

**Author's comments in response to the anonymous referees for "Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastal Antarctica" by S. Ishino et al.**

We thank the referees for their careful reading and helpful comments. Followings are the referee's comments in blue and our response in black, followed by the revised manuscript. We hope our response and the revised manuscript fully answer the referee's questions and suggestions.

Please see also Supplement materials since we modified our data, tables and figures as follows.

- We added  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of sulfate as supplement data in response to the question by Referee #1. Also, data for the uncertainty of  $[\text{nss-SO}_4^{2-}]$  and  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  were corrected after recalculation of error propagation through the response to Referee #2.
- Table 1 was added as summary of oxidation reactions and corresponding  $\Delta^{17}\text{O}$  values of sulfate and nitrate, in response to suggestion by Referee #2.
- Figure 2 was replaced into corrected version using the corrected uncertainty for  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$ .

In addition to the changes suggested by referees, we have made the following relevant change of the revised manuscript.

- Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) changed into Institut des géosciences de l'environnement (IGE) from January 1st of this year. Therefore, we changed our affiliation (p.1, 1.8) and two applicable part (p.4, 1.26 and p.7, 1.8).
- The explanation of the back trajectory analysis using NOAA's HYSPLIT was corrected as we used Windows-based version, not the on-line version (p.8, 1.13-15).

## Author Response to Referee #1

We thank Referee #1 for the helpful comment. Please find our responses below.

**This is the first simultaneous measurements of concentration as well as triple oxygen isotope composition of atmospheric sulfate, nitrate, and ozone in an air-shed. I am impressed by the quality of the dataset, especially its capability in revealing the role of ozone/ROx ratio, HOX, and the sulfate or nitrate precursor chemistry as demonstrated by the authors.**

We deeply appreciate for careful review by Referee#1 and understanding on the significance of this study.

### **A couple of general comments:**

**1. It seems to me that the variation seen in the  $\Delta^{17}\text{O}$  of nitrate and sulfate are due more to changes in oxidation pathways and less to the oxidative capacity of the atmosphere. The use of “oxidative capacity” to me is less accurate or at least poorly defined. I think the current atmosphere has plenty of “oxidative capacity” and is unlikely running below some kind of oxidative threshold. It’s the oxidation pathway, being different for different species, that changes spatially and temporarily. And that “pathway” is what this study is going after.**

Thanks to the pointing out. We agree with Referee#1.  $\Delta^{17}\text{O}$  values of sulfate and nitrate reflect the relative contribution of various oxidation pathways involved in sulfate and nitrate formation rather than the proxies of the oxidative capacity. Therefore, we changed the word ‘the oxidative capacity’ to ‘the oxidation pathways of  $\text{SO}_2$  and  $\text{NO}_x$ ’ throughout the manuscript as suggested by Referee#1.

We also modified Introduction section, where explaining what do  $\Delta^{17}\text{O}$  values of sulfate and nitrate mean and how they will be connected to the reconstruction of the oxidative capacity. The relative contribution of the oxidation pathways depends on the relative abundance of each oxidant, and therefore offers the possibility to probe the past relative concentration of  $\text{O}_3$ , OH and other oxidants, which are the main oxidative agents of the atmosphere. This was also mentioned by the comment of Referee#2 in terms of the interest of this study. Taking into consideration this comment and the comment of the same subject by Referee#2, 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.

**2. A positive correlation between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for nss sulfate is expected. Thus, the  $\delta^{18}\text{O}$ -nss  $\text{SO}_4$  would be a line of independent evidence for the conclusions. However, the  $\delta^{18}\text{O}$  data is never mentioned, which needs some explanation.**

As discussed by Schauer et al. (2012), the  $\text{Ag}_2\text{SO}_4$  thermo-decomposition method is not reliable for the  $\delta^{18}\text{O}$  of sulfate due to the oxygen isotope exchange between the  $\text{O}_2$  products and the quartz reactor, while  $\Delta^{17}\text{O}$  of  $\text{O}_2$  can be corrected from this effect as the  $\Delta^{17}\text{O}$  values of quartz materials is assumed to be 0 ‰. But for  $\delta^{18}\text{O}$  values, such correction is not available due to the unknown of  $\delta^{18}\text{O}$  value of the quartz reactor and isotopic fractionation associated with this exchange. The explanation is now added in section 2.2.2 of the revised manuscript to explain the unreliable  $\delta^{18}\text{O}$  measurement. This is the main reason why we don't discuss the  $\delta^{18}\text{O}$  values of sulfate.

However, the  $\delta^{18}\text{O}$  data is provided in Supplementary materials on demand in case if someone wants to calculate the  $\Delta^{17}\text{O}$  value with another definition. Note that those  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values are relative to reference  $\text{O}_2$ , not calibrated relative to VSMOW. Based on this data, the plot of  $\Delta^{17}\text{O}$  as a function of  $\delta^{18}\text{O}$  does not show the positive correlation (slope: -0.03,  $R^2$ : 0.02), despite the clear seasonal variation in  $\delta^{18}\text{O}$  values with the summer minimum and winter maximum. This may result from the different controlling factors in  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ . Whereas  $\Delta^{17}\text{O}$  signature depends on the oxidant which provides one of four oxygen atoms of sulfate,  $\delta^{18}\text{O}$  is expected to mainly depend on the oxygen atoms of water which provides three oxygen atoms of sulfate through the equilibrium between  $\text{SO}_2$  and water, as examined by the laboratory experiment by Holt et al. (1983). This is out of the main subject of our discussion about oxidation chemistry in the atmosphere.

Therefore, because of the unreliability of the data, as well as the inconsistency of the subject, we don't discuss the  $\delta^{18}\text{O}$  values of sulfate.

**3. Some apparent observational discrepancies are presented in Introduction but a clearer working hypothesis would improve the presentation. In other words, a recommended**

**approach is to predict a potential seasonal pattern based on previous observational data and atmospheric chemistry models, and then go on to say that there are a couple of key parameters that we have not yet monitored in coastal Antarctica. In the end, parameters can only make sense when they are incorporated into a comprehensive atmospheric chemistry-transport model.**

We thank to Referee #1 for the helpful suggestion. Based on previous observations,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are expected to show the seasonal variations with summer minima and winter maxima, because the oxidation pathways should shift from  $\text{O}_3$  oxidation in winter to  $\text{HO}_x$  or  $\text{H}_2\text{O}_2$  oxidations in summer along with sunlight driven changes in the relative abundance of those photochemical oxidants. However, due to the lack of  $\Delta^{17}\text{O}(\text{O}_3)$  values at coastal Antarctica, the possibility had been remaining that the seasonal variations of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values at the site are influenced not only by the oxidation chemistry but also the variations in  $\Delta^{17}\text{O}(\text{O}_3)$  values. If the  $\Delta^{17}\text{O}(\text{O}_3)$  values are examined to have the flat value throughout the year, we can remove the possibility of the influence by  $\Delta^{17}\text{O}(\text{O}_3)$  values, and go on to the interpretation of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values in terms of the chemistry. This is the main working hypothesis of this study.

We agree to Referee#1 that estimates by atmospheric chemistry-transport model are necessary when we want to check if the present understanding on sulfur and nitrogen chemistry can explain the observation. However, the observational data is indispensable to constrain the models. Therefore, the second purpose of this study is to provide the reliable observational data for the future model analyses. Nevertheless, we observed the discrepancy between our data and the present understanding on the chemistry for sulfate production.

Along with the response to the first comment, we have re-written the Introduction to present clear working hypotheses and the purpose of this study, as suggested by Referee#1. Few sentences are also added in the Summary to emphasize the necessity of model analyses in the future.

**Specifics:**

**Abstract and the rest: I suggest when it's the first time mention "summer", add that it is the warm months or the austral summer.**

We modified the expressions as follows.

-- p.1, 1.21: ‘characterized by summer minima and winter maxima’ → ‘characterized by minima in the austral summer and maxima in winter’

-- p.3, 1.10: ‘showing an austral summer minimum and a winter maximum’

-- p.8, 1.26-27: ‘The [nss-SO<sub>4</sub><sup>2-</sup>] had a summer maximum of up to ~280 ng m<sup>-3</sup> from January to February,’ → ‘The [nss-SO<sub>4</sub><sup>2-</sup>] had a maximum of up to ~280 ng m<sup>-3</sup> from January to February, the months corresponding to the austral summer,’

**Page 3 line 1: “This” is ambiguous.**

**Page 3 line 12-13: The final sentence can be deleted.**

Since we changed a large part of our Introduction, those parts were all deleted.

**2.1.1.: Can you offer quantitative data instead of saying that “: : the atmosphere is highly oxidative”?**

We added the quantitative explanation to suggest how the atmosphere at DDU is oxidative at section 2.1.1., as suggested by Referee#1.

**Page 6 line 28: Cited reference “Bhattacharya et al 2008” is not found in the reference list.**

We thank to Referee#1 for careful reading. We added Bhattacharya et al. (2008) in the reference list (p.19, 1.5).

## **References**

Schauer, A. J., Kunasek, S. A., Sofen, E. D., Erbland, J., Savarino, J., Johnson, B. W., Amos, H. M., Shaheen, R., Abaunza, M., Jackson, T. L., Thiemens, M. H., and Alexander, B.: Oxygen isotope exchange with quartz during pyrolysis of silver sulfate and silver nitrate, Rapid Commun. Mass. Sp., 26, 2151–2157, 2012.

Holt, B. D., Cunningham, P. T., Engelkemeir, A. G., Graczyk, D. G., and Kumar, R.: Oxygen-18 study of

nonaqueous-phase oxidation of sulfur dioxide, *Atmos. Env.*, 17, 625-632, 1983.

## 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 O<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup> 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  $\Delta^{17}\text{O}$  tracer. By essence,  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$ , we can extract the OCA.  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  values of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{O}_3$  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 than each taken separately.

- 2- Demonstrating that the seasonality of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is a direct consequence of the oxidation scheme and not the seasonality of  $\Delta^{17}\text{O}(\text{O}_3)$  (This is the first time the seasonality of  $\Delta^{17}\text{O}(\text{O}_3)$  is confronted with  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$ . 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  $\Delta^{17}\text{O}$  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 NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> 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 O<sub>2</sub>, O<sub>3</sub>, OH, HO<sub>2</sub>, RO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O(1D), O(3P), NO<sub>3</sub>, 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 SO<sub>2</sub> 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 O<sub>3</sub>/RO<sub>x</sub> 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. [O<sub>3</sub>] 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<sub>3</sub> and Δ<sup>17</sup>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 Δ<sup>17</sup>O). However, DDU with strong seasonal contrasts and proximity with the ocean

source is an interesting place to study  $\Delta^{17}\text{O}$  with the goal to understand the different mechanisms at play. For instance, we show that  $\Delta^{17}\text{O}(\text{O}_3)$  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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  (i.e. the transfer of the  $\Delta^{17}\text{O}$  of ozone to other compounds) than directly producing an oxidation proxy for ice core. It should be bare in mind that the  $^{17}\text{O}$  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,  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  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, 1.30). It is due to the formation of the mirabilite, a  $\text{Na}_2\text{SO}_4$  crystal phase that precipitates at  $-8^\circ\text{C}$  and thus depleting the seawater in  $\text{SO}_4^{2-}$  relative to  $\text{Na}^+$ .

**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  $[\text{nss-SO}_4^{2-}]$  propagated from the uncertainty in concentration measurement by IC (i.e., 5%) and standard deviation ( $1\sigma$ ) of filter blank values, and  $k$  value ( $0.13 \pm 0.04$  in winter). The error propagated to  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  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  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values was also slightly changed, which is now applied to Figure 2. Also the explanation for the uncertainty analysis was modified (p.5, 1.7-12 and p.6, 1.31 - p.7, 1.2).

**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 SO<sub>2</sub>. Why wasn't a similar correction applied to summer sulfate?**

In our study,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  measurement was performed only on the submicron (fine) particles, as sulfate in the supermicron (coarse) mode particles consists of more than 80% of  $\text{ss-SO}_4^{2-}$ , and will result in a large uncertainty in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  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, 1.3-5).

**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  $0.13 \pm 0.04$  is derived from the examination of the  $[\text{SO}_4^{2-}]/[\text{Na}^+]$  ratio of aerosol present in supermicron modes at DDU (Jourdain and Legrand, 2002) from May to October. Also for our dataset of the  $[\text{SO}_4^{2-}]/[\text{Na}^+]$  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  $-8^{\circ}\text{C}$  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  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  anomaly results from a combination of four mechanisms. The  $\Delta^{17}\text{O}(\text{NO}_3^-)$  anomaly depends on  $\Delta^{17}\text{O}$  of  $\text{NO}_2$ , and of the oxidation mechanism. The authors discuss that  $\text{NO}_2$  formed from  $\text{NO} + \text{O}_3$  will contain a terminal oxygen atom from ozone, and these carry the  $\Delta^{17}\text{O}$  anomaly, resulting in preferential transfer to the  $\text{NO}_2$ . First, what is known about photolysis? It plays a role in the equilibrium between  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ , but does it produce an isotope anomaly?**

A study of the  $\text{NO}_2$  photo-dissociation dynamic (Jost et al, 2005) has not been able to demonstrate the MIF nature of this photo-dissociation. Thus,  $\text{NO}_2$  photolysis is believed to be a reaction without a detectable oxygen isotope anomaly, and the  $\text{NO}$  products preserve  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  from a statistical point of view.

**Second, in Section 4.1.2 I would have appreciated an estimate of the  $\Delta^{17}\text{O}$  value in nitrate for each of the mechanisms discussed.**

We added Table 1 to show both  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values for each reaction and added the reaction schemes of nitrate formation at section 4.1.2 (p.11, 1.4-25). The  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values shown in Table 1 were estimated by Morin et al. (2011), using photochemical box model with photochemical steady state approximation. Since  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values are also summarized in Table 1, we also modified section 4.1.1 (p.10, 1.11-28),  $\Delta^{17}\text{O}$  values of sulfate, to avoid the repetition and the lack of information. Additionally, to make the explanation clearer, we summarized the principle of  $\Delta^{17}\text{O}$  estimations in section 4.1 (p.10, 1.2-9).

**Third, would the authors estimate how much of NO<sub>3</sub><sup>-</sup> is produced via NO<sub>2</sub> + OH + M → HNO<sub>3</sub> + M, and how much by the dark reaction NO<sub>2</sub> + O<sub>3</sub> → NO<sub>3</sub>, NO<sub>3</sub> + RH → HNO<sub>3</sub>.**

We added one paragraph in section 4.2 (p.13, 1.7-26) to mention about the relative contribution of oxidation pathways, estimated from observed  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. For sulfate, the relative contribution of only  $\text{SO}_3^{2-} + \text{O}_3$  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<sub>2</sub> + 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  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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 [O<sub>3</sub>] 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, NO<sub>x</sub>, 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  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values to [O<sub>3</sub>]. We also found correlations between  $\Delta^{17}\text{O}$  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 qualified. 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  $\Delta^{17}\text{O}$  of sulfate and nitrate. It is still too early to for that. The main difficulty resides in the fact that the different oxidants ( $\text{O}_3$ ,  $\text{OH}$ ,  $\text{XO}$ ) 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  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}$  build up. We think that a major result of our study is to show that the seasonal trend of  $\Delta^{17}\text{O}$  sulfate and nitrate has nothing to do with the seasonal trend of  $\Delta^{17}\text{O}$  ozone, which is a new and important result for the interpretation of the  $\Delta^{17}\text{O}$  sulfate and nitrate. This result demonstrates that all the variability of  $\Delta^{17}\text{O}$  of sulfate and nitrate is somehow embedded in the oxidation schemes of  $\text{NO}_x$  and  $\text{SO}_2$ . As a last thought, it may in fact be impossible to establish an oxidant proxy from  $\Delta^{17}\text{O}$  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 of RO<sub>x</sub>, which would seem to indicate organic odd oxygen species (organic oxy and peroxy radicals). Is it standard to include OH and H<sub>2</sub>O<sub>2</sub>?**

As suggested by Referee #2, we changed the 'RO<sub>x</sub>' into 'HO<sub>x</sub>, RO<sub>x</sub>, and H<sub>2</sub>O<sub>2</sub>' 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 HO<sub>x</sub> 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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# Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastal Antarctica

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## Abstract

Triple oxygen isotopic compositions ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of atmospheric sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) in the atmosphere reflect the relative contribution of oxidation pathways involved in their formation processes, which potentially provides information to reveal missing reactions in atmospheric chemistry models. However, there remain many theoretical assumptions for the controlling factors of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values in those model estimation. To test one of those assumption that  $\Delta^{17}\text{O}$  values of ozone have a flat value and does not influence the seasonality of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values, we performed the first simultaneous measurement of  $\Delta^{17}\text{O}$  values of atmospheric sulfate, nitrate, and ozone collected at Dumont d'Urville station (66°40'S, 140°01'E) throughout 2011.  $\Delta^{17}\text{O}$  values of sulfate and nitrate exhibited seasonal variation characterized by minima in the austral summer and maxima in winter, within the ranges of 0.9–3.4 ‰ and 23.0–41.9 ‰, respectively. In contrast,  $\Delta^{17}\text{O}$  values of ozone showed no significant seasonal variation, with values of  $26 \pm 1$  ‰ throughout the year. These contrasting seasonal trends suggest that seasonality in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are not the result of changes in  $\Delta^{17}\text{O}(\text{O}_3)$  but the changes in oxidation chemistry. The summer/winter trends for  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are caused by sunlight-driven changes in the relative contribution of  $\text{O}_3$  oxidation to the oxidation by  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$ . In addition to that general trend, by comparing  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values to ozone mixing ratios, we found  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values observed in spring (September to November) were lower than in fall (March to May), while there is no significant spring/fall difference in  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. The relatively lower sensitivity of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values to the ozone mixing ratio in spring compared to fall is possibly explained by (i) increased contribution of  $\text{SO}_2$  oxidations by OH and  $\text{H}_2\text{O}_2$  caused by  $\text{NO}_x$  emission from snowpack and/or (ii)  $\text{SO}_2$  oxidation by hypohalous acids ( $\text{HOX} = \text{HOCl} + \text{HOBr}$ ) in the aqueous phase.

Sakiko ISHINO 15/2/2017 14:56

削除: Bruno Jourdain, Susanne

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削除: Laboratoire de Glaciologie et Géophysique de l'Environnement, 38000 Grenoble, France

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Sakiko ISHINO 12/1/2017 17:45

削除: Reconstruction of the oxidative capacity of the atmosphere is of great importance to understanding climate change, because of its key role in determining the life times of trace gas

## 1 Introduction

Triple oxygen isotopic compositions ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of atmospheric sulfate and nitrate have shown potential to probe the relative importance of various oxidation pathways involved in their formations (e.g., Michalski et al., 2003; Lee and Thiemens, 2001). Atmospheric ozone ( $\text{O}_3$ ) possesses high  $\Delta^{17}\text{O}$  values of approximately 26 ‰ (Krankowsky et al., 1995; Johnston and Thiemens, 1997; Vicars et al., 2012, 2014), contrary to most of the oxygen bearing compounds such as  $\text{O}_2$  and  $\text{H}_2\text{O}$ , which have  $\Delta^{17}\text{O}$  values of approximately 0 ‰ (Barkan and Luz, 2003, 2005). Oxygen atoms of  $\text{O}_3$  are directly or indirectly transferred to sulfate and nitrate through various oxidation pathways of their precursors,  $\text{SO}_2$  and  $\text{NO}_x$  ( $= \text{NO} + \text{NO}_2$ ), respectively. Therefore,  $\text{O}_3$  oxidation produces sulfate and nitrate possessing high  $\Delta^{17}\text{O}$  values, whereas oxidation by OH,  $\text{RO}_2$  and  $\text{H}_2\text{O}_2$  produces sulfate and nitrate with low  $\Delta^{17}\text{O}$  values. In general, the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values can be prognosticated using the given  $\Delta^{17}\text{O}(\text{SO}_2)$  and  $\Delta^{17}\text{O}(\text{NO}_2)$  values for each reaction pathways and the estimates of relative contribution of each oxidation pathways by atmospheric chemistry/transport models (e.g., Alexander et al., 2009; Morin et al., 2011; Sofen et al., 2011). Considering the higher  $\text{HO}_x$  levels in summer due to enhanced photochemical activity relative to winter,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are expected to show the specific seasonal trend with summer minima and winter maxima in the mid to high latitude regions. By comparing those expected values to observations, missing processes for sulfate and nitrate formation in the models have been proposed. For example, McCabe et al. (2006) performed an year-round observation of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values at Alert, Canada, showing lower  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values during winter compared to the calculated values using a model of Feitcher et al. (1996); they suggest a twofold overestimate of  $\text{O}_3$  oxidation in sulfate formation during winter in the Northern hemisphere, and pointed out 10-18% contribution of metal catalyzed  $\text{O}_2$  oxidation in aqueous phase. An observation of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values in Alert by Morin et al. (2008) revealed significantly higher values during spring compared to the calculated values, which is expected to be a result of  $\text{NO}_2$  oxidation by BrO. Savarino et al. (2013) also had shown significantly higher  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values at the marine boundary layer compared to an estimate of chemical transport model by Alexander et al. (2009), while the mismatch was fixed by considering a contribution of BrO in nitrate formation. The  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are thus used to examine the lack of oxidation schemes in the models. However, the observational data of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  to constrain these models are still not enough to demonstrate theoretical assumptions of the controlling factors of  $\Delta^{17}\text{O}$  signatures in these model estimation (e.g., Morin et al., 2011).

One of the important parameters which have to be confirmed by observations is  $\Delta^{17}\text{O}$  value of ozone, because of the possibility that  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are influenced not only by changes in oxidation chemistry but also variations in  $\Delta^{17}\text{O}(\text{O}_3)$  values. Indeed, various  $\Delta^{17}\text{O}(\text{O}_3)$  values ranging 25-35 ‰ are used for model calculations to reproduce the observed variations in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values (Alexander et al., 2009; Morin et al., 2011; Sofen et al., 2011). Those varied  $\Delta^{17}\text{O}(\text{O}_3)$  values were assumed based on the observations using the cryogenic collection method (Johnston and Thiemens, 1997; Krankowsky et al., 1995), which showed highly varied values of 6-54 ‰. However, the

Sakiko ISHINO 12/1/2017 17:57

削除: The reconstruction of changes in the past oxidative capacity of the atmosphere over preindustrial–industrial and glacial–interglacial scales is of great importance for understanding climate change because of its key role in determining the lifetimes of trace gases, such as  $\text{CH}_4$ , CO and hydrochlorofluorocarbons (Alexander and Mickley, 2015; Wang and Jacob, 1998). In early studies, attempts to reconstruct the past oxidative capacity were based on  $\text{H}_2\text{O}_2$  and HCHO in polar ice cores (Neftel et al., 1984; Staffelbach et al., 1991). However, it was found that these two chemical species are not irreversibly trapped in snow and some evaporation and/or decomposition occur after their deposition in surface snow (Hutterli et al., 2001). Thus, the interpretation of past atmospheric concentrations from ice records was not as straightforward as originally thought.

Sakiko ISHINO 19/1/2017 21:33

削除: as stable proxies of

Sakiko ISHINO 3/12/2016 10:53

削除: the oxidative capacity of the atmosphere, because they indicate

Sakiko ISHINO 4/12/2016 19:20

削除: past

Sakiko ISHINO 20/1/2017 11:21

削除: Erbland et al., 2013; Frey et al., 2009;

Sakiko ISHINO 19/1/2017 22:35

削除: Kunasek et al., 2010; Sofen et al., 2014

Sakiko ISHINO 7/12/2016 06:19

削除: Atmospheric sulfate and nitrate are produced from  $\text{SO}_2$  and  $\text{NO}_x$  ( $= \text{NO} + \text{NO}_2$ ), respectively, and are the ultimate products of the sulfur and nitrogen cycles as results of oxidation reactions by various oxidants such as OH radicals,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{RO}_2$  and/or halogen oxides (Seinfeld and Pandis, 2012). In general,

Sakiko ISHINO 7/12/2016 07:21

削除: since  $\text{O}_3$  has high  $\Delta^{17}\text{O}$  values approximately 26 ‰ (Vicars et al., 2012, 2014),

Sakiko ISHINO 4/12/2016 17:16

削除:  $\text{RO}_x$  species such as

5 recent observations of  $\Delta^{17}\text{O}(\text{O}_3)$  values using the nitrite-coated filter method, which was developed by Vicars et al. (2012), and applied at Grenoble, R/V Polarstern Campaign (Vicars et al., 2014) and Dome C (Savarino et al., 2016), had shown the insignificant spatial and temporal variability with values ranging 23-27 ‰. This result suggests that the variations observed in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are not the result of changes in  $\Delta^{17}\text{O}(\text{O}_3)$  values, but mainly explained by the changes in oxidation pathways. To test this hypothesis, it is necessary to investigate the spatial and temporal variability of  $\Delta^{17}\text{O}(\text{O}_3)$  values, which is expected to have the stable value, simultaneously with variations in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. Antarctica is a suitable site to test this hypothesis, because of the clear seasonality in solar radiation, which is one of the main factors influencing  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values through the changes in photochemical oxidants variations. In fact, several studies have been reported the clear seasonal variations in  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values at coastal and inland Antarctica, Dumont d'Urville and Dome C, showing an austral summer minimum and a winter maximum (Erbland et al., 2013; Frey et al., 2009; Savarino et al., 2007). This trend is mainly explained by increased  $\text{NO}_x$  oxidation by OH and  $\text{RO}_2$  under solar radiation in summer, relative to winter when  $\text{NO}_x$  oxidation is dominated by the reaction transferring the oxygen atoms from  $\text{O}_3$  to nitrate in dark polar winter, when assuming the values are mainly controlled by oxidation chemistry. The similar trend following solar cycle is expected for  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values, which is mainly controlled by the relative importance of  $\text{SO}_2$  oxidation by OH,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ . The first attempt of the monthly scale observation of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values at Dome C showed the increasing trend from January to June (summer to winter) and decreasing trend from October to next January (spring to summer), despite the unexpected decline during mid-winter, July-August (Hill-Falkenthal et al., 2013). Nevertheless, the variability of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value throughout the year is larger than those which have ever been observed on the earth (Lee and Thiemens, 2001; Li et al., 2013; McCabe et al., 2006). It is thus ideal to examine if at Antarctica, the  $\Delta^{17}\text{O}(\text{O}_3)$  values show a flat value throughout a year in contrast to those seasonal variability in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values, for demonstrating that the seasonality of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values is a direct consequence of changes in chemistry and not the variation in  $\Delta^{17}\text{O}(\text{O}_3)$  values.

10 In this study, we present the first simultaneous observations of  $\Delta^{17}\text{O}$  values of sulfate, nitrate and ozone at the coastal Antarctic site, Dumont d'Urville Station (DDU) throughout 2011, to answer the key question about the controlling factors of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values as well as to provide a set of data that can be used to constrain chemistry/transport model scheme in the future study. The series of oxidants observations such as  $\text{O}_3$  (Legrand et al., 2009, 2016a),  $\text{HO}_x$  (Kukui et al., 2012, 2014) and  $\text{NO}_x$  (Grilli et al., 2013) have demonstrated that due to the katabatic winds, air masses on the East Antarctic Plateau enriched in oxidants produced via reactive nitrogen emission from surface snow and subsequent interactive reactions between  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{RO}_2$ , are frequently exported to DDU. They also suggested the influence of bromine chemistry is much less significant in East Antarctica compared to West coastal site such as Halley and Neumayer. However, besides the framework of that project, model-aided analyses of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  observations by Chen et al. (2016) pointed the significant contribution (33-50%) of  $\text{SO}_2$  oxidation by hypohalous acids on total sulfate production in remote marine boundary layer including Southern Ocean, indicating the possibility of its influence in coastal Antarctic site. Hence, we

Sakiko ISHINO 6/12/2016 21:31

削除: since  $\text{RO}_x$  have  $\Delta^{17}\text{O}$  values of approximately 0 ‰ (Morin et al., 2011).

Sakiko ISHINO 7/12/2016 08:32

削除: Thus, the  $\Delta^{17}\text{O}$  values of both species trapped in ice cores reflect the past regional oxidation chemistry involved in sulfur and nitrogen cycles, and can provide insight into past oxidant variations (e.g., Alexander et al., 2004; Kunasek et al., 2010; Sofen et al., 2014).

Sakiko ISHINO 15/2/2017 15:46

削除: These measurements were conducted within the framework of the Oxidant Production over Antarctic Land and its Export project (OPALE; Preunkert et al., 2012), which enabled us to combine the isotopic measurements of sulfate and nitrate with various meteorological and other oxidant observations.

Sakiko ISHINO 14/12/2016 12:49

削除: The primary purpose of this study was to examine the relationship between  $\Delta^{17}\text{O}$  values of sulfate and nitrate to determine their complex chemistry in the Antarctic atmosphere.

secondary aimed to reveal any features of oxidation mechanisms of their precursors based on seasonality of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values at this specific site.

## 2 Samples and analytical methods

### 5 2.1 Sampling site and aerosol sample collection

#### 2.1.1 Sampling site

Samples were collected at DDU (66°40'S, 140°01'E; 40 m above the sea level), located on a small island, 1 km off the coast of Antarctica. The climate of DDU is described in König-Langlo et al. (1998). Compared with other parts of Antarctica, DDU is temperate, with temperatures ranging from -30 to 5°C throughout the year. Most parts of the island are free of snow, and the sea ice disappears completely during summer. Recent observations of surface ozone and the OH radical (Legrand et al., 2016a; Kukui et al., 2012) revealed that at DDU,  $\text{O}_3$  and OH levels are approximately 2 and 10 times higher, respectively, compared to the Palmer station (Jefferson et al., 1998), due to the transportation of air masses influenced by the snowpack emission of reactive nitrogen species on the East Antarctic Plateau and the subsequent oxidants productions.

#### 2.1.2 Aerosol sample collection

Aerosol samples were collected using a high-volume air sampler (HVAS; General Metal Works GL 2000H Hi Vol TSP; Tisch Environmental, Cleves, OH, USA). Coarse ( $> 1 \mu\text{m}$ ) and fine ( $< 1 \mu\text{m}$ ) particles were collected separately, using a four-stage cascade impactor and a backup glass fiber filter, respectively. The slotted 12.7 cm  $\times$  17.8 cm glass fiber filters were mounted on the cascade impactor, while 20.3 cm  $\times$  25.4 cm glass fiber filters were used for backup. The HVAS was placed on a platform, 1 m above ground, 50 m from the coast, and 20 m away from the closest building. Aerosol collection was carried out at weekly intervals, with flow rates of  $\sim 1.5 \text{ m}^3/\text{min}$ , yielding an average pumped air volume of 15000  $\text{m}^3$  per sample. Samples collected between January 2011 and January 2012 were used for this study. Once per month, a field blank was checked by mounting filters onto the filter holder, and running the cascade impactor for 1 min.

After each collection period, the filters were removed from the cascade impactor inside a clean chemical hood; they were wrapped in aluminum foil and stored in plastic bags at -20°C. The four filters on the impactor stage were grouped together as "coarse" particle samples, while the backup filters were kept as "fine" particle samples. Samples were transported back to University Grenoble Alpes (France) for chemical and isotopic analyses, while frozen.

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### 2.1.3 Quantification of ionic species

The soluble compounds in the aerosols were extracted with ultra-pure water (Millipore filter, 18 MΩcm; EMD Millipore, MA, USA), according to the process described in Savarino et al. (2007); more than 98% of the initial water volume was recovered. Field blank filters were processed in the same way.

- 5 Small aliquots of these sample solutions were taken for quantification of ionic species. Anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and sodium ( $\text{Na}^+$ ) concentrations were analyzed using ion chromatography systems described in Savarino et al. (2007) and Jourdain and Legrand (2002), respectively.

10 Atmospheric concentrations of these ionic species were calculated using the aerosol loading for each filter, the mean filter blank values, and the air volume pumped through the filter. The air volume was corrected to standard temperature and pressure ( $T = 273.15 \text{ K}$ ,  $p = 101325 \text{ Pa}$ ) based on meteorological data from DDU provided by Meteo France. The uncertainties for atmospheric concentrations were calculated by propagating the typical uncertainty of the ion chromatography analysis (5%) and standard deviation ( $1\sigma$ ) of filter blank values.

## 2.2 Oxygen isotopic analyses of sulfate and nitrate in aerosols

### 2.2.1 Definition of triple oxygen isotopic compositions

- 15 Given the two isotope ratios, notated as  $^{17}R$  ( $= ^{17}\text{O}/^{16}\text{O}$ ) and  $^{18}R$  ( $= ^{18}\text{O}/^{16}\text{O}$ ), stable oxygen isotope ratios are conventionally scaled using a delta ( $\delta$ ) notation:

$$\delta^x\text{O} = \frac{x_{R_{\text{sample}}}}{x_{R_{\text{VSMOW}}}} - 1 \quad (1)$$

20 where  $R_{\text{VSMOW}}$  denotes the isotope ratio of the standard material, Vienna Standard Mean Ocean Water (VSMOW); and  $x$  is 17 or 18. Despite the robust relationship of the mass-dependent law ( $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ ) in most of the oxygen-containing species, (e.g.,  $\text{O}_2$  and  $\text{H}_2\text{O}$ ), atmospheric ozone does not follow mass-dependent fractionation and possesses a significant positive  $\Delta^{17}\text{O}$  ( $= \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ), inherited from mass-independent fractionation associated with its formation process (Gao and Marcus, 2001). Since non-zero  $\Delta^{17}\text{O}$  values can be observed in various atmospheric species bearing oxygen atoms inherited from  $\text{O}_3$  (e.g., sulfate and nitrate), the  $\Delta^{17}\text{O}$  signature is a powerful tracer, used to investigate the relative contribution of  $\text{O}_3$  to oxidation processes.

- 25 **2.2.2 Oxygen isotopic analysis of sulfate and data correction**

All  $\Delta^{17}\text{O}$  values of sulfate were measured with an isotope ratio mass spectrometer (IRMS) (MAT253; Thermo Fisher Scientific, Bremen, Germany), coupled with an in-house measurement system at Tokyo Institute of Technology. The measurement system for  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  follows Savarino et al. (2001), with modifications described in several studies

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(Schauer et al., 2012; Geng et al., 2013). Briefly, 1  $\mu\text{mol}$  of sulfate is separated from other ions using ion chromatography and chemically converted to silver sulfate ( $\text{Ag}_2\text{SO}_4$ ). This  $\text{Ag}_2\text{SO}_4$  powder is transported in a custom-made quartz cup, which is dropped into a furnace at  $1000^\circ\text{C}$  within a high temperature conversion elemental analyzer (TC/EA; Thermo Fisher Scientific, Bremen, Germany) and thermally decomposed into  $\text{O}_2$  and  $\text{SO}_2$ . Gas products from this sample pyrolysis are carried by ultrahigh-purity He ( $>99.99995\%$  purity; Japan Air Gases Co., Tokyo, Japan), which is first purified using a molecular sieve ( $5\text{\AA}$ ) held at  $-196^\circ\text{C}$  (Hattori et al., 2015). The gas products  $\text{O}_2$  and  $\text{SO}_2$  are carried through a cleanup trap (trap 1) held at  $-196^\circ\text{C}$  to trap  $\text{SO}_2$  and trace  $\text{SO}_3$ , while  $\text{O}_2$  continues to another molecular sieve ( $5\text{\AA}$ ) in a 1/16 inch o. d. tubing trap (trap 2) held at  $-196^\circ\text{C}$  to trap  $\text{O}_2$  separately from the other gas products. The  $\text{O}_2$  is purified using a gas chromatograph, with a CP-Molsieve ( $5\text{\AA}$ ) column (0.32 mm i.d., 30 m length,  $10\ \mu\text{m}$  film; Agilent Technologies Inc., Santa Clara, CA, USA) held at  $40^\circ\text{C}$ , before being introduced to the IRMS system to measure  $m/z = 32, 33,$  and  $34$ . The inter-laboratory calibrated standards (Sulf- $\alpha, \beta$  and  $\epsilon$ ; Schauer et al., 2012) were used to assess the accuracy of our measurements; our values were in good agreement with published ones (Fig. 1). As discussed by Schauer et al. (2012), this method results in the oxygen isotope exchange between the  $\text{O}_2$  products and the quartz cups as well as the quartz reactor, which shifts  $\delta^{17}\text{O}, \delta^{18}\text{O}$ , and thus  $\Delta^{17}\text{O}$  measurements. The shift in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value is corrected by estimating the magnitude of the oxygen isotope exchange with quartz materials, whose  $\Delta^{17}\text{O}$  value is assumed to be approximately  $0\ \text{‰}$  (Matsuhisa et al., 1978). The intercept of  $-0.03$  in Fig. 1 also supports this assumption. Since  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of each quartz materials used in this study are not known, the corrected  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$  shown in Supplementary materials are unreliable, and therefore we don't discuss these values. Note that those  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$  are relative values to our  $\text{O}_2$  reference gas. The precision of  $\Delta^{17}\text{O}$  is typically better than  $\pm 0.2\ \text{‰}$  based on replicate analyses of the standards.

Since sea salt sulfate aerosols ( $\text{ss-SO}_4^{2-}$ ) are of little importance to atmospheric sulfur oxidation processes (i.e.,  $\Delta^{17}\text{O}(\text{ss-SO}_4^{2-}) = 0\ \text{‰}$ ), both total sulfate concentrations and  $\Delta^{17}\text{O}$  values were corrected for their  $\text{ss-SO}_4^{2-}$  component to obtain their non-sea salt sulfate ( $\text{nss-SO}_4^{2-}$ ) content, using Eq. (2) and (3) below.

$$[\text{nss} - \text{SO}_4^{2-}] = [\text{total} - \text{SO}_4^{2-}] - k \times [\text{Na}^+] \quad (2)$$

$$\Delta^{17}\text{O}(\text{nss} - \text{SO}_4^{2-}) = \frac{[\text{total} - \text{SO}_4^{2-}]}{[\text{nss} - \text{SO}_4^{2-}]} \times \Delta^{17}\text{O}(\text{total} - \text{SO}_4^{2-}) \quad (3)$$

where “total” is the quantity measured by ion chromatography, corresponding to the sum of  $\text{ss-}$  and  $\text{nss-SO}_4^{2-}$  components; and  $k$  is the mass ratio of  $[\text{SO}_4^{2-}]/[\text{Na}^+]$  in sea water (0.25; Holland et al., 1986). To take into account sea salt chemical fractionation processes that affect the Antarctic region in winter, when temperatures drop below  $-8^\circ\text{C}$  in the presence of sea ice (Wagenbach et al., 1998), we used a  $k$  value of  $0.13 \pm 0.04$ , estimated from the average at winter DDU previously by Jourdain and Legrand (2002) as well as confirmed by our own dataset; this was applied to samples collected from May to October. Note that the sea salt fractionation is a chemical fractionation and is different from an isotopic fractionation. Eq. (3) is the isotope mass balance equation between  $\text{ss-}$  and  $\text{nss-SO}_4^{2-}$ , with  $\Delta^{17}\text{O}(\text{ss-SO}_4^{2-}) = 0\ \text{‰}$ . The total uncertainties for  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values were calculated using the precision of  $\Delta^{17}\text{O}$  measurement and the uncertainty of  $k$  value, resulting in

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the uncertainty of  $\pm 1.9\%$  at maximum. The propagated error for both  $[\text{nss-SO}_4^{2-}]$  and  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values are shown in Supplementary material.

The measurement of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value were performed only for the fine mode samples, because sulfate in the coarse mode samples consists of more than 80% ss-SO<sub>4</sub><sup>2-</sup>. The influence of prnithogenic soil emission on Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> concentration was not taken into account, since it mainly affects supermicron (coarse) aerosols (Jourdain and Legrand, 2002).

### 2.2.3 Oxygen isotopic analysis of nitrate

The  $\Delta^{17}\text{O}$  value of nitrate was measured simultaneously with  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values using a bacterial denitrifier method (Casciotti et al., 2002), coupled with IRMS measurement using our in-house peripheral system at University Grenoble Alpes (Morin et al., 2009). All nitrates in our samples were converted to N<sub>2</sub>O via bacterial denitrification. This N<sub>2</sub>O was introduced to the measurement system, separated from CO<sub>2</sub>, H<sub>2</sub>O and other volatile organic compounds, and pre-concentrated in a cold trap. The trapped N<sub>2</sub>O was converted into O<sub>2</sub> and N<sub>2</sub> by pyrolysis at 900°C, using a gold tube furnace, followed by separation of O<sub>2</sub> and N<sub>2</sub> via a 10 m Molsieve (5Å) gas chromatography column, before being introduced to the IRMS system. Measurements were performed simultaneously for samples equivalent to 100 nmol nitrate, as well as a subset of international nitrate reference materials (US Geological Survey 32, 34, and 35, as well as their mixtures) for correction and calibration of  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values relative to VSMOW and  $\delta^{15}\text{N}$  values relative to air N<sub>2</sub>. Analytical uncertainty was estimated based on the standard deviation of the residuals from a linear regression between the measured reference materials and their expected values. The uncertainties ( $1\sigma$ ) for  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\delta^{15}\text{N}(\text{NO}_3^-)$  were 0.4 ‰ and 0.3 ‰, respectively.

### 2.3 Sampling and analytical methods of oxygen isotopic composition of ozone

The sampling and isotopic analysis of surface ozone were performed by coupling the nitrite-coated filter method with nitrate isotopic measurements described in Vicars et al. (2012, 2014). The principle of ozone collection underlying this technique is the filter-based chemical trapping of ozone via its reaction with nitrite:



During R1, one of the three oxygen atoms of nitrate is transferred from one of the two terminal oxygen atoms of ozone, while the other two oxygen atoms are derived from the reagent nitrite. Since the  $\Delta^{17}\text{O}$  signature of ozone is located only on the terminal atoms of ozone (Bhattacharya et al., 2008; Janssen and Tuzson, 2006), simple mass balance implies that  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$  is 2/3 of  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ . Thus,  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$  values can be inferred using the simple mass-balance of Eq. (4):

$$\Delta^{17}\text{O}(\text{O}_3)_{\text{term}} = 3 \times \Delta^{17}\text{O}(\text{NO}_3^-) - 2 \times \Delta^{17}\text{O}(\text{NaNO}_2), \quad (4)$$

where  $\Delta^{17}\text{O}(\text{NaNO}_2)$  of the reagent is confirmed to be zero (Vicars et al., 2012). Therefore, the  $\Delta^{17}\text{O}$  value of ozone can be determined from the oxygen isotopic composition of nitrate produced on the coated filter via R1, determined by the same measurement system described above.

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上へ移動 [1]: Eq. (3) is the isotope mass balance equation between ss- and nss-SO<sub>4</sub><sup>2-</sup>, with  $\Delta^{17}\text{O}(\text{ss-SO}_4^{2-}) = 0\%$ .

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上へ移動 [2]: The total uncertainties for  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values were calculated using the precision of  $\Delta^{17}\text{O}$  measurement and the uncertainty of  $k$  value.

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Ozone sampling was carried out by pumping ambient air, using a low-volume vacuum pump (Model 2522C-02; Welch, IL, USA), through a glass fiber filter ( $\emptyset$  47 mm, GF/A type; Whatman, UK), pre-coated with a mixture of  $\text{NaNO}_2$ ,  $\text{K}_2\text{CO}_3$  and glycerol. Sampling was conducted once per week from May 2011 to April 2012, with 24–48 h sampling intervals. After sampling, filter samples and procedural blanks were extracted in  $18\text{M}\Omega$  water. Any unreacted nitrite reagent was removed using the reaction with sulfamic acid, neutralized later with NaOH solutions (Granger and Sigman, 2009; Vicars et al., 2012). The sample solutions were stored in the dark at  $-20^\circ\text{C}$ , and transported back to Grenoble. After nitrate concentration analysis using a colorimetric technique (Frey et al., 2009), the isotopic analysis of nitrate (i.e., ozone) was performed using the same protocol as the nitrate isotope analysis. In addition to the isotope measurements of ozone, we aligned the mixing ratio of surface ozone to the weekly average using data reported in Legrand et al. (2016a) to fit the time resolution of our aerosol sampling.

## 2.4 Complementary analyses

To investigate relationships between the origins of the air masses and the  $\Delta^{17}\text{O}$  signatures of sulfate and nitrate, transport pathways of sampled air masses were analyzed using the NOAA's HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (Stein et al., 2015). The model was used with NCEP-NCAR reanalysis data fields using a regular  $2.5^\circ \times 2.5^\circ$  longitude-latitude grid. Five-day backward trajectories for air masses arriving at the DDU at an altitude of 40 m above sea level were computed twice per day for each day during sampling periods.

The sea ice area fraction around the Antarctic continent was derived from the Advanced Microwave Scanning Radiometer on-board NASA's Earth Observing System Aqua satellite using the ARTIST sea ice algorithm (Kaleschke et al., 2001). The contact times of these air masses with the Antarctic continent and sea ice were calculated using five-day backward trajectories and sea ice area fractions.

## 3 Results

### 3.1 Sulfate

Seasonal variations in atmospheric concentrations and  $\Delta^{17}\text{O}$  values of  $\text{SO}_4^{2-}$  are shown in Fig. 2a. Atmospheric concentrations of  $\text{nss-SO}_4^{2-}$  showed a clear seasonal trend. The  $[\text{nss-SO}_4^{2-}]$  had a maximum of up to  $\sim 280 \text{ ng m}^{-3}$  from January to February, corresponding to the austral summer period, but decreased to a background level ( $\sim 10 \text{ ng m}^{-3}$ ) during May to August, winter period, before increasing as summer returned. This trend in  $[\text{nss-SO}_4^{2-}]$  at coastal Antarctic sites results from enhanced marine biogenic activity, emitting dimethyl sulfide (DMS) in circum-Antarctic regions in summer, as has often been reported previously (e.g., Wagenbach et al., 1998; Minikin et al., 1998; Jourdain and Legrand, 2002;

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Preunkert et al., 2008). As Antarctica is surrounded by ocean, DMS is the major source of atmospheric non-sea salt sulfur (Minikin et al., 1998; Jourdain and Legrand, 2002). Interestingly, a sample from 18–25 July had an anomalously high value of  $46 \text{ ng m}^{-3}$ , four times the monthly mean level for July ( $\sim 12 \text{ ng m}^{-3}$ ).

5 The  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values showed the reverse trend, with a summer minimum and a winter maximum. The  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  value increased from 1.0 ‰ observed in January to a maximum of 3.4 ‰ at the end of June, decreasing to 0.9 ‰ in December. The annual weighted mean value of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  was  $1.4 \pm 0.1$  ‰. Higher values (greater than 2 ‰) were generally observed during April to July, but the anomalous peak from 18–25 July was characterized by a low  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  value of 0.9 ‰. Consequently, the monthly mean value had a maximum in July ( $2.6 \pm 0.6$  ‰), when the 18–25 July data were excluded.

### 10 3.2 Nitrate

Seasonal variations in atmospheric concentrations and  $\Delta^{17}\text{O}$  values for nitrate are shown in Fig. 2b. Nitrate concentrations increased to  $55 \text{ ng m}^{-3}$  in January but gradually decreased to less than  $10 \text{ ng m}^{-3}$  in March to May. In July, a significant peak of  $28 \text{ ng m}^{-3}$  was observed, followed by a seasonal increase as summer returned. The  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values showed a simple seasonal variation, with a summer minimum and a winter maximum.  $\Delta^{17}\text{O}(\text{NO}_3^-)$  increased from 27 ‰ in January to over 15 40 ‰ in July, decreasing moderately to a minimum value of 23 ‰ in December. These trends in nitrate concentrations and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are consistent with those observed at this site 10 years ago (Savarino et al., 2007).

### 3.3 Ozone

Daily averaged ozone mixing ratios are presented in Fig. 2c; these exhibit a distinct seasonal variation, with a summer minimum and a winter maximum. The minimum ozone mixing ratio was observed in January, having a value lower than 10 ppbv, while the maximum was observed during July to August, having a value higher than 35 ppbv. From November to December, sudden increases in ozone levels to values over 30 ppbv were observed a few times, consistent with seasonal trends for ozone at DDU (Legrand et al., 2009). The  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values showed an insignificant variation, with a summer maximum of 28 ‰ and a winter minimum of 23 ‰, and an annual mean  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  value of  $26 \pm 1$  ‰.

## 4 Discussion

### 4.1 $\Delta^{17}\text{O}$ values and atmospheric formation pathways of sulfate and nitrate

Atmospheric sulfate and nitrate are produced from the oxidation of their precursor,  $\text{SO}_2$  and  $\text{NO}_x$ , by various oxidants. Therefore,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values for sulfate and nitrate produced via each oxidation pathways are determined by the  $\Delta^{17}\text{O}$  values of their precursors and the  $\Delta^{17}\text{O}$  values of oxidants, which provides oxygen atom to the products in different transferring factors. To interpret the our data, we estimated the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values produced via each oxidation pathways. The  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values for the oxidation by  $\text{O}_3$  were estimated using the mean  $\Delta^{17}\text{O}(\text{O}_3)$  value (i.e., 26 ‰) observed in this study. Each oxidation pathways and corresponding  $\Delta^{17}\text{O}$  values of products sulfate and nitrate are summarized in Table 1.

#### 4.1.1 $\Delta^{17}\text{O}$ values of sulfate

Since  $\text{SO}_2$  quickly exchanges its oxygen atoms with abundant water vapor in the atmosphere, the  $\Delta^{17}\text{O}(\text{SO}_2)$  value is assumed to be 0 ‰ (Holt et al., 1983). Thus, the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value is dependent only on the oxidation pathway of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ .  $\text{SO}_2$  oxidation by OH ( $\Delta^{17}\text{O}(\text{OH}) = \sim 0$  ‰) in the gas phase produces sulfuric acid ( $\text{H}_2\text{SO}_4$ ) which possesses the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value of approximately 0‰.



$\text{SO}_2$  can also dissolve into the aqueous phase on aerosol surfaces, where it can be oxidized by  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  or metal-catalyzed oxidation by  $\text{O}_2$  to form sulfate (Seinfeld and Pandis, 2006). Given that  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values of approximately 26 ‰ have been observed, the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value of sulfate produced by ozone should be around 6.5 ‰, based on a  $\Delta^{17}\text{O}$  signature transfer factor of 0.25 (Savarino et al., 2000).



Give the  $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$  values of 1.6 ‰ on average (Savarino et al., 1999), the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  of sulfate produced by  $\text{H}_2\text{O}_2$  is estimated to be 0.8 ‰, using a transfer factor of 0.5 (Savarino et al., 2000).



The  $\Delta^{17}\text{O}(\text{O}_2)$  value was measured to be  $-0.3$  ‰ (Barkan and Luz, 2003), producing sulfate with a  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value of almost 0 ‰ (Savarino et al., 2000).



Additionally, aqueous phase  $\text{SO}_2$  oxidation by hypohalous acids ( $\text{HOX} = \text{HOCl}, \text{HOBr}$ ) has been proposed as one of the major reactions in marine boundary layer (Vogt et al., 1996; von Glasow et al., 2002). Details are discussed in section 4.3.

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削除:  $\Delta^{17}\text{O}(\text{SO}_4^{2-}) = 0.8$  ‰

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Thus,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  of nss- $\text{SO}_4^{2-}$  results from a subtle balance between various oxidation reactions, each one transferring a specific amount of  $\Delta^{17}\text{O}$  signature to sulfate.

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#### 4.1.2 $\Delta^{17}\text{O}$ values of nitrate

The  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value is dependent on both the  $\Delta^{17}\text{O}(\text{NO}_2)$  value and the oxidation pathways of  $\text{NO}_2$  to  $\text{NO}_3^-$ . The  $\Delta^{17}\text{O}(\text{NO}_2)$  is determined by the relative contribution of NO oxidation pathways during the following photochemical cycle.

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Since all non-zero  $\Delta^{17}\text{O}$  of ozone is positioned in the terminal oxygen atoms (Bhattacharya et al., 2008), which preferentially react with NO (Savarino et al., 2008),  $\text{NO}_2$  formed by ozone exhibits a higher isotopic value than the bulk  $\Delta^{17}\text{O}(\text{O}_3)$ . On the other hand,  $\text{NO} + \text{RO}_2$  reaction produces the nitrate with lower  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value because  $\Delta^{17}\text{O}(\text{RO}_2)$  is approximately 0 ‰ (Morin et al., 2007).  $\text{NO}_2$  is then converted into nitrate through one of the following reactions.



It has been pointed out that BrO plays a significant role in both NO and  $\text{NO}_2$  oxidation in marine boundary layer (Savarino et al., 2013) through the following reactions:



while they are thought to have little importance (2% at maximum) on the Antarctic Plateau during the austral summer, due to low BrO levels up to 2-3 pmol/mol (Frey et al., 2015; Savarino et al., 2016). The oxidation by BrO may also produce  $\text{NO}_2$  and nitrate with high  $\Delta^{17}\text{O}$  values (Morin et al., 2007), because BrO is thought to possess the terminal oxygen atom of ozone (Bhattacharya et al., 2008).

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Following the principle that two of the three oxygen atoms in  $\text{NO}_3^-$  come from  $\text{NO}_2$  and one arises through conversion of  $\text{NO}_2$  to  $\text{NO}_3^-$ , the  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value of nitrate produced by each pathway can be expressed as Eq. (5).

$$\Delta^{17}\text{O}(\text{NO}_3^-) = \frac{2}{3} \times \Delta^{17}\text{O}(\text{NO}_2) + \frac{1}{3} \times \Delta^{17}\text{O}(\text{Oxidant}) \quad (5)$$

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For a given value of  $\Delta^{17}\text{O}(\text{NO}_2)$ , the  $\text{NO}_2 + \text{OH}$  pathway produces the lowest  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value, while the  $\text{NO}_3 + \text{RH}$  pathway or  $\text{BrONO}_2$  hydrolysis produce the highest  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values.

#### 4.2 General trend of seasonal variations in $\Delta^{17}\text{O}$ values of sulfate and nitrate

The  $\Delta^{17}\text{O}$  signatures of atmospheric sulfate and nitrate originate from the oxygen transfers from ozone, via oxidation of their precursors. Thus, changes in  $\Delta^{17}\text{O}(\text{O}_3)$  values likely affect both  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. However, given the small seasonal variability of the  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  (ca. 5 ‰), and assuming that all oxygen atoms transferred to  $\text{NO}_x$  are from the terminal oxygen of ozone, the expected variability of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  should not exceed 1.3 ‰ and 7.5 ‰, respectively. Clearly, these upper limits do not explain the 2.5 ‰ and 19 ‰ seasonal variability observed in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  at DDU, respectively. Furthermore, the seasonal variation in  $\Delta^{17}\text{O}(\text{O}_3)$  values, with a summer maximum and a winter minimum, is the reverse pattern to  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values, with summer minima and winter maxima. These inconsistencies suggest that variability in  $\Delta^{17}\text{O}(\text{O}_3)$  values is not the major factor influencing the seasonal variations in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values.

Meanwhile,  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are dependent on the relative importance of various oxidation pathways involved in their formation as described in the previous sections. Since the relative importance of these oxidation pathways is sensitive to the relative concentrations of oxidants in the atmosphere, and there is seasonal variation for ozone mixing ratios at a continental scale (Crawford et al., 2001; Legrand et al., 2009), the mixing ratio of ozone is expected to correlate with  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. Indeed,  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values, as well as ozone mixing ratios, all display similar seasonal variations, as shown in Fig. 2. The seasonal variation in the ozone mixing ratios at DDU is generally explained by accumulation of ozone in winter, and its photochemical destruction in summer (Legrand et al., 2009; 2016a), which induces the production of  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$  in the summer period. Therefore, we propose that seasonal variations in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  result from a shift in oxidation pathways from  $\text{O}_3$  to  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$ . Decreases in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are caused by the combining effect of decrease in the ozone concentration and decrease in the transfer efficiency of  $\Delta^{17}\text{O}(\text{O}_3)$  to the final products. Thus, the changes in relative concentrations of  $\text{O}_3$  vs.  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$  along with the changes in sunlight level, are the main factors controlling the seasonal variations of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values.

A similar seasonal variation in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values has been observed at Dome C, an inland Antarctic site (Hill-Falkenthal et al., 2013). However, the  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values observed at Dome C significantly declined in July and August, in contrast to our observations that showed only a single significant decline in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values during the period of 18–25 July. This low  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  sample is also characterized by high  $\text{nss-SO}_4^{2-}$  concentration (Fig. 2a). We don't have any evidence of contamination from station activities or laboratory works. The preliminary result of sulfur isotope analysis of sulfate in the same sample, showing  $\delta^{34}\text{S}$  value of 17.6 ‰ (to be published), suggests that this sulfate results from marine

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biogenic sulfur (i.e., DMS) which possesses  $\delta^{34}\text{S}$  values ranging 16–20 ‰ (Oduro et al., 2012; Amrani et al., 2013). However, the results of the back trajectory analyses exhibit that DDU was under continental outflow condition over this period, as well as throughout July (Fig. 3). It is hence difficult to identify the origin of this low  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  value during 18–25 July. Nevertheless, this point doesn't change the interpretation that  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values are generally lower in summer and higher in winter. Thus, this sample was excluded from consideration for the following discussion and does not impair our further interpretation.

For sulfate, the relative contribution of  $\text{O}_3$  oxidation for sulfate formation ( $f(\text{nss-SO}_4^{2-})_{\text{O}_3}$ ) was calculated. Since positive  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values result from only  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  oxidation and the other pathways result in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  of approximately 0 ‰, we calculated the maximum and the minimum  $f(\text{nss-SO}_4^{2-})_{\text{O}_3}$  by assuming no contribution of  $\text{H}_2\text{O}_2$  oxidation, and assuming the contribution from only  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  oxidation, respectively, using the simple mass balance equation. Consequently, the mean summer (Jan., Feb., and Dec.)  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  value of 1.2 ‰ is corresponding to  $f(\text{nss-SO}_4^{2-})_{\text{O}_3}$  of 0.07-0.18, whereas the mean winter (Jun. - Aug.)  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  value of 2.4 ‰ is corresponding to  $f(\text{nss-SO}_4^{2-})_{\text{O}_3}$  of 0.28-0.37. The relative contribution of  $\text{O}_3$  oxidation is thus 2 to 4 folds higher in winter than in summer. However, it is important to mention that DMS levels are quite low at DDU in winter (Preunkert et al. 2007); the sulfate collected at DDU is likely produced at a lower latitude region under more sunlight. Thus, the observed  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values in winter may not solely reflect oxidation chemistry in the local atmosphere at DDU. The sulfur sources need to be constrained for the interpretation of winter data. Also for nitrate, it is believed that during Antarctic winter period, the atmospheric nitrate results mainly from the deposition of polar stratospheric clouds (Santacesaria et al., 2001; Savarino et al. 2007) and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are not representative of the oxidation chemistry of the atmosphere at this site. On the other hand, since a mean summer  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value of 27.1 ‰ requires the contribution of  $\text{NO}_2+\text{OH}$  pathway ( $f(\text{NO}_3^-)_{\text{OH}}$ ), the maximum and minimum  $f(\text{NO}_3^-)_{\text{OH}}$  value was calculated by assuming no contribution of  $\text{N}_2\text{O}_5$  hydrolysis, and by assuming no contribution of  $\text{NO}_3+\text{RH}$  and  $\text{BrONO}_2$  hydrolysis pathways, respectively. As a result,  $f(\text{NO}_3^-)_{\text{OH}}$  value corresponding to the summer  $\Delta^{17}\text{O}(\text{NO}_3^-)$  value of 27.1 ‰ is expected to range 0.28-0.52. However, this is in contradiction to an expectation that the termination reaction is only  $\text{NO}_2+\text{OH}$  pathway under permanent sunlight. For further constraints on oxidation chemistry, a coupled stratosphere/troposphere chemical transport model will be necessary, which is beyond the scope of this paper.

#### 4.3 Sensitivity of sulfate and nitrate $\Delta^{17}\text{O}$ values to the ozone mixing ratio

To examine the response of  $\Delta^{17}\text{O}$  values to the changes in oxidant concentration, we compared  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values to ozone mixing ratio (Figure 4), which was only one oxidant observed in year-round scale at the same time. In Fig. 4,  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are generally co-varied with ozone mixing ratios, suggesting that a change in the ozone mixing ratio is one of the main factors controlling  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. Note that as

mentioned in section 4.2, in winter,  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are not directly linked to ozone mixing ratios at DDU.

Excluding winter data (June to August), the regression lines for sulfate and nitrate have slopes, intercepts and correlation coefficients ( $R^2$ ) of 0.07, -0.01 and 0.50, and 0.55, 18.2 and 0.80, respectively (Fig. 4). These slopes indicate how sensitive  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are to ozone mixing ratios. Meanwhile, the intercepts indicate  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values when assuming ozone was not involved in the oxidation of  $\text{SO}_2$  and  $\text{NO}_2$ . If this was true, it would imply that the seasonal cycles of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  are controlled largely by the last stage of oxidation and not by the  $\Delta^{17}\text{O}$  values of their precursors. In the case of sulfate, this is likely to be true, given that  $\Delta^{17}\text{O}(\text{SO}_2) = 0\text{‰}$  year-round, because of oxygen isotopic exchange between  $\text{SO}_2$  and water vapor. Therefore, the intercept for sulfate of approximately 0‰ is consistent with  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values for sulfate produced via the  $\text{SO}_2 + \text{OH}$  pathway. Meanwhile, the intercept of approximately 18‰ for nitrate (Fig. 4b) corresponds to a  $\Delta^{17}\text{O}(\text{NO}_2)$  value of 27‰, assuming all nitrate is produced via the  $\text{NO}_2 + \text{OH}$  pathway. This  $\Delta^{17}\text{O}(\text{NO}_2)$  value is in a good agreement with the value of 26‰ calculated for conditions at 80°N, under the assumption that  $\Delta^{17}\text{O}(\text{OH}) = 0\text{‰}$  (Morin et al., 2011). Using the calculation processes of Morin et al. (2011), we calculated  $\Delta^{17}\text{O}(\text{NO}_2)$  to be 26.5‰, consistent with the intercept value. In this calculation, we employed DDU conditions for summer, with a mean temperature of about 0°C,  $\Delta^{17}\text{O}(\text{O}_3) = 26\text{‰}$ , mixing ratios of  $\text{O}_3$  and  $\text{RO}_2$  of  $5.6 \times 10^{11}$  molecules  $\text{cm}^{-3}$  and  $3.3 \times 10^8$  molecules  $\text{cm}^{-3}$ , respectively (Legrand et al., 2009; Kukui et al., 2012). Thus, the plot of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values as a function of ozone mixing ratios has potential to be used for estimating  $\Delta^{17}\text{O}(\text{NO}_2)$  values, which they have never been measured.

The sensitivity of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values to ozone mixing ratios in spring (September to November) seems to be lower than in fall (March to May) (Fig. 4). Fixing the intercept to -0.01, the slopes between  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values and ozone mixing ratios for spring and fall were  $0.063 \pm 0.004$  and  $0.084 \pm 0.005$ , respectively, showing a clear difference over their range of deviation. In contrast to  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values, the slopes between  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values and ozone mixing ratios for an intercept fixed to 18.2 show less difference between spring and fall, with the values of  $0.54 \pm 0.02$  and  $0.57 \pm 0.01$ , respectively. However,  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  is also sensitive to  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$ . If the relative abundance of  $\text{O}_3$  vs.  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$  are regulated only by changes in solar irradiation as discussed in section 4.2, then the slopes between  $\Delta^{17}\text{O}$  values for sulfate and nitrate against ozone mixing ratios should be the same for spring and fall. The different slopes observed for sulfate in spring and fall indicate the effects of various oxidation processes, decreasing  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  in spring and/or increasing  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  in fall. There are several processes that could explain such a spring/fall difference.

One possible explanation involves the influence of  $\text{NO}_x$  emissions from snowpack covering the East Antarctic Plateau (Davis et al., 2001; Crawford et al., 2001; Chen et al., 2001). The Antarctic atmosphere is strongly affected by  $\text{NO}_x$  emissions from snowpack, starting at the beginning of spring with the return of the sunlight. These snow  $\text{NO}_x$  emissions subsequently enhance both  $\text{O}_3$  and  $\text{OH}$  productions, with  $\text{OH}$  in greater proportion than  $\text{O}_3$ . This is particularly true at DDU

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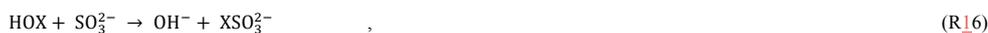
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in summer, where katabatic air from the East Antarctic Plateau causes the ozone mixing ratio to be in the range of 10–40 ppbv (Legrand et al., 2009; 2016a), with a mean OH concentration of  $2.1 \times 10^6$  molecules  $\text{cm}^{-3}$  (Kukui et al., 2012). In contrast, Palmer Station is exposed to oceanic air, producing ozone mixing ratios within the range of 9–20 ppbv, with a mean OH concentration of about  $1.0 \times 10^5$  molecules  $\text{cm}^{-3}$  (Jefferson et al., 1998). These observations suggest that  $\text{NO}_x$  emissions increase oxidants at DDU, compared with the Palmer Station, about 2-fold for  $\text{O}_3$  and more than 10-fold for OH. Chemical transport models over the Antarctic continent show that  $\text{NO}_x$  emitted from snow during summer increase  $\text{O}_3$  and OH by a factor of 2 and 7, respectively, compared with estimations not including snow  $\text{NO}_x$  emissions (Zatko et al., 2016). Additionally,  $^{15}\text{N}$  depletion in nitrate starts from the beginning of September (See Supplement), which is consistent with previous measurement at DDU (Savarino et al., 2007), supporting that the snow  $\text{NO}_x$  emission happens in early spring at DDU. Thus, by snow  $\text{NO}_x$  emission, OH production is enhanced more efficiently than  $\text{O}_3$  production in spring, possibly resulting in lower  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  spring values.

Another possible explanation is that hypohalous acids ( $\text{HOX} = \text{HOCl}, \text{HOBr}$ ) act as important oxidants of  $\text{SO}_2$  via the aqueous phase reaction (R16 and R17) in the marine boundary layer (Fogelman et al., 1989; von Glasow, 2002):



This reaction is expected to produce sulfate with  $\Delta^{17}\text{O} = 0$  ‰, as all oxygen atoms of sulfate originate from water (Fogelman et al., 1989; Troy and Margerum, 1991; Yiin and Margerum, 1988), leading to lower  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values in the atmosphere. Indeed, unexpectedly low  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values have been observed in marine aerosols, which is possibly explained by a contribution of HOX oxidation of 33%–50% to total sulfate production in the marine boundary layer (Chen et al., 2016). Chen et al. (2016) estimated that a minimum concentration of gaseous HOX of 0.1 pptv could account for half of the sulfate production in the marine boundary layer. At DDU, year-round observations of gaseous inorganic bromine species ( $[\text{Br}_y^*] = [\text{HBr}] + [\text{HOBr}] + 0.9[\text{Br}_2] + 0.4[\text{BrO}] + [\text{BrNO}_2] + [\text{BrONO}_2] + [\text{Br}]$ ) revealed that maximum concentrations are observed in September, with values of  $13.0 \pm 6.5$  ng  $\text{m}^{-3}$  ( $\sim 3.6$  pptv) (Legrand et al., 2016b). Even if only one third of the  $\text{Br}_y^*$  corresponds to HOBr, as estimated using the model calculations by Legrand et al. (2016b) under summer conditions, then it is expected that HOX at DDU in spring is  $> 1$  pptv; thus, HOX could play a significant role in sulfate production in spring. Likewise,  $\text{Br}_y^*$  concentration at DDU is at minimum in May, with values of  $3.4 \pm 1.0$  ng  $\text{m}^{-3}$  (Legrand et al., 2016b), corresponding to less than one third of spring values. This would lead to a lower contribution of HOX to sulfate production in fall, compared with spring. Hence, sulfate production via aqueous oxidation by HOX may explain the lower  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in spring, relative to fall.

A change in pH of the aqueous phase on the aerosol surfaces may also explain the spring/fall difference in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$ . Given that  $\text{SO}_2$  oxidation by ozone in the aqueous phase is favored at high pH ( $> 5.5$ ) (Seinfeld and Pandis, 2006), if the pH of aerosol droplets is higher in fall than in spring, then the relative importance of the  $\text{SO}_2 + \text{O}_3$  reaction resulting in higher  $\Delta^{17}\text{O}$  values would increase in fall. However, ion concentration analyses of aerosols collected at DDU exhibited higher

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alkalinity in spring than in fall (Jourdain and Legrand, 2002; Legrand et al., 2016b), which is inconsistent with this explanation. Hence, this process can be excluded from further consideration.

It should be noted that smaller difference was observed between spring and fall  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values, which would be also affected by the above two processes. Snow  $\text{NO}_x$  emission would decrease  $\Delta^{17}\text{O}(\text{NO}_3^-)$  through depression of the contribution of  $\text{O}_3$  oxidation relative to the other oxidation pathways by  $\text{HO}_x$  and  $\text{RO}_x$ , while halogen chemistry would lead to high  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values through an oxygen atom transfer from  $\text{O}_3$  to  $\text{BrO}$  and consequently to nitrate (Morin et al., 2007; Savarino et al., 2013). Although it is difficult to identify the precise processes involved, observations of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values at an inland site (e.g., Concordia Station) would enable us to determine which process causes the spring/fall difference in the oxidation chemistry in the DDU atmosphere. If snow  $\text{NO}_x$  emission is the source of low  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  at DDU in spring, then  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  at an inland site would also exhibit lower values in spring than in fall.

#### 4.4 Air mass origin analysis

Using observations of several oxidants at DDU and Concordia Station (e.g., Legrand et al., 2009, 2016a; Kukui et al., 2012, 2014; Grilli et al., 2013), it has been suggested that the oxidative capacity of the atmosphere at DDU is influenced by air masses transported from the East Antarctic Plateau during katabatic wind outflows. The  $\text{NO}_x$  emission from snowpack in inland Antarctica stimulates the ozone,  $\text{HO}_x$ ,  $\text{RO}_x$ , and  $\text{H}_2\text{O}_2$  production through the enhanced  $\text{NO}_x$  cycle. Thus, the atmosphere at DDU is enriched in all of those photochemical oxidants, when air masses are from inland regions, compared to when air masses are from the ocean (Legrand et al., 2009). Therefore, we expected that  $\Delta^{17}\text{O}$  values for sulfate and nitrate also depend on air mass origin.

In Fig. 5, the  $\Delta^{17}\text{O}$  values for sulfate and nitrate are given as a function of the time that air masses were over the continent during the five-days travel prior to arriving at DDU. Summer data show that the contact times of air masses with the continent varied between 20 and 120 h (i.e., continental air and oceanic air are well mixed). Similarly, their  $\Delta^{17}\text{O}$  values show insignificant variation, having low values of around 1‰ and 25‰ for sulfate and nitrate, respectively. This trend reflects two different phenomena, decreased  $\Delta^{17}\text{O}$  values in summer because of the high contribution of photo-oxidants to atmospheric chemistry, and increased import of oceanic air. In contrast, plots for other seasons show that the  $\Delta^{17}\text{O}$  values exhibit high variation, although most of the air masses originate from the continent. It is important to note that this non-correlation does not mean that there is no link between  $\Delta^{17}\text{O}$  values and air mass origin. The influence of air mass transport on oxidative capacity has been demonstrated in daily observations of oxidants (e.g., Legrand et al., 2009). Given that air masses at this site are from a variety of directions, and are mixed together, this makes interpretation of weekly averaged analyses more complicated. Hence, no significant correlation between  $\Delta^{17}\text{O}$  values and air mass origin in weekly data could reflect a real lack of correlation or a too broad time resolution for these data.

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## 5 Summary

To develop an understanding of the **factors influencing  $\Delta^{17}\text{O}$  values of atmospheric sulfate and nitrate**, seasonal variations of  $\Delta^{17}\text{O}$  values of atmospheric sulfate, nitrate and ozone were analyzed using the aerosol samples collected at DDU throughout 2011. Both  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values exhibited clear seasonal variations, with summer minima and winter maxima. In contrast,  $\Delta^{17}\text{O}$  values of ozone showed limited variability throughout the year, indicating that  $\Delta^{17}\text{O}(\text{O}_3)$  values do not significantly influence summer/winter trends in  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values. **We hence, for the first time, demonstrated that  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are direct results of local oxidation chemistry of their precursors.**

The summer/winter trends of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values **are likely to** reflect sunlight-driven changes in the relative importance of **oxidation pathways; oxidation by  $\text{HO}_x$ ,  $\text{RO}_x$  and  $\text{H}_2\text{O}_2$  are increased during summer when the solar radiation enhances the production of those oxidants, whereas the relative contribution of oxidation reaction transferring oxygen atoms of  $\text{O}_3$  to sulfate and nitrate is increased during winter period.** Interestingly, by comparing  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values to ozone mixing ratios, we found that the  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  values in spring months were lower than in fall months despite of similar ozone levels for spring and fall, whereas there was no clear difference between  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values.

Possible explanations for the spring/fall differences for sulfate include: (i) low **relative contribution of  $\text{O}_3$  oxidation** in spring induced by reactive nitrogen emissions from snowpack at inland sites being transported to coastal sites; and (ii) effects of  $\text{SO}_2$  oxidation by hypohalous acids ( $\text{HOCl}$ ,  $\text{HOBr}$ ), enhanced in spring by interaction of sea salt particles with photo-oxidants. Further observations of  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in aerosols collected at Antarctic inland sites will help us to identify the processes causing such different sulfate and nitrate formation in spring and fall. **Nevertheless, the dataset of this study can be dedicated to atmospheric chemical transport models to better constraints on unique local oxidation chemistry at DDU.**

## Author contributions

S. Ishino, S. Hattori and J. Savarino designed the research. M. Legrand, B. Jourdain and S. Preunkert provided qualified complementary data, organized the Antarctic field campaign, and collected samples. S. Ishino, S. Hattori, J. Savarino, A. Barbero and N. Caillon performed experiments. S. Ishino, S. Hattori, J. Savarino, K. Kuribayashi, and N. Yoshida analyzed data. S. Ishino, S. Hattori and J. Savarino prepared the manuscript, with contributions from all other co-authors.

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削除: We concluded that the main factor controlling the  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values is

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削除: (i.e.,  $\text{O}_3/\text{RO}_x$  ratios) in oxidation,

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削除: which is supported by co-variation of the  $\Delta^{17}\text{O}(\text{nss-SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values with ozone mixing ratios. ... 16

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削除: Clearly, chemical transport models, connecting  $\Delta^{17}\text{O}$  values with the oxidation processes involved in sulfate and nitrate formation are necessary for quantitative interpretation of the spatio-temporal patterns of  $\Delta^{17}\text{O}$  signatures.

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## Data availability

The data used for the figures and the interpretations are shown in Supplement materials.

## Acknowledgments

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10 (INSU). This work is also supported by a Grant in-Aid for Scientific Research (S) (23224013) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, a Grant in-Aid for Young Scientist (A) (16H05884) of MEXT, Japan, and by a research fund from Asahi Group Foundation. S.H., S. I., and N. Y. are supported by a Japan–France Research Cooperative Program (SAKURA and CNRS) of MEXT, Japan. J. S. and N. C. thank the CNRS/INSU (PRC program 207394) and the PH-SAKURA program of the French Embassy in Japan (project 31897PM) for financial support  
15 for this collaboration. [This work has been supported by a grant from Labex OSUG@2020 \(Investissements d’avenir – ANR10 LABX56. S. I. thanks the Academy for Co-creative Education of Environment and Energy Science for financial support.](#) We are grateful to Basile de Fleurian who carried out winter sampling at DDU in 2011. The authors gratefully acknowledge Erwann Vince of the Laboratoire d’étude des Transferts en Hydrologie & Environnement for preparation of bacterial cultures used for nitrate and ozone isotope analyses. Meteo France are acknowledged for providing meteorological  
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Table 1: Summary of  $\Delta^{17}\text{O}$  values of sulfate and nitrate produced via each reaction pathways with oxidants.  $\Delta^{17}\text{O}$  values of sulfate are calculated based on Savarino et al. (2000).  $\Delta^{17}\text{O}$  values of nitrate refer to estimate of box model by Morin et al. (2011).  $\Delta^{17}\text{O}$  value of nitrate produced by  $\text{BrONO}_2$  hydrolysis is assumed to be equal to the value for  $\text{NO}_3 + \text{RH}$  pathway.

	Oxidation pathway	$\Delta^{17}\text{O}$ (oxidant) (‰)	Transferring factor	$\Delta^{17}\text{O}$ (product) (‰)
$\text{SO}_4^{2-}$	$\text{SO}_2 + \text{OH}$	0 <sup>a</sup>	-	0
	$\text{SO}_3^{2-} + \text{O}_3$ (aq.)	26 <sup>b</sup>	$0.25 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$	6.5
	$\text{HSO}_3^- + \text{H}_2\text{O}_2$ (aq.)	1.6 <sup>c</sup>	$0.50 \times \Delta^{17}\text{O}(\text{H}_2\text{O}_2)$	0.8
	$\text{SO}_3^{2-} + \text{O}_2$ (cat. Fe, Mn)	-0.3 <sup>d</sup>	$0.25 \times \Delta^{17}\text{O}(\text{O}_2)$	-0.1
	$\text{SO}_3^{2-} + \text{HOX} + \text{H}_2\text{O}$	39 (HOX) <sup>e</sup> , 0 ( $\text{H}_2\text{O}$ ) <sup>f</sup>	-	0
$\text{NO}_3^-$	$\text{NO}_2 + \text{OH}$	0	$2/3 \times \Delta^{17}\text{O}(\text{NO}_2)$	17.3-25.1
	$\text{N}_2\text{O}_5$ hydrolysis	26 ( $\text{O}_3$ ), 0 ( $\text{H}_2\text{O}$ )	$2/3 \times \Delta^{17}\text{O}(\text{NO}_2) + 1/6 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	31.0-35.2
	$\text{NO}_3 + \text{RH}$	26 ( $\text{O}_3$ )	$2/3 \times \Delta^{17}\text{O}(\text{NO}_2) + 1/3 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	38.0-42.7
	$\text{BrONO}_2$ hydrolysis	39 ( $\text{BrO}$ ) <sup>e</sup>	$2/3 \times \Delta^{17}\text{O}(\text{NO}_2) + 1/3 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	38.0-42.7

<sup>a</sup> Holt et al. (1983); <sup>b</sup> Vicars et al. (2014); <sup>c</sup> Savarino et al. (1999); <sup>d</sup> Barkan and Luz (2003); <sup>e</sup> assumed based on Bhattacharya (2008); <sup>f</sup> Barkan and Luz (2005)

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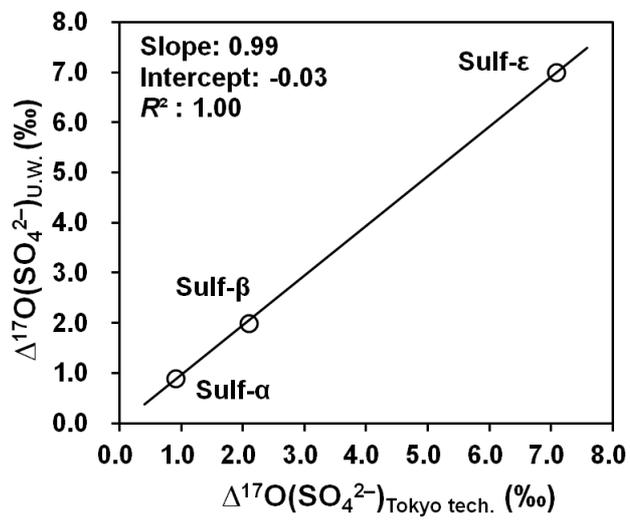


Figure 1: Comparison of  $\Delta^{17}\text{O}$  values of sulfate for standard materials measured at the University of Washington (U.W.) and Tokyo Institute of Technology (Tokyo tech.).

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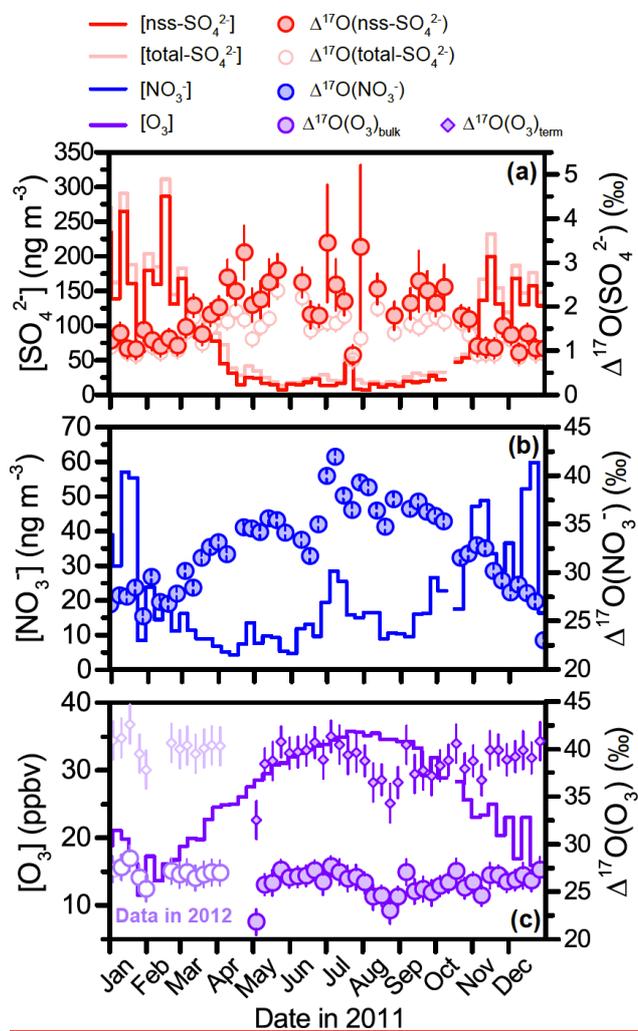


Figure 2: Seasonal variations of concentrations (solid line) and  $\Delta^{17}\text{O}$  values (circles) of sulfate (red), nitrate (blue), and ozone (purple) at Dumont d'Urville Station during 2011.  $\Delta^{17}\text{O}$  values of ozone are shown as bulk (circle) and terminal (square) values.  $\Delta^{17}\text{O}$  values of ozone include samples collected from January to April 2012.

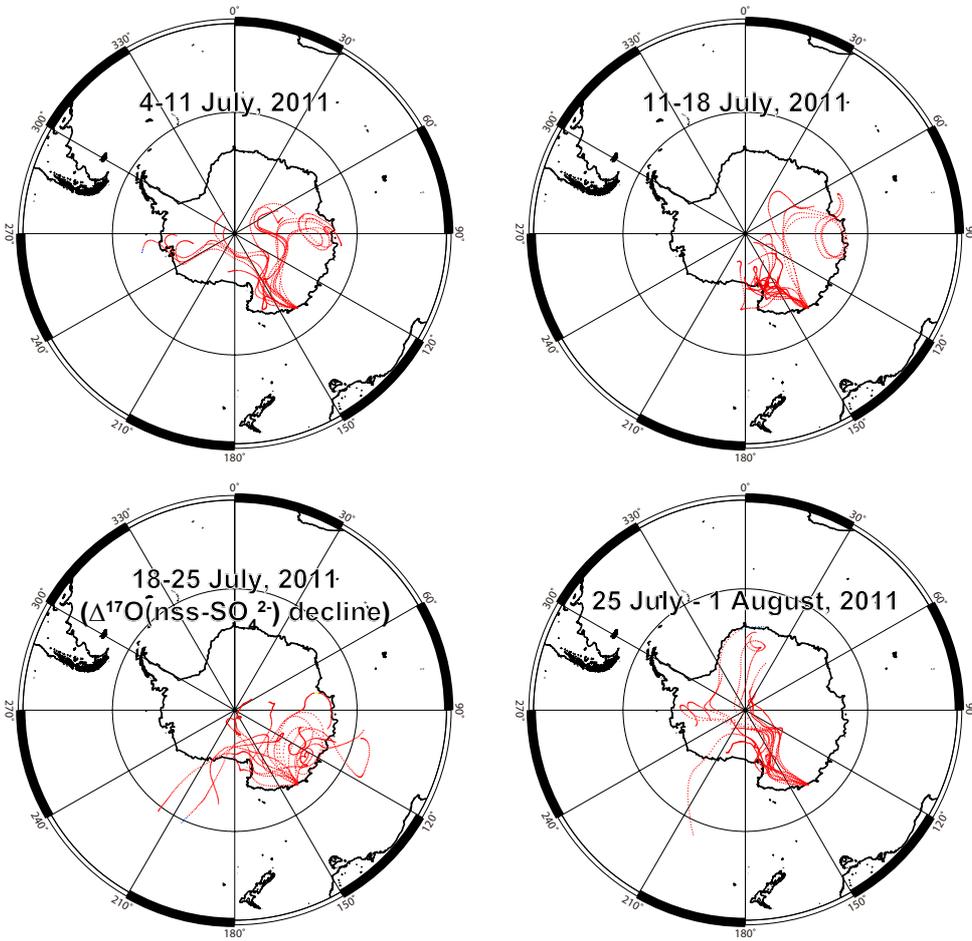


Figure 3: Air mass pathways arriving at Dumont d'Urville Station during sampling periods in July 2011.

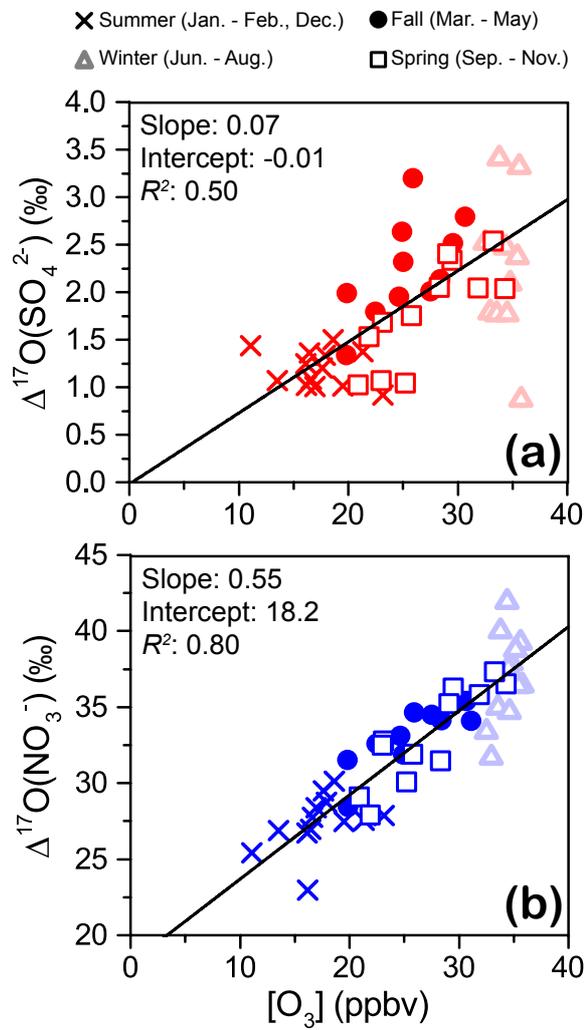


Figure 4:  $\Delta^{17}\text{O}$  values of (a) sulfate, and (b) nitrate as a function of ozone mixing ratios  $[\text{O}_3]$ . Winter values were not taken into account in the calculation of slopes and intercepts.

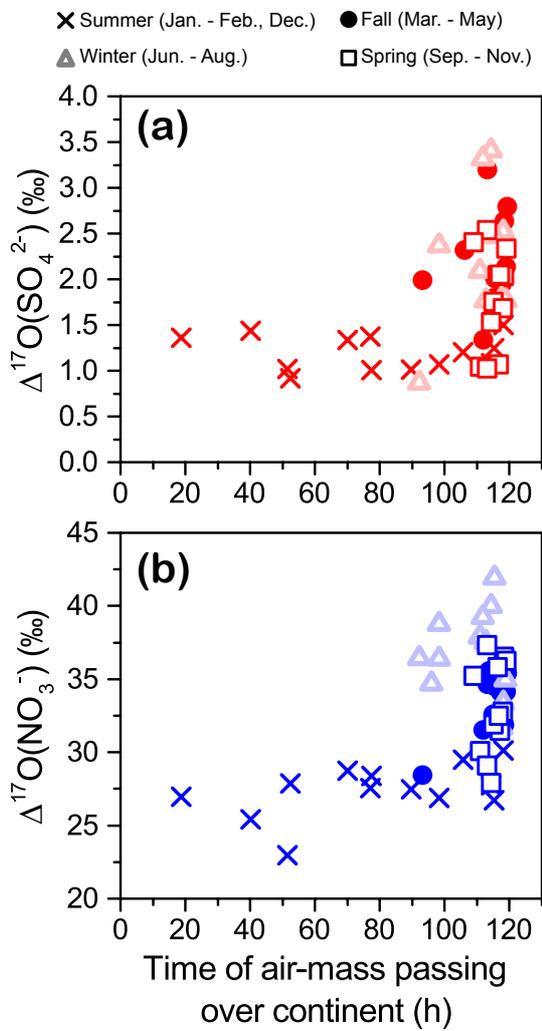


Figure 5: Relationship between  $\Delta^{17}\text{O}$  values of (a) sulfate, and (b) nitrate, with the time taken for air masses to pass over the Antarctic continent (i.e., air mass contact time with surface snow).