Determination on the triple oxygen isotopic compositions of tropospheric ozone

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Tropospheric ozone (O_3) is important as a greenhouse gas, as well as having harmful effects on respiration and photosynthesis. In addition, O_3 is important as an oxidant in the tropospheric photochemical reactions. In recent years, tropospheric ozone have been increasing in Eastern Asia, and thus we must understand the origin and behavior of tropospheric ozone accurately.

In this study, we determined the oxygen isotopic compositions including the triple oxygen isotopic compositions ($\Delta^{17}O$), by passing air sample through nitrite (NO_2^-)-coated filters, which allows the reaction of O_3 with NO_2^- to produce NO_3^-. The oxygen isotopic composition of $NO_3^-$was then determined to estimate the oxygen isotopic composition of O_3. To remove atmospheric HNO_3 prior to the reaction between O_3 and NO_2^-, nylon filters were placed before the nitrite-coated filters. In order to obtain a high collection efficiency for the reaction between O_3 and NO_2^-, the O_3 collection was conducted at a flow rate less than 0.5L/min. The NO_2^- on the filter was removed by adding hydrogen azide (N_3H) which selectively converts NO_2^- to N_2O. Then, NO_3^- was converted to N_2O, which is converted to O_2 to be injected into an isotope mass spectrometer (MAT252), allowing quantification on the $\Delta^{17}O$ value of NO_3^-. From the values determined for NO_3^-, the oxygen atoms derived from NO_2^- was subtracted to determine the oxygen isotopic compositions of O_3. Please note that the oxygen isotopic composition determined through this method is not the average isotope composition of oxygen atoms in O_3 ($\Delta^{17}O\ (O_3)_{bulk}$), but is the isotope composition of the oxygen atoms in the terminal positions ($\Delta^{17}O\ (O_3)_{terminal}$) of O_3.
Observation on the atmospheric O_3 was conducted from August to December, 2017, at Nagoya University. The $\Delta^{17}O$ values of ozone were between +32‰~+39‰ which coincided well with those previously determined for tropospheric ozone (35‰±4‰). Besides, the $\Delta^{17}O$ values of ozone were the lowest in August, and were the highest in November. The seasonal variation in the $\Delta^{17}O$ values is most likely due to the stratospheric influence on the tropospheric O_3. We also found about 1‰ differences in the $\Delta^{17}O$ values between day and night. We concluded that the formation of an inversion layer in night time was responsible for the lower $\Delta^{17}O$ values. That is to say, while the ^{17}O-depleted O_3 produced at ground level heights under the high pressure condition occupied major portion of O_3 in night time due to the inversion layer, the ^{17}O-enriched O_3 produced at the upper layers contributed to O_3 in day time through the active vertical convection.

Keywords: ozone, triple oxygen isotopic composition, troposphere

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