3 'complex photochemistry' 'strong oxidizing canopy' 'highly oxidative' in each case I am wondering what these modifiers mean. Complex, strong and highly relative to what? I think many locations could be found with a much higher oxidizing capacity than DDU, and also, with photochemistries more complex than at DDU.

We modified the sentence as follows to avoid ambiguous expression (p.16, l.16-18).

- 'complex photochemistry' → 'the enhanced HOx cycle'
- 'strong oxidizing canopy' → Deleted.
- 'highly oxidative' → 'compared to when air mass come from inland and ocean side. '

19, 33 Seinfeld and Pandis published the second edition of their book Atmospheric Chemistry and Physics in 2006 and the third edition in 2016. They did not publish any book with this title in 2012? Please specify edition and year.

We deeply thank to Referee#2 for careful reading. We checked the edition and published year, and corrected the reference list; Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics, 2nd edition, Wiley & Sons, New York, USA, 2006.

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