

# Response to the referee #1 (egusphere-2023-744)

Dear Lei Geng,

We thank you for your valuable review of this work and relevant comments that greatly improved the manuscript. Your comments/suggestions are given below in bold, followed by our answers. Changes/new elements added to the manuscript are presented in blue.

## Major comments:

- 1) **The way to derive  $\text{RO}_2$  using measured  $\Delta^{17}\text{O}(\text{NO}_2)$ : I don't think it make any sense to use the other method (i.e., Case B) to estimate  $\text{RO}_2$  and compare the results with Case A.**

First of all, as shown in Table 1, in both SP1 and SP2, neither the derived  $\text{RO}_2$  concentration at each sampling period nor the averages can be considered as “consistent”; Don't get the points how can these values can be called “closeness”.

Secondly, to derived  $\text{RO}_2$  from  $\Delta^{17}\text{O}(\text{NO}_2)$  (i.e., Case A), one simply assumes that it is only  $\text{RO}_2$  completes with  $\text{O}_3$  to oxidize  $\text{NO}$  as indicated by Equation 13. This ignores the contributions of  $\text{HO}_2$ . While in Case B, a  $\text{RO}_2/\text{HO}_2$  ratio of 0.859 was applied. So does this mean that in Case A the same ratio of  $\text{RO}_2/\text{HO}_2$  can also be applied and then compared with Case B? In fact, it is highly doubtful that the same ratio in one study can be applied to another, given variations in concentrations of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{NMVOCs}$ , don't even to mention the uncertainties associated with the empirical formula of  $\text{HO}_2$  calculation using  $\text{O}_3$ .

So just saying from  $\Delta^{17}\text{O}(\text{NO}_2)$  to estimate  $\text{RO}_2$  and note it is actually representing the sum of  $\text{RO}_2$  and  $\text{HO}_2$  is enough here. This provides a new method to estimate  $\text{RO}_2$  and  $\text{HO}_2$  radicals, and can be verified with actual measurements in the future. The current way of Case B is just too uncertain and the results are not comparable.

Thank you for pointing this out, which was also a concern for Reviewer #2. We agree with your comments and have removed the comparison with Case B in the revised version of the manuscript which now only discusses RO<sub>2</sub> derived from isotopic measurements. We invite you to read our answers to Reviewer #2 pages 26-27 and pages 30-32, where you will find the revised manuscript structure and the reworded/modified section 3.2 on isotopically derived RO<sub>2</sub>.

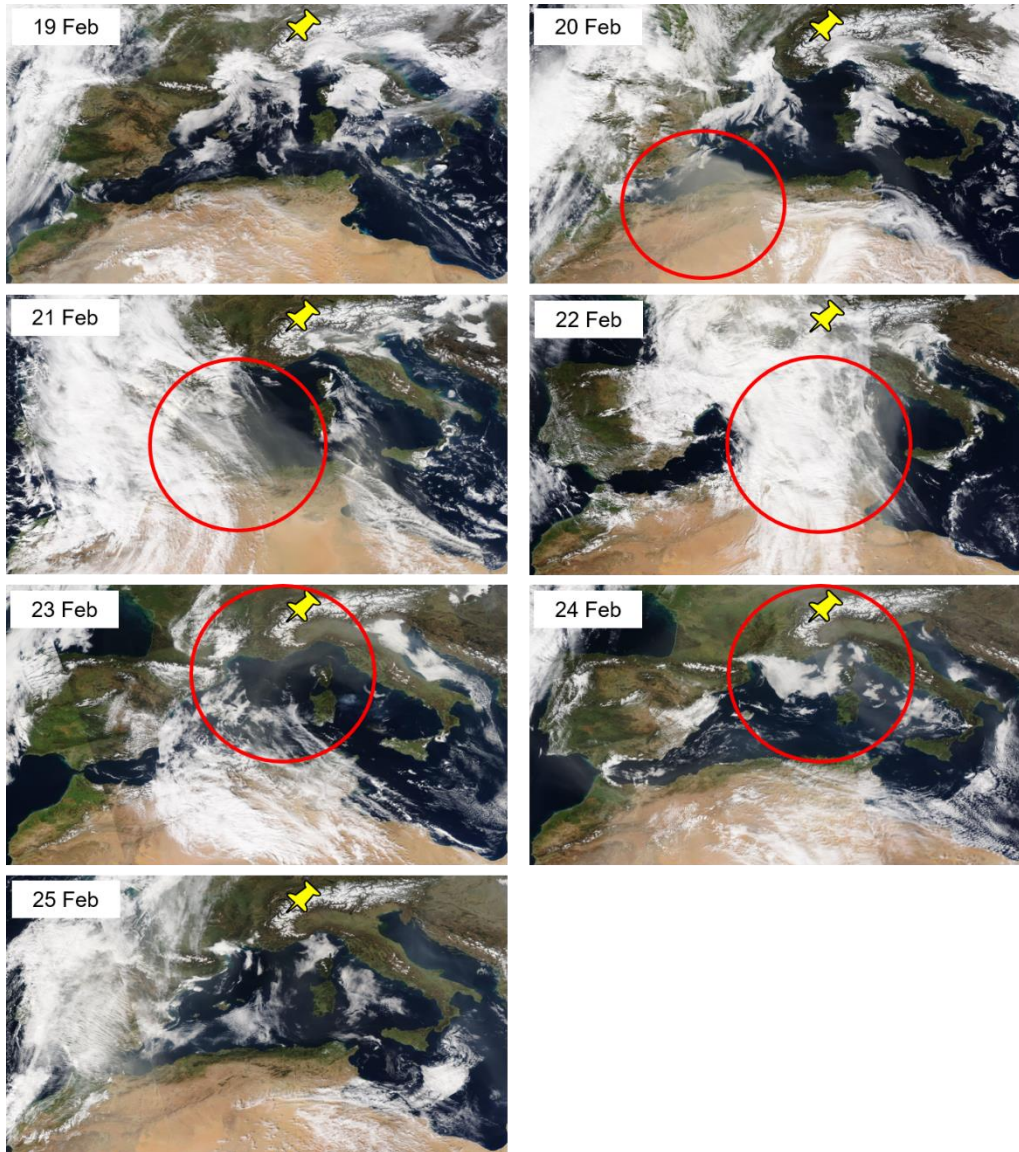
**The authors paid too much attentions to the observations of Beijing and tried to make analogies between the two in order to explain their observations. However, the authors overlooked the differences in concentrations of PM<sub>2.5</sub>, PM<sub>10</sub> and nitrate between the two days, and all of these concentrations in SP 2 are higher in SP 2 than SP 1, would this suggest a transport events and non-local sources of nitrate? Note the  $\delta^{15}\text{N}(\text{NO}_3^-)$  values and its relationship with  $\delta^{15}\text{N}(\text{NO}_2)$  are also different in SP 2 compared to SP 1, this may indicate the same thing: a regional transport event occurred and which brought non-local nitrate. The  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  data should be combined to discuss at this point.**

We were not sought to draw analogies but rather to show how an interpretation of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  variabilities without taking into account of the stratification of  $\Delta^{17}\text{O}(\text{NO}_2)$  at night in polluted environments could lead to biased conclusions. We believe it is important to alert the community on such over-interpretations, which could arise from poor considerations of  $\Delta^{17}\text{O}(\text{NO}_2)$  dynamics.

**The last, references or other evidence should be provided when attributed the high load of PM<sub>10</sub> in SP 2 to Saharan dust, e.g., back trajectory analysis or something similar.**

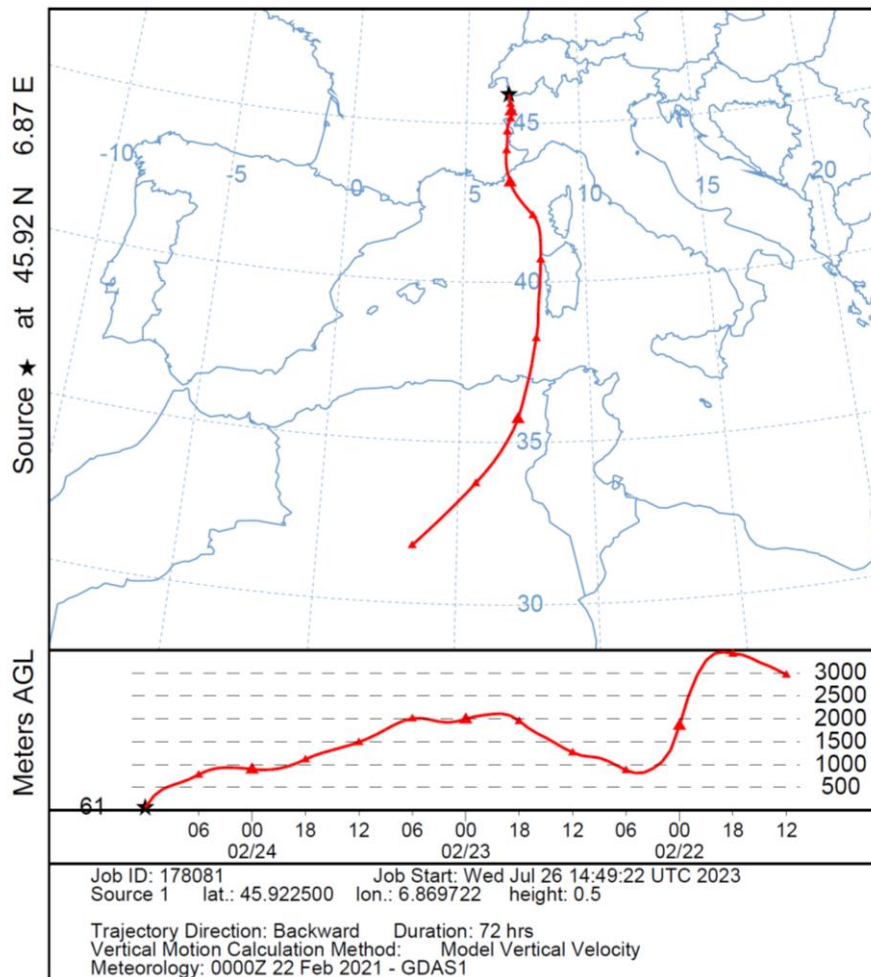
The Saharan dust episode which began around 23 February was indeed more diffuse than that of 7 February. NASA AQUA MODIS satellite images show the formation of a dusty air mass over the Saharan region on February 20 and the displacement of this air mass over the following days towards the south of France (**Erreur ! Source du renvoi introuvable.**). In addition, backtracking trajectory (HYSPLIT) shows the air mass from the south entering the Chamonix valley on 24 February (**Figure 1**). Figure 1 and 2 have been added to the revised Supplement.

To note, we had visual evidence of the presence of Saharan dust in the Chamonix atmosphere during SP 2 and the extractions from the GF filters collected during SP 2 showed a yellow coloration, very distinct from the filter extractions from SP 1.



**Figure 1.** Images from the AQUA satellite (MODIS; © NASA) from 19 February 2021 to 25 February 2021. One can see a plume of Saharan dust forming over North Africa on 20 February (localised by the red circle) and moving above the south of France and the Alps until 24 February. The yellow pin points to Chamonix, France.

NOAA HYSPLIT MODEL  
 Backward trajectory ending at 1200 UTC 24 Feb 21  
 GDAS Meteorological Data



**Figure 1.** HYSPLIT 72 hours backward trajectory on 24 February 2021 ending at Chamonix, France, at 12:00 UTC (13:00 local time). The model was run every 6 hours. The starting height (in meter above ground level) is half of the boundary layer height estimated by the model from meteorological data set.

## Technical comments:

- **Blank correction of isotope measurement of NO<sub>2</sub>: I wondered where the blank comes from, if it is coming from the chemicals used to trap NO<sub>2</sub>, there is no problem to correct as what was done here; however, if the blank NO<sub>2</sub> was coming from absorption of atmospheric NO<sub>2</sub> during the preparation and the installation of the coated denuder tubes, it won't make sense to do the correction by assuming blank  $\Delta^{17}\text{O}(\text{NO}_2) = 0$  permil, which would over correct.**

Although difficult to assess, it is unlikely that this blank came from atmospheric NO<sub>2</sub> as the denuders of the batches used for SP 1 and SP 2 were handled using the same procedure. It is more likely that this contamination came from the batch of MQ water used to extract the SP 2 denuders or from a contaminated pipette. Since the sample collected between 13:30 and 16:30 LT during SP 2 captured less atmospheric NO<sub>2</sub> than other samples (due to lower ambient NO<sub>2</sub> during this period), the blank has more impact.

- **Equation (4) and relatives in the text: don't get the point why defines a new term  $T_{\text{NO}+\text{O}_3}$  instead of using what has been long used in the literature, i.e., the  $A$  value to represent the fraction of O<sub>3</sub> oxidation of NO and this “ $A$ ” is almost reserved in the study of  $\Delta^{17}\text{O}$  of nitrate. I suggest to keep consistent with the literature and do not define new terms unless necessary so that peers can easily follow. I understand here the authors used “ $A^*$ ” later to define the lifetime differences, but it can be simply replaced with any other symbols.**

We understand your concern. However, the “ $A^*$ ” notation was initially used in Albertin et al. (2021) to be consistent with the literature (see Li et al., 2020), so it follows that we could not use this letter for the term relating to  $T_{\text{NO}+\text{O}_3}$ . Thus, for the sake of consistency with Albertin et al. (2021), we would like to keep the term “ $T_{\text{NO}+\text{O}_3}$ ”. In addition, “ $T$ ” symbolises the word “transfer”, a more explicit letter than  $A$ . Nonetheless, to avoid confusing, we have added in the revised manuscript that this term can also be called  $A$  in part of the literature.

- **Line 246: These latter, not “later”**

Thank you for pointing this mistake out, which has been corrected.

- **Line 409, I would not call 29.0 +/- 2.2 is consistent with the values of 26 +/- 1 in the literature. In fact, why not just use the relationship of  $\Delta^{17}\text{O}(\text{O}_3^*) = 1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ ? The latter would derive a lower  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  which is more consistent with Vicars and Savarino 2014.**

Regarding the point that we state  $(29.0 \pm 2.2) \text{‰}$  to be consistent with the values of  $(26.2 \pm 1.3) \text{‰}$ , in view of the uncertainty range, this is acceptable in terms of overlapping. However, although our mean value remains consistent with previous studies, we recognise that it is at the lower end of the SD of 29.0 ‰ and at the upper range of the SD of 26 ‰. To support the consistency of our derived  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  at  $(29.0 \pm 2.2) \text{‰}$  with the study of Vicars and Savarino (2014), we propose to add to the revised manuscript a comparison of our derived  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  with the measurements of Vicars and Savarino (2014) performed in February-March. Indeed, it is interesting to note that, over year-round measurements of  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  in Grenoble, France (120 km south-west of Chamonix), Vicars and Savarino (2014) reports a large peak of  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values in February-March, 2-3 ‰ greater than the annual mean of  $(26.2 \pm 1.3) \text{‰}$ . Although the reasons for the higher values at that period remain unknown, our derived  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  is surprisingly in very good agreement with the values reported for this period by Vicars and Savarino (2014). We have added this point to the revised manuscript (lines 484-495) as:

“Assuming that their maximum measured daytime  $\Delta^{17}\text{O}(\text{NO}_2)$  reflects the conversion of NO to NO<sub>2</sub> only through Reaction (R3) (i.e.,  $T_{\text{NO}+\text{O}_3} = 1$ ), Albertin et al. (2021) derived a  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  value of 39.2 ‰ from Eq. (3). Given the respective analytical uncertainties (around  $\pm 1 \text{‰}$ ), their value is in very good agreement with the maximum daytime value of 40.8 ‰ we observed in Chamonix. Similarly to Albertin et al. (2021), assuming that the highest daytime  $\Delta^{17}\text{O}(\text{NO}_2)$  value at our site corresponds to  $T_{\text{NO}+\text{O}_3} \approx 1$  leads to  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2) = 40.8 \text{‰}$ . Using the experimental  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  transfer function determined by Savarino et al. (2008), we estimate a bulk <sup>17</sup>O-excess of O<sub>3</sub> ( $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ ) at  $(29.0 \pm 2.2) \text{‰}$ . This value is consistent with the range of direct  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  measurements at mid-latitudes (mean of  $(26.2 \pm 1.3) \text{‰}$ ; Vicars and Savarino, 2014), although falling at the upper end of the range. Interestingly, Vicars and Savarino (2014) reported a significant peak in  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  during February-March in Grenoble, France (located 120 km southwest of Chamonix), based on year-round measurements with  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values 2–3 ‰ higher than the annual mean of 26.2 ‰. Although the cause of increased values during this period is unknown, our derived  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  matches remarkably well the February-March measurements reported by Vicars and Savarino (2014).”

Now, regarding the relationship of  $\Delta^{17}\text{O}(\text{O}_3^*) = 1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ , a clarification is needed because there is too much confusion on this, even in published literature.  $\Delta^{17}\text{O}(\text{O}_3^*)$  is defined as the  $\Delta^{17}\text{O}$  bears by the terminal atoms of O<sub>3</sub> (we can also find in the literature  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ ). It does not represent in any way the actual  $\Delta^{17}\text{O}$  transfer of O<sub>3</sub> to the species with which it reacts, in our case NO. The relation  $\Delta^{17}\text{O}(\text{O}_3^*) = 1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  is theoretically justified as well as observed in laboratory and follows

that the  $\Delta^{17}\text{O}$  is only borne by the terminal atoms of  $\text{O}_3$ . The  $\Delta^{17}\text{O}$  transfer from  $\text{O}_3$  to  $\text{NO}$  can only be equal to  $1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  if for example  $\text{NO}$  reacts only with the terminal atoms of  $\text{O}_3$ . Actually, the work of Savarino et al. (2008) did show that  $\text{NO}$  does not react only with the  $\text{O}_3$  terminal atoms, but also, albeit to a lower extent, with its central atom (probability of  $(8 \pm 5) \%$  for the abstraction of central atoms during the reaction  $\text{NO} + \text{O}_3$ ). As a result, the  $\Delta^{17}\text{O}$  transfer of  $\text{O}_3$  to  $\text{NO}$  is slightly lower than  $1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ . Therefore, one need to define the term  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  which represents the true  $\Delta^{17}\text{O}$  transfer during the reactions  $\text{NO} + \text{O}_3$  and this has been quantified by Savarino et al. (2008) with:

$$\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2) = (1.18 \pm 0.07) \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} + (6.6 \pm 1.5) \text{‰}$$

Unfortunately, the literature is very heterogeneous in the choice of the  $\Delta^{17}\text{O}$  transfer functions, mainly due to confusion in the definition of  $\Delta^{17}\text{O}(\text{O}_3^*)$ , which is wrongly associated with the transfer of  $\Delta^{17}\text{O}$  from  $\text{O}_3$  to  $\text{NO}$ . This is why, in the interests of clarification for the community and in order to minimise the uncertainties that can arise from a poor choice of  $\Delta^{17}\text{O}$  transfer function, we have added few lines on this to our revised manuscript (lines 471-482) as:

“At this point, it is important to recall that the choice of the  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  in Eq. (12) is of a particular importance for quantifying  $T_{\text{NO}+\text{O}_3}$  (as for  $\text{RO}_2$ ). In the literature,  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  varies between 35 ‰ and 41 ‰ (Michalski et al., 2003; Savarino et al., 2016; Vicars et al., 2012; Li et al., 2022; Zhang et al., 2022). This relatively wide range of values is partly a result of some confusion in defining  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$ , the  $\Delta^{17}\text{O}$  transfer from  $\text{O}_3$  to  $\text{NO}$ . Indeed, the term  $\Delta^{17}\text{O}(\text{O}_3^*)$  is sometimes erroneously used as the transfer function of  $\Delta^{17}\text{O}$  from  $\text{O}_3$  to  $\text{NO}_2$  during Reaction (R3).  $\Delta^{17}\text{O}(\text{O}_3^*)$  is actually defined as  $\Delta^{17}\text{O}$  of  $\text{O}_3$  terminal atoms and is also named  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$  in the literature. As the  $\Delta^{17}\text{O}$  in  $\text{O}_3$  is borne by its terminal atoms,  $\Delta^{17}\text{O}(\text{O}_3^*) = 1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ . However,  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  can be equal to  $1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  if only terminal atoms of  $\text{O}_3$  reacts with  $\text{NO}$ . But laboratory experiments by Savarino et al. (2008) did show that  $\text{O}_3$  does react with  $\text{NO}$  not solely with its terminal atoms but also, to a small but significant extent, with its central atom (probability of  $(8 \pm 5) \%$  for the abstraction of central atoms during the reaction  $\text{NO} + \text{O}_3$ ). Consequently,  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  is slightly lower than  $1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  and the  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)$  expression determined by Savarino et al. (2008) should be used:  $\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2) = 1.18 \pm 0.07 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} + (6.6 \pm 1.5) \text{‰}$ .”

- **Line 458: it should be  $\Delta^{17}\text{O}_{\text{NO}_2+\text{O}_3}(\text{NO}_3)$ ? Again, if considering terminal O transfer when reacting with  $\text{O}_3$ , why not simply using the relationship of 1.5? The transfer function  $\Delta^{17}\text{O}$  from  $\text{O}_3$  to  $\text{NO}$  and  $\text{NO}_2$  are different?**

Similarly to our comment above,  $\Delta^{17}\text{O}_{\text{NO}_2+\text{O}_3}(\text{NO}_3)$  can be associated to  $1.5 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  only if  $\text{O}_3$  reacts solely with  $\text{NO}_2$  with its terminal atoms. Berhanu et al. (2012) quantified this transfer in the gas phase and found :

$$\Delta^{17}\text{O}_{\text{NO}_2+\text{O}_3}(\text{NO}_3) = (1.23 \pm 0.19) \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} + (9.02 \pm 0.99) \%$$

However, it should be noted that, unlike reaction  $\text{NO} + \text{O}_3$ ,  $\text{O}_3$  do indeed reacts with  $\text{NO}_2$  almost entirely with its terminal atoms (see Berhanu et al., 2012 for more details).



## References

- Albertin, S., Savarino, J., Bekki, S., Barbero, A., and Caillon, N.: Measurement report: Nitrogen isotopes ( $\delta^{15}\text{N}$ ) and first quantification of oxygen isotope anomalies ( $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ) in atmospheric nitrogen dioxide, *Atmospheric Chemistry and Physics*, 21, 10477–10497, <https://doi.org/10.5194/acp-21-10477-2021>, 2021.
- Berhanu, T. A., Savarino, J., Bhattacharya, S. K., and Vicars, W. C.:  $^{17}\text{O}$  excess transfer during the  $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$  reaction, *The Journal of Chemical Physics*, 136, 044311, <https://doi.org/10.1063/1.3666852>, 2012.
- Li, Y., Shi, G., Chen, Z., Lan, M., Ding, M., Li, Z., and Hastings, M. G.: Significant Latitudinal Gradient of Nitrate Production in the Marine Atmospheric Boundary Layer of the Northern Hemisphere, *Geophysical Research Letters*, 49, e2022GL100503, <https://doi.org/10.1029/2022GL100503>, 2022.
- Michalski, G., Scott, Z., Kabling, M., and Thiemens, M. H.: First measurements and modeling of  $\Delta^{17}\text{O}$  in atmospheric nitrate., *Geophysical Research Letters*, 30, 1870, <https://doi.org/10.1029/2003GL017015>, 2003.
- Savarino, J., Bhattacharya, S. K., Morin, S., Baroni, M., and Doussin, J.-F.: The  $\text{NO}+\text{O}_3$  reaction: A triple oxygen isotope perspective on the reaction dynamics and atmospheric implications for the transfer of the ozone isotope anomaly, *J. Chem. Phys.*, 128, 194303, <https://doi.org/10.1063/1.2917581>, 2008.
- Savarino, J., Vicars, W. C., Legrand, M., Preunkert, S., Jourdain, B., Frey, M. M., Kukui, A., Caillon, N., and Roca, J. G.: Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign, *Atmos. Chem. Phys.*, 16, 2016.
- Vicars, W. C. and Savarino, J.: Quantitative constraints on the  $^{17}\text{O}$ -excess ( $\Delta^{17}\text{O}$ ) signature of surface ozone: Ambient measurements from  $50^\circ\text{N}$  to  $50^\circ\text{S}$  using the nitrite-coated filter technique, *Geochimica et Cosmochimica Acta*, 135, 270–287, <https://doi.org/10.1016/j.gca.2014.03.023>, 2014.
- Vicars, W. C., Bhattacharya, S. K., Erbland, J., and Savarino, J.: Measurement of the  $^{17}\text{O}$ -excess ( $\Delta^{17}\text{O}$ ) of tropospheric ozone using a nitrite-coated filter, *Rapid Communications in Mass Spectrometry*, 26, 1219–1231, <https://doi.org/10.1002/rcm.6218>, 2012.
- Zhang, Y.-L., Zhang, W., Fan, M.-Y., Li, J., Fang, H., Cao, F., Lin, Y.-C., Wilkins, B. P., Liu, X., Bao, M., Hong, Y., and Michalski, G.: A diurnal story of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in urban Nanjing and its implication for nitrate aerosol formation, *npj Clim Atmos Sci*, 5, 1–10, <https://doi.org/10.1038/s41612-022-00273-3>, 2022.