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主 論 文 の 要 旨

論文題目 Determination on the triple oxygen isotopic composition of tropospheric ozone

(対流圏オゾンの三酸素同位体組成定量)

氏 名 許 昊

論 文 内 容 の 要 旨

About 90% of ozone (O_3) is in the stratosphere, with only about 10% in the troposphere. The tropospheric O_3 , however, causes harmful effects on human health and plants. It has been identified as a major greenhouse gas as well. Additionally, tropospheric O_3 and its byproducts, such as hydroxyl radicals, play essential roles in controlling oxidizing capacity of the troposphere and thus controlling oxidation pathways of trace gases, such as NO_x ($NO_x = NO + NO_2$) and SO_2 .

Because the stratosphere is a large reservoir of O_3 , stratosphere-troposphere transport (STT) is one of the most important factors controlling the levels of tropospheric O_3 . However, the STT events are sporadic and not well characterized. Therefore, to better understand the factors controlling the levels of tropospheric O_3 , I must clarify the origin and behavior of O_3 in the troposphere, especially the temporal changes in STT.

Traditionally, radionuclide Beryllium-7 (7Be ; half-life of 53.3 days) has been used to trace stratospheric O_3 in the troposphere. Because of its short half-life and well-

defined source term, the naturally occurring radionuclide ^7Be can be a sensitive indicator for quantifying the influence of STT in each tropospheric air. However, besides STT, both the long-range transport and in-situ photochemical reactions (such as the photolysis of NO_2) are responsible for the concentration of tropospheric O_3 . Therefore, the correlations between the concentrations of tropospheric O_3 and ^7Be are often unclear. As a result, it was difficult to quantify the influence of STT on tropospheric O_3 .

The stable isotopic compositions of the trace gases have been widely used to identify the origin and the oxidation mechanisms of these gases. Unique and distinctive triple oxygen isotopes ($\Delta^{17}\text{O}$) of O_3 provide a powerful tool in studies of the origin and behaviors of O_3 , particularly in the mixing from the stratosphere. However, due to (i) the low O_3 collection efficiency and the interference of atmospheric Xe using the cryogenic trapping technique (ii) and significant nitrate blank produced ($2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$) using the single nitrite-coated filter method, it is difficult to quantify an accurate $\Delta^{17}\text{O}$ of O_3 from ambient air using these two classical methods.

Here, I developed a method to determine the triple oxygen isotopic composition ($\Delta^{17}\text{O}$) of tropospheric O_3 in the terminal positions [$\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$] using a multistep nitrite-coated filter-pack system by transferring the O-atoms in the terminal positions of O_3 to nitrite on each filter ($\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$). The NO_3^- produced by this reaction is chemically converted to N_2O , and continuous-flow isotope ratio mass spectrometry (CF-IRMS) is used to determine the oxygen isotopic compositions. Artificial O_3 gas with known oxygen isotopic compositions was also

measured to verify the accuracy of the $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ obtained using my filter-pack system.

Then by using this new method, I measured the $\Delta^{17}\text{O}$ of tropospheric O_3 at Niigata and Nagoya of Japan from 2017 to 2020. By using the relationship between the reciprocal of concentrations and $\Delta^{17}\text{O}_{\text{term}}$ of tropospheric O_3 , I estimated the $\Delta^{17}\text{O}$ of stratospheric O_3 supplied through the STT ($\Delta^{17}\text{O}_{\text{STT}}$), together with that produced through the photochemical reactions at surface altitude ($\Delta^{17}\text{O}_{\text{sur}}$). Moreover, using the $\Delta^{17}\text{O}_{\text{STT}}$ and $\Delta^{17}\text{O}_{\text{sur}}$, I estimated the mixing ratios of stratospheric O_3 (i.e., O_3 produced in stratosphere and supplied to troposphere through STT) in each tropospheric O_3 (f_{STT}), as well as the absolute concentrations of stratospheric O_3 supplied through STT in troposphere ($[\text{O}_3]_{\text{STT}}$).

As a result, the reciprocal of the NO_3^- quantities on the nitrite-coated filters in each sample showed a strong linear relationship with $\Delta^{17}\text{O}$ of NO_3^- . Using the linear relation, I corrected the changes in $\Delta^{17}\text{O}$ of NO_3^- on the filters owing to nitrate blank. I verified the accuracy of this new method by measuring artificial O_3 with a known $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ determined from the changes in $\Delta^{17}\text{O}$ of O_2 . Moreover, my new method provided a reliable $\delta^{18}\text{O}$ of O_3 in the terminal positions from which the kinetic isotope fractionation associated with O_3 collection on filters had been corrected successfully. Therefore, I conclude that the multistep nitrite-coated filter-pack system technique is a sufficiently robust and reliable method for accurately and precisely determining the oxygen isotopic compositions of tropospheric O_3 .

The $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ determined in this study [$+37.5 \pm 1.4\text{‰}$ (1 σ) for Nagoya; $+37.0 \pm 1.6\text{‰}$ (1 σ) for Niigata] was in agreement with previous studies. Moreover,

measurements of $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ showed $1.3 \pm 0.7\%$ (1 σ) diurnal variations between daytime (higher) and nighttime (lower) in Nagoya, due to the formation of the stable boundary layer during nighttime, which hindered the vertical convection in the troposphere.

The $\delta^{18}\text{O}$ of O_3 in terminal positions ($\delta^{18}\text{O}_{\text{term}}$) determined in this study was somewhat higher than the previous studies. The kinetic isotope fractionation during the collection was responsible for this discrepancy. Moreover, The isotope enrichment factors (ϵ) determined through my multistep nitrite-coated filter-pack method ($-7.5 \pm 1.6\%$) implied that the kinetic isotope fractionation during the collections on the filters was considerable.

Additionally, I found a significant normal correlation between ^7Be concentrations and $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$, implying that the STT process was highly responsible for the elevated $\Delta^{17}\text{O}_{\text{term}}$ of O_3 in the troposphere, especially in April. Moreover, the $[\text{O}_3]_{\text{STT}}$ exhibited minimum values in summer (5.3 ± 1.0 ppb) and maximum in late winter to spring (15.9 ± 2.1 ppb). Although the f_{STT} values were higher than those estimated using the chemistry climate models in past studies, the trend of the seasonal variations was consistent with them. I concluded that the $\Delta^{17}\text{O}$ successfully provided observational constraints on the STT of O_3 . Overall, my study provided an observational constraint on STT of O_3 using this new index, and such identification of the transport processes provides an important basis for a better understanding of the O_3 behavior in the troposphere.