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Reply on RC1

Hao Xu et al.

Author comment on "Diagnosing the stratospheric proportion in tropospheric ozone using triple oxygen isotopes as tracers" by Hao Xu et al., Atmos. Chem. Phys. Discuss.,
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Dear Savarino,

Thank you very much for your valuable comments on our manuscript. We have responded to each of your comments and questions.

1) At no point in the article is the contradiction brought about by an interpretation involving ozone mixing from two regions of the atmosphere with radically different P and T conditions discussed. Indeed, it is well established that ozone formation and destruction are in dynamic equilibrium and that its isotopic composition is controlled by P and T conditions. Although the lifetime of ozone is a few days to a few weeks, at the molecular scale, ozone is destroyed and then reformed at the half-hour scale (i.e. $1/J(O_1D)$). Moreover, the isotopic exchanges resulting from the equilibrium $O + O_2 \leftrightarrow O_3^*$ are themselves 50 times faster than the stabilization of O_3^* into O_3 . Therefore, ozone is considered to be permanently in isotopic equilibrium with the environment in which it is found (Vicars 2014, Yeung 2012). As a result, stratospheric ozone entering the troposphere almost instantaneously acquires an isotopic composition corresponding to the P and T conditions of the troposphere. The interpretation of the $\Delta^{17}O$ peak observed in spring is therefore in contradiction with what we know about ozone formation and it is never discussed.

We will make the suggested revision and discuss it in Section 4.2. Because the $\Delta^{17}O_{\text{term}}(O_3)$ values in April were 2.2–4.6 ‰ greater than the annual mean, a significant increase when considering the ± 1 ‰ uncertainty associated with the analytical technique. Moreover, the $\Delta^{17}O$ of O_3 increased at high altitudes (Lyons, 2001). Furthermore, the significant correlation between 7Be data and $\Delta^{17}O_{\text{term}}(O_3)$ implies that the STT is highly responsible for the elevated $\Delta^{17}O_{\text{term}}(O_3)$ in the troposphere. However, as you point out, the $\Delta^{17}O_{\text{term}}(O_3)$ value of stratospheric O_3 changes rapidly when it enters the troposphere. Thus, to clarify the reasons for this contradiction, we must collect samples on the different altitudes of tropospheric O_3 in future studies (e.g., planetary boundary layer, free troposphere, upper troposphere).

2) On the other hand, since the sampling is not continuous but at the frequency of about one weekly collection per month, it is difficult to measure the natural variability of the isotopic composition of ozone, especially in spring when the stratospheric contributions are considered as maximum, and thus to see the

dynamics of this spring peak and its statistical significance between years.

Because the archived samples were precious and the measurements of the $\Delta^{17}\text{O}$ values of O_3 were costly and time-consuming, the number of samples for stable isotopes was limited to one weekly collection per month. Despite this, 210 $\Delta^{17}\text{O}$ values (all nitrite-coated filters) are reported in this manuscript (supplement). We repeated the analysis for each sample at least three times to attain high precision (see section 2.3). We hope our results, including these many data values, are worthy of publication. We will collect samples with higher frequency (in spring) and high-altitude resolution in future studies.

3) The interpretation of the diurnal variability based again on air-mass mixing could have been easily tested. I have no doubt that there is a possibility in Japan to install their very simple collection device at an altitude above the boundary layer and to test the hypothesis that the free troposphere has a higher $\Delta^{17}\text{O}$. This hypothesis is currently based on modeling work (Lyons, 2001) that has otherwise never been confronted with observation. Here the authors have missed an occasion to improve our understanding of the ozone isotopic composition and check the hypothesis they are using. Could for instance the difference between day and night been the result of the temperature difference alone? All chemical sinks of O_3 is currently considered as mass-dependent but is it true? For instance we know that the $\text{CO}+\text{OH}$ sink is not.

We appreciate the referee's comments. We will collect O_3 samples at different altitudes in future studies. Because the diurnal temperature variability is generally less than 10°C in Nagoya city. Moreover, isotopic enrichment ($\Delta^{17}\text{O}$) increases very slowly with increasing temperature (Krankowsky et al., 2007). Thus, we do not think the temperature is the main reason for the diurnal variation in $\Delta^{17}\text{O}_{\text{term}}(\text{O}_3)$. Because oxygen isotopic fractionations associated with the most important chemical reaction processes are mass-dependent, such as the reactions of $\text{NO} + \text{O}_3$ and $\text{NO}_2 + \text{O}_3$ (Berhanu et al., 2012; Chakraborty and Chakraborty, 2003; Savarino et al., 2008), we assumed that $\Delta^{17}\text{O}$ was almost stable during the sink of O_3 .

4) There may be some processes other than P & T that influence the ozone $\Delta^{17}\text{O}$. There is now a body of evidence (e.g. diurnal variation, seasonal maximum, hemispheric difference) that ozone isotopic composition varies well beyond what PBL P and T range allows but the isotopic equilibrium during ozone formation cannot be ignore in the discussion.

We will make the suggested revision and discuss it in Section 4.2.

5) In Vicars 2014, nitrogen isotopes of the nitrate produced by ozone is used as a quality check, and to correct ozone $\Delta^{17}\text{O}$ variability, why in Xu et al 2021 and in this paper, nitrogen isotopes are not reported? Checking $\Delta^{17}\text{O}$ versus 15N may reveals some artefacts.

In the study of Vicars and Savarino (2014), the single nitrite-coated filter method was corrected using nitrogen isotopes, because of nitrate blank produced (NaNO_2 reagent and $2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$ reaction) and the kinetic isotope fractionation (for $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$) during the collections. In this study, we used a multistep nitrite-coated filter-pack method developed by Xu et al. (2021) for the correction of nitrate blank produced ($2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$ reaction) and the kinetic isotope fractionation (for $\delta^{18}\text{O}$). Moreover, we found that the NO_3^- on the filters of the control group (only NaNO_2 reagent) was negligible at less than $0.08 \mu\text{mol}$, which was less than 1% on average of that produced by the reaction of NO_2^- and O_3 . Furthermore, Xu et al. (2021) also verified the accuracy of this method through the measurement of artificial O_3 with known $\Delta^{17}\text{O}_{\text{term}}(\text{O}_3)$ that had been determined from the changes in $\Delta^{17}\text{O}$ of O_2 . Thus, we did not measure the nitrogen

isotopes in this study.

6) A revised version where ozone formation is discussed in light of its isotopic equilibrium is definitely required before the paper can be published. Without it, it gives the false impression that interpretation $\Delta^{17}\text{O}$ of ozone is just a question of air-mass mixing.

We will make the suggested revision; the following sentences are added to the manuscript (Section 4.2).

Considering that the lifetime of O_3 is important for controlling the levels of tropospheric O_3 , variations in the isotopic lifetimes of the O_3 molecules are the potential factor to impact $\Delta^{17}\text{O}$ values of O_3 . Although the chemical lifetime of the O_3 molecule can be of the order of months, the isotopic lifetime will generally be much shorter (Johnston and Thiemens, 1997; Vicars and Savarino, 2014; Yeung et al., 2012). Previous studies have suggested that the isotopic lifetime of the O_3 molecule is approximately 30 min in the daytime by measuring the absolute O_3 photolysis frequency, $j(\text{O}^3\text{P})$; however, in the absence of photolytic cycling, the isotopic lifetime of O_3 is extended at night (Vicars and Savarino, 2014). The new O_3 molecules formed through the photolytic cycling depend only on local temperature and pressure, which determine the isotope enrichments. As a result, stratospheric O_3 entering the troposphere may lose the isotopic compositions of the original O_3 . However, the $\Delta^{17}\text{O}_{\text{term}}(\text{O}_3)$ values in April were 2.2–4.6 ‰ greater than the annual mean, a significant increase when considering the $< \pm 1$ ‰ uncertainty associated with the analytical technique. Moreover, the significant correlation between ^7Be data and $\Delta^{17}\text{O}_{\text{term}}(\text{O}_3)$ implies that the STT is highly responsible for the elevated $\Delta^{17}\text{O}_{\text{term}}(\text{O}_3)$ in the troposphere (see Section 4.3). Thus, to clarify the reasons for this contradiction, we must collect samples on the different altitudes of tropospheric O_3 in future studies (e.g., planetary boundary layer, free troposphere, upper troposphere).

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