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 Δ17O 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. $\Delta^{17}O$ 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 SO_2 and NO_X' throughout the manuscript as suggested by Referee#1.

We also modified Introduction section, where explaining what do $\Delta^{17}O$ 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 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 $\Delta^{17}O$ and $\delta^{18}O$ for nss sulfate is expected. Thus, the $\delta^{18}O$-nss SO_4 would be a line of independent evidence for the conclusions. However, the $\delta^{18}O$ data is never mentioned, which needs some explanation.

As discussed by Schauer et al. (2012), the Ag_2SO_4 thermo-decomposition method is not reliable for the $\delta^{18}O$ of sulfate due to the oxygen isotope exchange between the O_2 products and the quartz reactor, while $\Delta^{17}O$ of O_2 can be corrected from this effect as the $\Delta^{17}O$ values of quartz materials is assumed to be 0 ‰. But for $\delta^{18}O$ values, such correction is not available due to the unknown of $\delta^{18}O$ 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 $\delta^{18}O$ measurement. This is the main reason why we don't discuss the $\delta^{18}O$ values of sulfate.

However, the $\delta^{18}O$ data is provided in Supplementary materials on demand in case if someone wants to calculate the $\Delta^{17}O$ value with another definition. Note that those $\delta^{18}O$ and $\delta^{17}O$ values are relative to reference O_2, not calibrated relative to VSMOW. Based on this data, the plot of $\Delta^{17}O$ as a function of $\delta^{18}O$ does not show the positive correlation (slope: -0.03, R^2: 0.02), despite the clear seasonal variation in $\delta^{18}O$ values with the summer minimum and winter maximum. This may result from the different controlling factors in $\Delta^{17}O$ and $\delta^{18}O$. Whereas $\Delta^{17}O$ signature depends on the oxidant which provides one of four oxygen atoms of sulfate, $\delta^{18}O$ is expected to mainly depend on the oxygen atoms of water which provides three oxygen atoms of sulfate through the equilibrium between 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 $\delta^{18}O$ 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, $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are expected to show the seasonal variations with summer minima and winter maxima, because the oxidation pathways should shift from O_3 oxidation in winter to HO_X or H_2O_2 oxidations in summer along with sunlight driven changes in the relative abundance of those photochemical oxidants. However, due to the lack of $\Delta^{17}O(O_3)$ values at coastal Antarctica, the possibility had been remaining that the seasonal variations of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values at the site are influenced not only by the oxidation chemistry but also the variations in $\Delta^{17}O(O_3)$ values. If the $\Delta^{17}O(O_3)$ values are examined to have the flat value throughout the year, we can remove the possibility of the influence by $\Delta^{17}O(O_3)$ values, and go on to the interpretation of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ 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, l.21: 'characterized by summer minima and winter maxima' → 'characterized by minima in the austral summer and maxima in winter'

-- p.3, l.10: 'showing an austral summer minimum and a winter maximum'

-- p.8, l.26-27: 'The [nss-SO$_4^{2-}$] had a summer maximum of up to ~280 ng m^{-3} from January to February,' → 'The [nss-SO$_4^{2-}$] had a maximum of up to ~280 ng m^{-3} 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, l.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.