

Determination on ^{17}O -excess ($\Delta^{17}\text{O}$) of tropospheric ozone using a multi-step nitrite-coated filter pack system

Running Head : Filter pack system for the isotopic compositions of tropospheric ozone

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RATIONALE: The oxygen-17 excess ($\Delta^{17}\text{O}$) of tropospheric ozone (O_3) is useful as a tracer to identify the source of O_3 . Additionally, $\Delta^{17}\text{O}$ of tropospheric O_3 is essential to clarify the atmospheric chemistry of the oxidants, such as the nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and sulfur dioxide (SO_2) in the atmosphere, because ^{17}O -excess in the oxides is a function of that in O_3 . The current method for measuring $\Delta^{17}\text{O}$ of O_3 used a single nitrite-coated filter to transfer the oxygen atoms of O_3 to nitrate (NO_3^-). However, we found that the $\Delta^{17}\text{O}$ values determined by the method were often inaccurate due to nitrate blank produced through the reaction between nitrite and some oxygen compounds other than O_3 . We present an improved approach for the accurate measurement of the oxygen isotopic compositions ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) of tropospheric O_3 using nitrite-coated filters. We also

20 present a method to calibrate the $\Delta^{17}\text{O}$ of O_3 in this study.

METHODS: The multi-step nitrite-coated filter pack system was newly adopted to transfer the oxygen atoms in the terminal positions of O_3 to nitrite on each filter to determine the oxygen isotopic compositions of O_3 in the terminal positions (denoted as $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$). The NO_3^- produced by this reaction was chemically converted to N_2O , followed by continuous-flow isotope ratio mass spectrometry (CF-IRMS) to determine the stable oxygen isotopic compositions.

RESULTS: The reciprocal of the NO_3^- quantities on the multi-step nitrite-coated filters in each sampling showed a strong linear relationship with $\Delta^{17}\text{O}$ of NO_3^- . Using the linear relation, we corrected the changes in $\Delta^{17}\text{O}$ of NO_3^- on the filters due to the contribution of nitrate blank and determined the accurate $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$. The $\delta^{18}\text{O}$ values of O_3 were estimated using a method for correcting for changes in $\delta^{18}\text{O}$ due to the nitrate blank contribution and the Rayleigh fractionation during the nitrite oxidation. We also clarified that the $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values determined using the new method to be accurate by measuring the O_3 produced artificially in our laboratory, based on the changes in $\Delta^{17}\text{O}$ values of O_2 before and after the O_3 production. The $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values determined for ambient tropospheric O_3 in mid-latitudes were in good agreement with these reported in previous studies.

CONCLUSIONS: This new method using the multi-step nitrite-coated filter pack system enabled us to obtain accurate $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of tropospheric O_3 , particularly through the blank correction. Measurements on the $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values of the ambient troposphere on day-night separation clarified

significant diurnal variations: higher in daytime and lower in nighttime, probably due to the formation
40 of the temperature inversion layer at night.

1. INTRODUCTION

Tropospheric ozone (O_3) together with its byproducts such as hydroxyl radical (OH) and nitrate
radical (NO_3), plays an essential role as an oxidant, which controls the oxidizing capacity of the
troposphere and the lifetimes of the most reduced trace gases (Thompson, 1992; Finlayson-Pitts and
45 Pitts, 1997). It also has harmful effects on respiration (Zhang et al., 2019) and photosynthesis in
plants (Reich and Amundson 1985). Moreover, tropospheric O_3 is important as a greenhouse gas as
well. Reduction in the concentration of tropospheric O_3 attracts attention as an effective measure to
mitigate near-term climate change (Hansen and Sato, 2001; UNEP and WMO, 2011). Therefore, it
is essential to understand the origin and behavior of O_3 in the troposphere.

50 Tropospheric O_3 is produced through a complex series of reactions involving the photochemical
cycling of nitrogen oxides ($NO_x = NO + NO_2$) and hydrocarbons (Logan 1985). As a result, the
distribution of O_3 is heterogeneous spatially and temporally in the troposphere, reflecting both
anthropogenic and natural activities at the surface (Logan 1985; Hauglustaine and Brasseur 2001).
Additionally, O_3 transport from the stratosphere also significantly impacts on the spatiotemporal
55 variations in tropospheric O_3 (Husain et al., 1977; Cristofanelli et al., 2003; Hsu et al., 2005).

Stable isotopic compositions of atmospheric trace gases have been widely used as tracers to clarify
the sources and behaviors (e.g., Thiemens et al., 1983; Kendall, 1998; Whiticar, 1999; Thiemens,

1999; Hoag et al., 2005; Kendall et al., 2007). For instance, in the case of atmospheric nitrate, both $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios have been used as tracers to clarify the sources and behaviors (Durka et al., 1994; Kendall, 1998; Kendall et al., 2007). Besides, the ^{17}O -excess of atmospheric nitrate has been used as a unique and robust tracer of the reaction path from NO to nitrate in recent years (Brenninkmeijer et al., 2003; Morin et al., 2008; Alexander et al., 2009). The ^{17}O -excess of atmospheric nitrate has been applied as a robust tracer to quantify nitrate dynamics in the biosphere (Michalski et al., 2004; Tsunogai et al., 2010) and hydrosphere (Tsunogai et al., 2011; Tsunogai et al., 2018) as well because ^{17}O -excess of nitrate is almost stable during biological processing. To promote these studies using ^{17}O -excess as a tracer, we must quantify the ^{17}O -excess of tropospheric O_3 , together with the temporal variations, accurately and precisely, because tropospheric O_3 characterized by the ^{17}O -excess significantly deviated from the other most terrestrial oxygen molecules, as well as a major source of the ^{17}O -excess found in atmospheric nitrate (Lyons 2001; Thiemens 2006). Additionally, the oxygen isotopic compositions of tropospheric O_3 can be a useful tracer to identify the sources and variations, especially for mixing stratospheric O_3 (Krankowsky et al., 2000; Lyons 2001; Vicars and Savarino, 2014).

Two methods were reported to determine oxygen isotopic compositions of tropospheric O_3 under the concentration parts per billion (ppb) level, including $\Delta^{17}\text{O}$. The classical method used the cryogenic trapping technique to isolate O_3 in the air from oxygen gas (O_2) and converted O_3 to O_2 for the measurements using isotope ratio mass spectrometry (IRMS) (Krankowsky et al., 1995; Johnston

and Thiemens, 1997). The oxygen isotopic compositions of O₃ determined through the classical method, however, can sometimes be inaccurate due to the low O₃ collection efficiency and the interference in IRMS from atmospheric xenon (Brenninkmeijer et al., 2003). Vicars et al. (2012) developed an alternative new method, in which the oxygen atoms in the terminal positions of O₃ were transferred to nitrite ($\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$) on a nitrite-coated filter and the oxygen isotopic composition of O₃ were estimated from nitrate produced on the filter. The NaNO₂ reagent used to coat the filter for O₃ collection, however, usually contains significant nitrate (Vicars et al., 2012; Vicars and Savarino, 2014). Besides, the gaseous nitrate in the air could be gathered on the nitrite-coated filter during the O₃ collection and mixed with O₃-derived nitrate (Vicars et al., 2012; Vicars and Savarino, 2014). Furthermore, our preliminary experiments clarified that a significant quantity of nitrate blank was produced on the nitrite-coated filters during O₃-free air collection, probably due to the reaction between nitrite and atmospheric O₂ ($2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$). As a result, it was difficult to quantify the accurate value for $\Delta^{17}\text{O}(\text{O}_3)$ from nitrate gathered on a single nitrite-coated filter.

In this study, we used a multi-step nitrite-coated filter-pack system instead to collect O₃ in the air. In this system, the same O₃ collected on different filters as nitrate, which enabled us to correct for the changes in oxygen isotopic compositions due to the contribution of nitrate blank, such as that derived from NaNO₂ reagent, atmospheric O₂, and the other possible contamination sources and to determine $\Delta^{17}\text{O}(\text{O}_3)$ in the troposphere accurately. Because the $\Delta^{17}\text{O}$ value of O₃ should be stable during the

partial removal reaction on each nitrite-coated filter, we can quantify the nitrate blank by changing the quantities of O₃ collected on the multi-step filters. Here we report details of the new collection system. Moreover, to confirm Δ¹⁷O(O₃) accuracy determined through our filter-pack system, we analyzed the Δ¹⁷O(O₃) with the known oxygen isotopic compositions. We determined these in
100 ambient tropospheric O₃ as well.

2. EXPERIMENTAL

2.1 Definitions

The stable isotopic compositions of O₃ are presented by its δ¹⁷O (or δ¹⁸O) values calculated from
105 $R_{\text{sample}} / R_{\text{standard}} - 1$, where R_{sample} demotes ¹⁷O/¹⁶O ratio (or ¹⁸O/¹⁶O ratio) in sample and R_{standard} demotes that of the standard reference material (Vienna standard mean ocean water, VSMOW). Because the oxygen isotopic compositions of O₃ were determined from those of nitrate produced via NO₂⁻ + O₃ reaction, we use the Δ¹⁷O signature (the magnitude of ¹⁷O-excess) defined by the following equation (Miller, 2002; Kaiser et al., 2007):

$$\Delta^{17}\text{O} = \frac{1 + \delta^{17}\text{O}}{(1 + \delta^{18}\text{O})^\beta} - 1$$

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(1)

where the constant β is 0.5279 (Kaiser et al., 2007), which have been often used for the Δ¹⁷O values of NO₃⁻ (Kaiser et al., 2007; Tsunogai et al., 2016; Nakagawa et al., 2018; Nelson et al., 2018).

Please note that the $\Delta^{17}\text{O}$ values defined by the power-law (Eq. 1) are different from those defined
115 by the linear definition ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) used for O_3 in many of the previous studies
(Vicars et al., 2012; Vicars and Savarino, 2014). Our $\Delta^{17}\text{O}$ values of O_3 would have been $1.4 \pm$
0.08 ‰ higher if we had used this linear definition for calculation. Compared with the linear
definition, $\Delta^{17}\text{O}$ values based on the power-law definition are more stable during 'mass-dependent'
isotope fractionation processes (Kaiser et al., 2007). Thus, we used the $\Delta^{17}\text{O}$ values as always stable
120 irrespective to the progress of any partial removal reactions, such as reaction between O_3 and nitrite
($\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$). As a result, we can obtain the accurate $\Delta^{17}\text{O}$ values of O_3 from those of
 NO_3^- based on the power-law definition. On the other hand, variations in the $\Delta^{17}\text{O}$ values based on
the power-law definition are nonlinear distributions during mixing processes between fractions
having different $\Delta^{17}\text{O}$ values. In the calculation done in this study, the deviations in the $\Delta^{17}\text{O}$ values
125 of O_3 , however, were less than 0.2‰. Because these deviations are smaller than the standard error
in the determinations on the $\Delta^{17}\text{O}$ values of O_3 , we disregarded this effect in our discussions.

2.2 Principle of O_3 collection

In this study, tropospheric O_3 was collected by passing air through the multi-step nitrate-coated
filter-pack system, in which O_3 reacted with nitrite (NO_2^-) in the aqueous phase to form nitrate
130 (NO_3^-):



Details of the $\text{NO}_3^- + \text{O}_3$ reaction have been studied well (Liu et al., 2001; Michalski and Bhattacharya, 2009; Vicars et al., 2012). They clarified the reaction rates of NO_2^- with O_3 were rapid, especially in the alkaline solution (Liu et al., 2001). Additionally, the oxygen exchange reaction rate between NO_3^- and water is negligibly small at pH above 7 (Kaneko and Poulson, 2013). Moreover, Liu et al. (2001) and Bhattacharya (2009) clarified that only the oxygen atom in the terminal positions of O_3 reacts with NO_2^- . As a result, $\Delta^{17}\text{O}$ of O_3 in the terminal positions ($\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) can be estimated from that of NO_3^- produced on nitrite-coated filters via the reaction R1.

140 **2.3 Reagents preparation and multi-step nitrite-coated filter pack system**

The NO_2^- solution to coat glass fiber filters (ADVANTEC® GB-100R) was prepared following the method described in Vicars et al. (2012) adding slight modifications. The coating solution (0.15 mol L⁻¹ NaNO_2 , 0.2 mol L⁻¹ Na_2CO_3 , and 0.04 mol L⁻¹ glycerol) was prepared using the reagents with the purities of more than 98.5%, 99.8%, and 99.5% for NaNO_2 , Na_2CO_3 , and glycerol, respectively. The glass fiber filters, rinsed twice with Milli-Q water and dried using a filter paper (ADVANTEC® No. 590) to remove extra water, were immersed into the 500 mL of the coating solution for 3 minutes. The extra coating solution on the coating filters was then removed using the filter paper. At this time, the coating filters were covered with more than 100 μmol of NO_2^- , more than 10 times of the quantities needed to react with O_3 . They were then immediately placed in sterile plastic Petri dishes, sealed in aluminum bags, and stored at 4 °C for up to two months until

sampling. One nitrite-coated filter per batch (control group) was just stored without sampling to quantify the nitrate blank on the nitrite-coated filter derived from the NaNO_2 reagent used in the coating solution.

Based on the methods outlined by [Noguchi et al. \(2007\)](#), [Vicars et al. \(2012\)](#), and [Hayasaka et al. \(2014\)](#), a five-stage filter pack system was constructed and used for O_3 collection ([Fig. 1](#)). The first and second stages of the filter pack system were $0.45 \mu\text{m}$ Nylon filters (PALL ULTIPOR N66-NX047100) that collected particulate nitrate, gaseous nitrate, SO_2 , HCl , HONO , NH_3 , and NO_2 . Then O_3 was collected by the nitrite-coated filters via aqueous-phase reaction with NO_2^- at the third (F1), fourth (F2), and fifth stages (F3; [Fig. 1](#)).

160 **2.4 Ambient ozone collections**

In this study, tropospheric O_3 samples were obtained from the outside of our laboratory building in Nagoya, Japan ($35^\circ 9' 7'' \text{ N}$, $136^\circ 58' 19'' \text{ E}$, $\sim 67 \text{ m a.s.l.}$) once every month from September 2017 to May 2018. Nagoya is located on the Pacific coast of central Japan, with a population size of ~ 2.3 million (density: $\sim 7133 \text{ people km}^{-2}$). The tropospheric O_3 in the ambient air was collected using the multi-step nitrite-coated filter pack system ([Fig. 1](#)) under the flow rate of 3.0 L min^{-1} for one week during daytime and nighttime ($n = 18$) separately to capture possible diurnal variations in $\Delta^{17}\text{O}$ of O_3 . The daytime period started at 6:00 a.m. and ended at 6:00 p.m., and nighttime period started at 6:00 p.m. and ended at 6:00 a.m., respectively.

To determine the isotopic compositions of nitrate blank produced on nitrite-coated filters during
170 sampling, additional air collections were performed under the flow rate of 1.5 L min⁻¹ for two
weeks (n = 3). The collections were conducted by connecting an activated carbon pre-filter (4-8 mm
mesh, 48mm diameter, 212mm long, 3001-17201 GL Sciences Inc., Japan) before the multi-step
nitrite-coated filter pack system to remove O₃ in the air (Metts and Batterman, 2006).

After each collection period, NO₃⁻ on the nitrite-coated filters were extracted to 400 mL of Milli-
175 Q water, passed through a 0.2 μm filter, and stored at 4 °C until the measurements of concentrations
and isotopic compositions of NO₃⁻.

2.5 Experiments using an electrochemical ozone generator

By introducing ultrahigh-purity O₂ (> 99.99995 vol. % purity; Japan Fine Products, Japan) into
an ozone generator (ED-OG-R6, Ecodesign-Labo Co., Japan) under the flow rate of 15 mL min⁻¹,
180 highly concentrated O₃ in O₂ stream (ca. 5%) was produced via electrical discharge under a fixed
pressure (0.15 MPa) and temperature (293K). To check the accuracy of the oxygen isotopic
compositions of O₃ determined using our multi-step nitrite-coated filter pack system, we determined
O₃ isotopes produced by the ozone generator independently through two different methods.

Warm-up operation of the ozone generator was operated for 10 min. Then, the highly
185 concentrated O₃ stream was introduced into the multi-step nitrite-coated filter pack system to collect
O₃ (flow path A of Fig. 2) via Teflon-PFA tubing connected to the outlet of the O₃ generator under
the flow rate of 15 mL min⁻¹ for 30 min. Then, NO₃⁻ on the filters were immediately extracted with

Milli-Q water and stored at 4 °C until the measurements in a similar manner with the ambient ozone samples.

190 Additionally, we also determined the oxygen isotopic compositions of O₃ produced by the ozone generator through the changes in the oxygen isotopic compositions of O₂. To remove O₃ in the O₂ stream eluted from the outlet of the O₃ generator, the outlet was introduced into a traditional gas-washing bottle containing 300 mL of NO₂⁻ solution using a PFA tubing (flow path B of Fig. 2). The NO₂⁻ solution was prepared following the method present in section 2.3 adding slight modifications
195 of the composition (0.15 mol L⁻¹ NaNO₂ and 0.2 mol L⁻¹ Na₂CO₃). The water vapor in the O₂ stream was removed by passing a dry ice-ethanol trap, and the quantity of total O₂ that passed through the trap was measured using a flowmeter (MC-3102E-NC, LINTEC, Co., Ltd.; flow path B of Fig. 2) with an analog input integration (CU-651-A4, UINICS Co., Ltd., Japan). Then a portion of O₂ was collected using a glass bottle with two stopcocks for the measurements on the oxygen
200 isotopic compositions of O₂ (flow path B of Fig. 2). Besides, the NO₂⁻ solution was diluted 100 times with Milli-Q water and stored in polyethylene bottles under the refrigeration (4 °C) until analysis on both concentrations and the oxygen isotopic compositions.

2.6 O₂ analysis

The oxygen isotopic compositions ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) of O₂ samples obtained in the experiments
205 using the ozone generator were determined precisely by using a MAT 252 system in dual-inlet mode at Nagoya University. The output of the major signals (m/z 32) was arranged to be 4.0 V for

both sample and our working standard O₂ (> 99.99995 vol. % purity; TAIYO NIPPON SANSCO Co., Ltd., Tokyo, Japan) in the reference side throughout the runs. The output signals of m/z 18, 28, 32, and 40 were determined as well to confirm the purities of O₂. Each sample was measured 3
210 times with each time having 30 cycles to obtain higher precisions.

The oxygen isotopic compositions of the working standard O₂ ($\delta^{17}\text{O} = +8.20 \pm 0.01\text{‰}$ vs. VSMOW, $\delta^{18}\text{O} = +16.24 \pm 0.02\text{‰}$ vs. VSMOW, 1 σ) had been calibrated on the VSMOW-SLAP scale by analyzing the working standard O₂ relative to three different O₂ gases which had been converted from our intra-laboratory H₂O standards quantitatively through the reaction with BrF₅ at
215 250°C for 1 hour. The oxygen isotopic compositions of the intra-laboratory H₂O standards had been calibrated on the VSMOW-SLAP scale using a cavity ring-down spectrometer (L2140-i, Picarro Inc., Santa Clara, CA, USA). All the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values were normalized to VSMOW scale.

2.7 Analysis of nitrate and nitrite

The concentrations of both NO₃⁻ and NO₂⁻ were measured simultaneously by ion chromatography
220 (Prominence HIC-SP, Shimadzu, Japan) within a few days after the sampling. The error (standard error of the mean) in the determined concentration was $\pm 3\%$. NO₂⁻ occupied more than 76 % of the total (NO₂⁻ + NO₃⁻) in the samples obtained during the experiments using the O₃ generator, and more than 80 % in the samples of ambient air.

To determine the stable isotopic compositions of NO₃⁻, NO₃⁻ in each sample solution was
225 chemically converted to N₂O by using the method originally developed to determine the $\delta^{18}\text{O}$ of

NO_3^- (McIlvin and Altabet, 2005) with several modifications for $\Delta^{17}\text{O}$ (Tsunogai et al., 2008, 2016).

The procedures were as follows. Approximately 10 mL of each solution was pipetted into a vial with butyl rubber caps. To increase the reaction rate (McIlvin and Altabet, 2005), sodium chloride (NaCl) was added until the final concentration was 0.5 mol L^{-1} . The solution was then added with
230 0.45 mL of an azide-acetic acid buffer ($0.1 \text{ mol L}^{-1} \text{ NaN}_3$ in 1% vol. acetic acid), which had been purged using high purity helium for 45 min. Subsequently, the vials were shaken for 1 h at a rate of 2 cycles s^{-1} , and then purged using high-purity helium again for 1.5 min to remove N_2O produced through the reaction of $\text{NO}_2^- + \text{HN}_3 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$. Then, 0.5 g of spongy cadmium was added, followed by $200 \mu\text{L}$ of a $1 \text{ mol L}^{-1} \text{ NaHCO}_3$ solution. The vials were shaken for 20 h at a rate of 2
235 cycles s^{-1} . Then, each solution was decanted into a different glass with a septum cap. After re-purging the solution using high purity helium for 3 min., 0.45 mL of an azide-acetic acid buffer ($1 \text{ mol L}^{-1} \text{ NaN}_3$ in 10 % vol. acetic acid) was added again. After 1 hour, the solution was made basic by adding 0.225 mL of $8 \text{ mol L}^{-1} \text{ NaOH}$.

To determine the stable isotopic compositions of NO_2^- , NO_2^- in solution samples were diluted to a
240 concentration of approximately $40 \mu\text{mol L}^{-1}$. Then, 0.3 g of NaCl and $150 \mu\text{L}$ of $1 \text{ mol L}^{-1} \text{ NaHCO}_3$ solution were added into the NO_2^- solution samples in 10 mL vials. After purging the solution with high-purity helium for 3 min., both the azide-acetic acid buffer and NaOH were added in a similar manner with the samples of NO_3^- .

The stable isotopic compositions ($\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$) of N_2O converted from NO_3^- or NO_2^- in each
245 vial were determined using a continuous-flow IRMS (CF-IRMS) system. The analytical procedures
using the CF-IRMS system were the same as those detailed in previous studies (Komatsu et al.,
2010; Hirota et al., 2010). We repeated the analyses for each solution sample at least three times to
attain high precision on the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values. The standard error of the mean was better than \pm
0.5 ‰ for $\delta^{18}\text{O}$, and ± 0.2 ‰ for $\Delta^{17}\text{O}$. The obtained $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of NO_3^- were normalized
250 to VSMOW scale using local laboratory nitrate standards calibrated against the international
standards of USGS34 and USGS35 (Nakagawa et al., 2013; Tsunogai et al., 2014, 2018). The
obtained $\Delta^{17}\text{O}$ values of NO_2^- were normalized to VSMOW scale as well, assuming that the changes
in $\Delta^{17}\text{O}$ values were negligible during the chemical conversion from NO_2^- to N_2O .

To calibrate the $\delta^{18}\text{O}$ values of NO_2^- , we prepared three nitrite reagents as the intra-laboratory
255 standards: STD1 (sodium nitrite, purity > 98.5%, JUNSEI Chemical Co., code: 10285-0301), STD2
(sodium nitrite, purity $\geq 99.0\%$, ACS, Reag. Ph Eur, code:106549), and STD3 (sodium nitrite,
99.5% purity, Sigma-Aldrich, code: 524379), the $\delta^{18}\text{O}$ values of which had been determined
through thermal conversion into carbon monoxide (CO) in a glassy carbon tube at 1400°C using a
thermal conversion/elemental analyzer isotope ratio mass spectrometer (TC/EA-IRMS; DELTA V
260 PLUS; Thermo Fisher Scientific) in SHOKO Science Co. Ltd. in Japan. The $\delta^{18}\text{O}$ values of the
intra-laboratory standards had been calibrated on the VSMOW scale by analyzing the international

nitrate standards of USGS34 and IAEA-NO-3 in a similar manner with the intra-laboratory standards.

2.8 Calculation

265 To estimate the $\Delta^{17}\text{O}$ of O_3 , we first measured the oxygen isotopic compositions of NO_3^- on each nitrite-coated filter of the filter pack system ($\Delta^{17}\text{O}(\text{NO}_3^-)_m$). Then, we obtained the oxygen isotopic compositions of NO_3^- produced via the reaction R1 ($\Delta^{17}\text{O}(\text{NO}_3^-)_c$) from which changes in $\Delta^{17}\text{O}$ due to the contribution of nitrate blank had been corrected, as the intercept of the linear relationship between reciprocal of the measured quantity NO_3^- ($1/[\text{NO}_3^-]_m$) and $\Delta^{17}\text{O}(\text{NO}_3^-)_m$ on each nitrite-
270 coated filter (Fig. 4) through least squares fitting of a straight line, assuming that the quantities and oxygen isotopic compositions ($\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$) of nitrate blank on each nitrite-coated filter of our multi-step nitrite-coated filter pack system were constant. From the value of $\Delta^{17}\text{O}(\text{NO}_3^-)_c$ estimated for each sampling, the $\Delta^{17}\text{O}$ value of O_3 in the terminal positions ($\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) can thus be estimated by using a simple mass balance (Vicars and Savarino, 2014):

$$275 \quad \Delta^{17}\text{O}(\text{O}_3)_{\text{term}} = 3 \times \Delta^{17}\text{O}(\text{NO}_3^-)_c - 2 \times \Delta^{17}\text{O}(\text{NO}_2^-) \quad (2)$$

where $\Delta^{17}\text{O}(\text{NO}_2^-)$ denotes the $\Delta^{17}\text{O}$ value of NO_2^- on each filter.

Additionally, we can relate the quantities of nitrate blank (n_b) with its $\Delta^{17}\text{O}$ ($\Delta^{17}\text{O}(\text{NO}_3^-)_b$) using the equations shown below:

$$m \times \Delta^{17}\text{O}(\text{NO}_3^-)_m = n_c \times \Delta^{17}\text{O}(\text{NO}_3^-)_c + n_b \times \Delta^{17}\text{O}(\text{NO}_3^-)_b \quad (3)$$

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$$n_c = m - n_b \quad (4)$$

where $\Delta^{17}\text{O}(\text{NO}_3^-)_b$ denotes $\Delta^{17}\text{O}$ of nitrate blank on the nitrite-coated filters; and m and n_c denote the quantities of measured NO_3^- and corrected NO_3^- (removing nitrate blank) on the nitrite-coated filters, respectively. In this study, the mean $\Delta^{17}\text{O}$ value of NO_3^- produced on the nitrite-coated filters during the ambient O_3 collections with the active carbon pre-filter was used for $\Delta^{17}\text{O}(\text{NO}_3^-)_b$. As a
 285 result, the quantities of nitrate blank (n_b) can be estimated from m and $\Delta^{17}\text{O}(\text{NO}_3^-)_m$ using the equation shown below:

$$n_b = m \times (\Delta^{17}\text{O}(\text{NO}_3^-)_c - \Delta^{17}\text{O}(\text{NO}_3^-)_m) / (\Delta^{17}\text{O}(\text{NO}_3^-)_c - \Delta^{17}\text{O}(\text{NO}_3^-)_b) \quad (5)$$

In this study, we estimated the mean value of n_b (n_b') on the nitrite-coated filter 1 (F1), 2 (F2), and 3 (F3) using both m and $\Delta^{17}\text{O}(\text{NO}_3^-)_m$ on each nitrite-coated filter of filter pack system.

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Compared to the quantities of NO_3^- on filter F1 (the first filter of the nitrite-coated filters), we can expect a significant reduction of NO_3^- quantities in the subsequent F2 and F3 filters due to the progress of O_3 reduction through the reaction R1. Assuming that nitrite oxidation in the multi-step nitrite-coated filter pack system was a first-order kinetic process to the quantities of O_3 , we can express the quantity of atmosphere O_3 that passed through a nitrite-coated filter using the equation
 295 shown below:

$$N_i = N_0 \times e^{-ki} \quad (6)$$

where N_0 and N_i denote the quantities of atmospheric O_3 at the initial (0), and the residual atmospheric O_3 that passed through the nitrite-coated filter i , respectively; i denotes the number of

the stage within the nitrite-coated filters ($i = 1, 2$ and 3); and k is the first-order rate constant for
 300 each ambient O_3 collection. Please note that the first (F1), second (F2) and third stages (F3) within
 the nitrite-coated filters correspond to the third, fourth, and fifth stages in the multi-step nitrite-
 coated filter pack system, respectively (Fig. 1).

On the other hand, the mass balance of the reaction R1 on the filter i of the multi-step nitrite-
 coated filter can be quantitatively described using the following equation (Fig. 3):

305
$$N_j = Q_i + N_i \quad (7)$$

where N_j denotes the quantities of atmospheric O_3 that passed through previous stage of filter i (j
 $= i - 1; j = 0, 1$ and 2) in the nitrite-coated filters, respectively; and Q_i denotes the quantities of the
 O_3 -derived O-atoms which reacted with NO_2^- at the filter i of the nitrite-coated filters through the
 reaction R1, respectively.

310 From the Eqs. (6) and (7), the quantities of NO_3^- (Q_i) on filter i of the nitrite-coated filters can be
 express as a function of the quantity of atmospheric O_3 at the initial (N_0) and the first-order rate
 constant k on the nitrite-coated filters shown below :

$$Q_i = N_0 \times (e^k - 1) \times e^{-k \times i} \quad (8)$$

$$\ln Q_i = -k \times i + \ln [N_0 \times (e^k - 1)] \quad (9)$$

315 By fitting a regression line to the relationships between i (in x-axis) and $\ln Q_i$ (in y-axis) of the
 nitrite-coated filters sampled simultaneously, we can estimate the values of k and N_0 from the slope
 and intercept of the regression line, respectively.

In accordance with the progress of the reaction R1 on nitrite-coated filters, the residual atmospheric O₃ in the air stream should present significant changes in δ¹⁸O values in the terminal positions due to the kinetic fractionation of oxygen isotopes during the reaction R1. The changes in the δ¹⁸O values of O₃ can be expressed by the Rayleigh equation (Coleman et al. 1981; Mariotti et al. 1981; Fig. 3) shown below:

$$\delta^{18}\text{O}_i - \delta^{18}\text{O}_0 = \varepsilon \times \ln f \quad (10)$$

where ε denotes the isotopic enrichment factor of the reaction R1; δ¹⁸O₀ and δ¹⁸O_i denote the δ¹⁸O values of atmospheric O₃ in the terminal positions at the initial (0), and the residual atmospheric O₃ passed through the nitrite-coated filter *i*, respectively; and *f* denotes the fraction of atmospheric O₃ remaining in the interlayers of the nitrite-coated filters (equal to *N_i/N₀*).

Because the O₃-derived O-atoms that reacted with NO₂⁻ through the reaction R1 had been converted to NO₃⁻ on filter *i*, we can relate *Q_i* and its δ¹⁸O (δ¹⁸O_{*Q_i*}) with *N_i* and δ¹⁸O_{*i*} of O₃ using a simple mass of this filter shown below:

$$N_j \times \delta^{18}\text{O}_j = Q_i \times \delta^{18}\text{O}_{Q_i} + N_i \times \delta^{18}\text{O}_i \quad (11)$$

where δ¹⁸O_{*j*} denotes the δ¹⁸O value of atmospheric O₃ that passed through previous stage of filter *i* (*j* = *i* - 1; *j* = 0, 1 and 2) in the nitrite-coated filters. As for *Q_i* and δ¹⁸O_{*Q_i*}, we can estimate these from the quantities and δ¹⁸O of NO₃⁻ measured on filter *i* by connecting the changes in δ¹⁸O owing to the contribution of NO₃⁻ on this filter using the relation on this filter shown below:

$$Q_i = m_i - n_b' \quad (12)$$

$$\delta^{18}\text{O}_{Q_i} = 3 \times \delta^{18}\text{O}(\text{NO}_3^-)_{c_i} - 2 \times \delta^{18}\text{O}(\text{NO}_2^-) \quad (13)$$

$$\delta^{18}\text{O}(\text{NO}_3^-)_{c_i} = (m_i \times \delta^{18}\text{O}(\text{NO}_3^-)_{m_i} - n_b' \times \delta^{18}\text{O}(\text{NO}_3^-)_b) / (m_i - n_b') \quad (14)$$

where m_i denotes the quantity of NO_3^- measured on the filter i of the nitrite-coated filters; n_b' denotes the mean value of nitrate blank on the nitrite-coated filters; $\delta^{18}\text{O}(\text{NO}_3^-)_{c_i}$ denotes the $\delta^{18}\text{O}$ value of NO_3^- from which the changes in $\delta^{18}\text{O}$ owing to the contribution of nitrate blank had been corrected; $\delta^{18}\text{O}(\text{NO}_3^-)_{m_i}$ denotes the $\delta^{18}\text{O}$ value of NO_3^- measured on the filter i of the nitrite-coated filters; and $\delta^{18}\text{O}(\text{NO}_2^-)$ denotes the $\delta^{18}\text{O}$ value of NO_2^- . In this study, the mean $\delta^{18}\text{O}$ value of NO_3^- produced on the nitrite-coated filters during ambient O_3 collections with the activated carbon pre-filter was used for $\delta^{18}\text{O}(\text{NO}_3^-)_b$. The mean value of nitrate blank (n_b') had been estimated from Eq. (5).

As a result, the initial $\delta^{18}\text{O}$ of O_3 in the terminal positions introduced into each multi-step nitrite-coated filter pack system ($\delta^{18}\text{O}_0$) can be estimated from the quantity of atmospheric O_3 at the initial (N_0), the quantities (Q_1, Q_2) and $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{Q_1}, \delta^{18}\text{O}_{Q_2}$) values of the O_3 -derived O-atoms which had reacted with NO_2^- at the nitrite-coated filter 1 (F1) and 2 (F2) of the nitrite-coated filters. The specific method for the calculation is as follows. We can obtain following relations from Eq. (7):

$$N_0 = N_1 + Q_1 \quad (15)$$

$$N_1 = N_2 + Q_2 \quad (16)$$

The following relations were obtained from Eq. (10):

$$\delta^{18}\text{O}_1 - \delta^{18}\text{O}_0 = \varepsilon \times \ln(N_1/N_0) \quad (17)$$

$$\delta^{18}\text{O}_2 - \delta^{18}\text{O}_0 = \varepsilon \times \ln(N_2/N_0) \quad (18)$$

The following relations were obtained from Eq. (11):

$$N_0 \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + N_1 \times \delta^{18}\text{O}_1 \quad (19)$$

$$N_1 \times \delta^{18}\text{O}_1 = Q_2 \times \delta^{18}\text{O}_{Q2} + N_2 \times \delta^{18}\text{O}_2 \quad (20)$$

360 By substituting N_1 and N_2 in Eq. (6) for Eqs. (17) and (18), the $\delta^{18}\text{O}$ value of the residual atmospheric O_3 passed through F2 ($\delta^{18}\text{O}_2$) can be expressed by $\delta^{18}\text{O}_1$ and $\delta^{18}\text{O}_0$:

$$\delta^{18}\text{O}_1 - \delta^{18}\text{O}_0 = -\varepsilon k \quad (21)$$

$$\delta^{18}\text{O}_2 - \delta^{18}\text{O}_0 = -2\varepsilon k \quad (22)$$

$$\delta^{18}\text{O}_2 = 2 \times \delta^{18}\text{O}_1 - \delta^{18}\text{O}_0 \quad (23)$$

365 By substituting $\delta^{18}\text{O}_2$ in this equation for Eq. (20), we can obtain the equation shown below:

$$N_1 \times \delta^{18}\text{O}_1 = Q_2 \times \delta^{18}\text{O}_{Q2} + N_2 \times (2 \times \delta^{18}\text{O}_1 - \delta^{18}\text{O}_0)$$

$$\delta^{18}\text{O}_1 = (Q_2 \times \delta^{18}\text{O}_{Q2} - N_2 \times \delta^{18}\text{O}_0) / (N_1 - 2N_2) \quad (24)$$

By combining Eq. (19) and (20), and substituting $\delta^{18}\text{O}_2$ in Eq. (23), we can obtain the equation shown below:

$$370 \quad N_0 \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} + N_2 \times (2 \times \delta^{18}\text{O}_1 - \delta^{18}\text{O}_0)$$

$$(N_0 + N_2) \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} + 2N_2 \times \delta^{18}\text{O}_1 \quad (25)$$

By substituting $\delta^{18}\text{O}_1$ in Eq. (24) for Eq. (25), we can obtain the equation shown below:

$$(N_0 + N_2) \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} + 2N_2 \times (Q_2 \times \delta^{18}\text{O}_{Q2} - N_2 \times \delta^{18}\text{O}_0) / (N_1 - 2N_2)$$

$$\delta^{18}\text{O}_0 = [(N_1 - 2N_2) \times Q_1 \times \delta^{18}\text{O}_{Q1} + N_1 \times Q_2 \times \delta^{18}\text{O}_{Q2}] / [(N_0 N_1 + N_1 N_2 - 2N_0 N_2)] \quad (26)$$

375 By substituting N_1 and N_2 in Eqs. (15) and (16) for Eq. (26), the initial $\delta^{18}\text{O}$ of O_3 in the terminal positions ($\delta^{18}\text{O}_0$) can be estimated from the equation shown below:

$$\delta^{18}\text{O}_0 = [(Q_1 + 2Q_2 - N_0) \times Q_1 \times \delta^{18}\text{O}_{Q1} + (N_0 - Q_1) \times Q_2 \times \delta^{18}\text{O}_{Q2}] / [N_0 \times (Q_2 - Q_1) + Q_1 \times (Q_1 + Q_2)] \quad (27)$$

By using the $\delta^{18}\text{O}_0$ value estimated from Eq. (27), we can estimate the isotopic enrichment factor (ε) of O_3 during each sample collection as well. From the Eqs. (17), (25) and (27), we can obtain the relations shown below:

$$(N_0 + N_2) \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} + 2N_2 \times (\delta^{18}\text{O}_0 - \varepsilon \times k)$$

$$(N_0 - N_2) \times \delta^{18}\text{O}_0 = Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} - 2N_2 \times \varepsilon \times k$$

$$\varepsilon = [Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} - (N_0 - N_2) \times \delta^{18}\text{O}_0] / (2N_2 \times k)$$

$$\varepsilon = [Q_1 \times \delta^{18}\text{O}_{Q1} + Q_2 \times \delta^{18}\text{O}_{Q2} - (Q_1 + Q_2) \times \delta^{18}\text{O}_0] / [2(N_0 - Q_1 - Q_2) \times k] \quad (28)$$

385

3. RESULTS AND DISCUSSION

3.1 Nitrate blank and interferences

As we expected in section 2.8, the $\Delta^{17}\text{O}$ values of NO_3^- on the filters decreased in accordance with decrease in the quantities of NO_3^- collected in the later stages of the multi-step filters (Fig. 4 (b)), implying that the contribution of nitrate blank became significant in the filters of the later stages, and that nitrate blank on the nitrite-coated filters potentially limits the accuracy and precision of the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of NO_3^- produced via the reaction R1.

To minimize nitrate blank derived from the NaNO₂ reagent, [Vicars et al. \(2012\)](#) used ultra-high purity reagent. Besides, they increased the quantity of NO₃⁻ produced via the reaction R1 on each filter to more than 0.2-0.5 μmol to minimize the relative contribution of nitrate blank ([Vicars et al., 2012](#)). In this study, however, we found that the NO₃⁻ on the filters of the control group stored at 4°C for two months was negligible, less than 0.08 μmol, while the mean value of nitrite blank (*n_b'*) during the sampling of ambient O₃ ranged from 0.1 to 0.7 μmol. It was difficult to explain the observed large nitrate blank on the filters by the contribution of NO₃⁻ derived from the NaNO₂ reagent.

The oxidation of NO₂⁻ by O₂ in the aqueous phase was studied by monitoring temporal variation in the concentration of NO₂⁻ and NO₃⁻ at different pH values ([Damschen and Martin, 1983](#); [Brida and Ong, 2000](#)). For example, the first order rate constants of the reaction between NO₂⁻ and O₂ were $(1.2 \pm 0.9) \times 10^{-6} \text{ s}^{-1}$ at pH 11.6 ([Brida and Ong, 2000](#)). Assuming that the aqueous phase on the nitrite-coated filters was saturated with atmospheric O₂ throughout the sampling, the total quantity of NO₃⁻ produced via NO₂⁻ + O₂ on the nitrite-coated filter during the sampling period of one week was estimated to be more than 9.1 μmol at 20 °C. Additionally, [Koutrakis et al. \(1993\)](#) and [Vicars et al. \(2012\)](#) suggested that the reaction between NO₂⁻ and weak atmospheric oxidant (such as O₂) could produce significant NO₃⁻ on nitrite-coated filters. As a result, the NO₂⁻ oxidation reaction with atmospheric O₂ was highly responsible for the primary source of nitrate blank produced on the nitrite-coated filters:



In order to verify this hypothesis, we performed additional nitrate blank experiments in which an activated carbon filter was used to remove O₃ during the additional air collections (see section 2.4 for the details). The quantities of NO₃⁻ on the nitrite-coated filters after the air collections for 2 weeks were 0.3 ± 0.1 μmol. In addition, the oxygen isotopic compositions of the nitrate blank (δ¹⁸O(NO₃⁻)_b and Δ¹⁷O(NO₃⁻)_b) on the nitrite-coated filters were +11.8 ± 0.4‰ (1σ) for δ¹⁸O, and – 0.12 ± 0.26‰ (1σ) for Δ¹⁷O in the experiments.

To check whether the observed oxygen isotopic compositions of NO₃⁻ obtained through the blank experiments were reasonable as those produced through the reaction R2 or not, we estimated the oxygen isotopic compositions of NO₃⁻ produced through the reaction R2. In NO₃⁻ produced via the reaction R2, two oxygen atoms are derived from the NaNO₂ reagent, while the other one oxygen atom is derived from atmospheric O₂. If the kinetic oxygen isotope fractionations were negligible in R2 and this simple stoichiometry determines the isotopic compositions of NO₃⁻ produced through the reaction R2, δ¹⁸O and Δ¹⁷O values of NO₃⁻ (δ¹⁸O(NO₃⁻)_{R2} and Δ¹⁷O(NO₃⁻)_{R2}) can be calculated by using a simple mass balance:

$$\delta^{18}\text{O}(\text{NO}_3^-)_{\text{R2}} = \frac{2}{3} \delta^{18}\text{O}_{\text{NaNO}_2} + \frac{1}{3} \delta^{18}\text{O}_{\text{O}_2} \quad (29)$$

$$\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{R2}} = \frac{2}{3} \Delta^{17}\text{O}_{\text{NaNO}_2} + \frac{1}{3} \Delta^{17}\text{O}_{\text{O}_2} \quad (30)$$

where δ¹⁸O_{O₂} and Δ¹⁷O_{O₂} denotes the δ¹⁸O and Δ¹⁷O of atmospheric O₂.

430 By using the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of the NaNO_2 reagent ($+5.74 \pm 0.1\text{‰}$ and $+0.02 \pm 0.03\text{‰}$,
respectively) and O_2 ($+23.5\text{‰}$ and -0.2‰ , respectively; Luz and Barkan, 2000; Kroopnick and
Craig, 1972), we estimated the oxygen isotopic compositions of NO_3^- produced through the reaction
R2 to be $+11.7 \pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $-0.07 \pm 0.06\text{‰}$ for $\Delta^{17}\text{O}$, respectively. These $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$
values were in agreement with those actually observed ($+11.8 \pm 0.4\text{‰}$ for $\delta^{18}\text{O}(\text{NO}_3^-)_b$ and $-0.12 \pm$
435 0.26‰ for $\Delta^{17}\text{O}(\text{NO}_3^-)_b$) during the nitrate blank experiments. As a result, we concluded that most
of the nitrate blank was derived from atmospheric O_2 via the reaction R2 on each nitrite-coated
filter.

3.2 Precision

To check the precision of the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values determined using our system, O_3 (ca. 5%) in
440 O_2 matrix eluted from the electrochemical ozone generator under the flow rate of 15 mL min^{-1} was
collected by changing the collection period (30 min. for Exp. A and 1 hour for Exp. B in Table 1)
using the system as schematically shown in Fig. 2 as path A and measured in a similar manner with
the ambient O_3 samples. Additionally, a duplicate collection of ambient ozone was performed using
the two of our filter pack systems (Exp. C-1 and C-2 in Table 1) simultaneously under the flow rate
445 of 3.0 L min^{-1} from 23rd to 27th in November 2017 and measured in a similar manner with the
ambient O_3 samples. The isotopic compositions of measured NO_3^- on filter pack system obtained
during these experiments ranged from $+43.5\text{‰}$ to $+53.6\text{‰}$ and from $+11.8\text{‰}$ to $+15.2\text{‰}$ for the
experiments using ozone generator (Exps. A and B in Table 1), and from $+49.2\text{‰}$ to $+54.0\text{‰}$ and

from +11.1‰ to +12.8‰ for the duplicate collection experiment, respectively (Exps. C-1 and C-2
450 in [Table 1](#)).

The reciprocal of the NO_3^- quantities ($1/[\text{NO}_3^-]$ (μmol^{-1})) on the nitrite-coated filters showed a strong linear relationship with the $\Delta^{17}\text{O}$ values ([Fig 4](#)). By extrapolating the linear relationships between $1/[\text{NO}_3^-]$ (μmol^{-1}) and $\Delta^{17}\text{O}$ to $1/[\text{NO}_3^-] = 0$ (μmol^{-1}) to exclude the contribution of blank NO_3^- (NO_3^- -depleted end-member) from the measured isotopic compositions through least-squares
455 fitting of the straight lines, we estimated the blank-corrected the $\Delta^{17}\text{O}$ values of NO_3^- (NO_3^- -enriched end-member) to be $+15.2 \pm 0.2\text{‰}$ (1σ) and $+15.1 \pm 0.2\text{‰}$ (1σ) for the Exp. A and B, respectively, and $+12.7 \pm 0.2\text{‰}$ (1σ) and $+12.8 \pm 0.1\text{‰}$ (1σ) for the Exp. C-1 and C-2, respectively ([Table 1](#) and [Fig. 4](#)). Using the Eq. (2), we estimated the $\Delta^{17}\text{O}$ values of O_3 in the terminal positions ($\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) to be $+45.7 \pm 0.6\text{‰}$ and $45.2 \pm 0.7\text{‰}$ for the Exp. A and B, respectively, and $+38.2 \pm$
460 0.7‰ (1σ) and $+38.3 \pm 0.3\text{‰}$ (1σ) for the Exp. C-1 and C-2, respectively ([Table 1](#) and [Fig. 4](#)). We concluded that we can determine the $\Delta^{17}\text{O}$ values of O_3 in the terminal positions with the precisions of $\pm 0.6\text{‰}$ (1σ) as the possible errors associated with the $\Delta^{17}\text{O}$ values. Compared with the single nitrite-coated filter technique ([Vicars and Savarino, 2014](#); [Savarino et al., 2016](#)), the standard errors associated with the $\Delta^{17}\text{O}$ values of O_3 in the terminal positions determined in this study using the
465 multi-step nitrite-coated filter system were improved (from $\pm 2.6\text{‰}$ to $\pm 0.6\text{‰}$). These observations suggest that our new sampling and analytical method, as well as the correction scheme, allows precise determinations on $\Delta^{17}\text{O}$ of tropospheric O_3 . The standard errors associated with the $\delta^{18}\text{O}$

values of O₃ in the terminal positions were estimated ± 3.4‰ for those produced by the ozone generator and ± 2.0‰ for those in ambient air.

470 As clearly shown in Fig. 4 (a), the quantities of nitrate blank in the experiments using the ozone generator (path A of Fig. 2) increased in accordance with the lengths of experiment time (1.6 μmol for 30 min. and 8.3 μmol for 1 hour), probably due to the production of NO₃⁻ from O₂ via the reaction R2 on each nitrite-coated filter. It was much higher than those in the ambient O₃ collection experiments with the mean value of 0.4 ± 0.2 μmol. The extradition enrichment of O₃ during the
475 experiments using the ozone generator (ca. 5%) might promote the reaction R2, by increasing catalytic activities on the surface of the nitrite-coated filters. Besides, the reaction efficiency between O₂ and NO₂ on the nitrite-coated filters could be higher under the low flow rate of 15 mL min⁻¹ adopted only in the experiments using the ozone generator (Fig. 4). That is to say, the high flow rate adopted in our filter pack system for sampling O₃ under the ambient level (3 L min⁻¹)
480 could be more suitable to minimize nitrite blank.

3.3 Accuracy

To verify the accuracy of the Δ¹⁷O determined through the multi-step nitrite-coated filter system, we determined the oxygen isotopic compositions of O₃ produced by the ozone generator using the traditional gas-washing bottle to remove O₃ and analyzed the changes in the oxygen isotopic
485 compositions of O₂ from those of the initial O₂ to those of final O₂ eluted from the gas-washing bottle (path B of Fig. 2).

Based on the mass of NO_3^- produced in the aqueous NO_2^- solution, the O_3 concentration produced by the generator was estimated to be 4.6% (4.6×10^4 ppm) under the flow rate of 15 mL min^{-1} adopted in this experiment. The O_3 concentration determined at the vent of the glass bottle was
 490 below the detection limit of an ozone detection tube (25 ppb; GASTEC Co., Ltd.) so that the efficiency of the gas adsorption in the gas-washing bottle was more than 99.9%.

One of the two O-atoms in the terminal positions of O_3 transferred to NO_2^- forming NO_3^- in the NO_2^- solution in the gas-washing bottle. As a result, the $\Delta^{17}\text{O}$ of O-atoms in the terminal positions ($\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) absorbed in the aqueous NO_2^- solution can be related with the changes in the $\Delta^{17}\text{O}$ of
 495 O_2 between that introduced into the generator (initial O_2) to final O_2 that eluted from the NO_2^- solution, a portion of which was sampled in a glass bottle with two stopcocks. If the production of NO_3^- through the reactions other than $\text{O}_3 + \text{NO}_2^-$ was negligible, we can obtain a mass balance equation of oxygen atoms shown below:

$$2 \times n(\text{O}_2)_I \times \Delta^{17}\text{O}(\text{O}_2)_I + 2 \times n(\text{NO}_2^-)_{R1} \times \Delta^{17}\text{O}_{\text{NaNO}_2} = n(\text{O}_3) \times \Delta^{17}\text{O}(\text{O}_3)_{\text{term}} + 2 \times n(\text{O}_2)_F \times \Delta^{17}\text{O}(\text{O}_2)_F \quad (31)$$

500 where $n(\text{O}_2)_I$, $n(\text{O}_2)_F$, $n(\text{NO}_2^-)_{R1}$ and $n(\text{O}_3)$ denote the quantities of initial O_2 , final O_2 , NO_2^- reacted with O_3 through the reaction R1, and O_3 produced through the reaction in the ozone generator ($3\text{O}_2 \rightarrow 2\text{O}_3$) during the experiments, respectively; and the $\Delta^{17}\text{O}(\text{O}_2)_I$ and $\Delta^{17}\text{O}(\text{O}_2)_F$ denote the oxygen isotopic compositions of initial O_2 and final O_2 , respectively. The quantities of initial O_2 ($n(\text{O}_2)_I$), NO_2^- reacted with O_3 in the NO_2^- solution ($n(\text{NO}_2^-)_{R1}$) and O_3 produced by the ozone generator

505 $(n(O_3))$ can be calculated from those of final O_2 ($n(O_2)_F$) and NO_3^- produced ($n(NO_3^-)_p$) in the NO_2^- solution of the gas-washing bottle using the equations shown below:

$$2 \times n(O_2)_I = [2 \times n(O_2)_F + n(O_3)]$$

(32)

$$n(NO_2^-)_{R1} = n(O_3) = n(NO_3^-)_p \quad (33)$$

510 The quantities of final O_2 ($n(O_2)_F$) were estimated from the volumes of O_2 measured using the flowmeter. The $n(NO_3^-)_p$ values corresponds to the quantities of NO_3^- in the NO_2^- solution of the gas-washing bottle. As a result, we can estimate the $\Delta^{17}O$ of O_3 in the terminal positions ($\Delta^{17}O(O_3)_{term}$) generated using the ozone generator independently from our method using the multi-step nitrite-coated filter pack system by combining Eqs. (31) - (33):

515
$$\Delta^{17}O(O_3)_{term} = \left[\frac{2 \times n(O_2)_F}{n(NO_3^-)_p} + 1 \right] \times \Delta^{17}O(O_2)_I + 2 \times \Delta^{17}O_{NaNO_2} - \frac{2 \times n(O_2)_F}{n(NO_3^-)_p} \times \Delta^{17}O(O_2)_F \quad (34)$$

The determined $\Delta^{17}O$ of initial O_2 , both $\Delta^{17}O$ and quantities of final O_2 , quantities of NO_3^- produced in the NO_2^- solution, and calculated $\Delta^{17}O$ of O_3 in the terminal positions produced by the generator are summarized in **Table 2**, together with the determined $\Delta^{17}O$ of NO_3^- in the NO_2^- solution. We could not find any significant variations in the determined $\Delta^{17}O$ values of O_2 , NO_3^- , and O_3 throughout the experiments, implying that the $\Delta^{17}O$ values of O_3 were stable throughout the experiments.

520

The $\Delta^{17}O(O_3)_{term}$ values determined by the multi-step nitrite-coated filter pack system (**Table 1**) were in good agreement with those determined by the gas adsorption method (**Table 2**). We

concluded that the $\Delta^{17}\text{O}$ of O_3 determined using the multi-step nitrite-coated filter pack system were
525 reliable, from which the changes in the $\Delta^{17}\text{O}$ due to the contribution of nitrate blank had been
corrected successfully.

The excellent agreement in the determined $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values also suggested that the quantities
of nitrate blank produced in the gas-washing bottle via the reaction R2 was negligibly small during
the experiments using path B of Fig. 2. In order to verify that the quantities of nitrate blank
530 produced via the reaction R2 in the NO_2^- solution was negligible in the experiments, we also
quantified NO_3^- produced by the flow of pure O_2 stream without electronic discharge (flow rate of
15 mL min^{-1} for 30 min.) and found that NO_3^- in the gas-washing bottle was below the detection
limit of ion chromatography, which corresponds to 1.8 μmol of NO_3^- in the NO_2^- solution, implying
that, differ from the nitrite-coated filters, the production of NO_3^- through $\text{O}_2 + \text{NO}_2^-$ reaction was
535 negligible in the gas-washing bottle. Some heterogeneous reactions on the surface of the nitrite-
coated filters might be responsible for the progress of the reaction R2 and those significant nitrate
blank on the filters when we used the nitrite-coated filters for collecting tropospheric O_3 .

3.4 $\Delta^{17}\text{O}$ of O_3 in ambient air

Our multi-step nitrite-coated filter pack system, together with the analytical system on $\Delta^{17}\text{O}$ of
540 NO_3^- , allows us to determine the oxygen isotopic composition of tropospheric O_3 . To validate the
method and to demonstrate its applicability, the ambient tropospheric air ($n = 18$) was collected
during daytime (D in [Table 3](#)) and nighttime (N in [Table 3](#)) separately by changing the pumping

time (6:00-18:00 for daytime samples and 18:00-6:00 for nighttime samples, [Table 3](#)). The temporal variations in the oxygen isotopic compositions of tropospheric O₃ are shown in [Fig. 5](#), along with
545 the average mixing ratio of O₃ during each sample collection period. The mean values and their standard deviations were $+150.2 \pm 13.5\text{‰}$ (daytime) and $+144.9 \pm 9.6\text{‰}$ (nighttime) for $\delta^{18}\text{O}$, $+38.1 \pm 1.0\text{‰}$ (daytime) and $+36.8 \pm 0.9\text{‰}$ (nighttime) for $\Delta^{17}\text{O}$ of O₃ in the terminal positions. ([Table 3](#)).

The average $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ value of the tropospheric O₃ determined in this study ($+37.4 \pm 1.1\text{‰}$) was consistent with those measured in mid-latitudes using cryogenic trapping technique in previous
550 studies, such as $+34.2 \pm 4.3\text{‰}$ ([Krankowsky et al., 1995](#)) and $+38.0 \pm 6.6\text{‰}$ ([Johnston and Thiemens, 1997](#)) (both of them were recalculated from the original to be the same $\Delta^{17}\text{O}$ definition). Moreover, our data are in good agreement with those obtained at Atlantic Ocean (50°N to 50°S) ($+37.3 \pm 1.1\text{‰}$; recalculated from the original to be the same $\Delta^{17}\text{O}$ definition) and at Grenoble, France ($+37.7 \pm 1.3\text{‰}$; recalculated from the original to be the same $\Delta^{17}\text{O}$ definition) using the
555 single nitrite-coated filter as well ([Vicars and Savarino, 2014](#); [Savarino et al., 2016](#)). The mean $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values in this study was in good agreement with the modeling calculation of $\Delta^{17}\text{O}$ transfer in the troposphere as well ([Lyons 2001](#)).

While the determined $\Delta^{17}\text{O}$ values of ambient O₃ in the terminal positions were almost stable, showing the mean $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ value of $+37.4\text{‰}$. However, the maximum $\Delta^{17}\text{O}$ value determined
560 daytime in April ($+39.7 \pm 1.0\text{‰}$) exceeded the 1σ variation range. This ¹⁷O-enrichment seems to occur in conjunction with the spring O₃ maximum in the tropospheric concentrations ([Monks, 2000](#);

Vicars and Savarino, 2014). Similar $\Delta^{17}\text{O}$ maximum of O_3 in spring had been found in Grenoble, France as well (Vicars and Savarino, 2014), so that the spring maximum in $\Delta^{17}\text{O}$ is likely to be common in mid-latitudes of the Northern Hemisphere. The $\Delta^{17}\text{O}$ of O_3 became larger in higher altitude (Lyons 2001). Besides, the enhanced stratosphere-troposphere exchange became active during the winter-spring transition (Austin and Follows, 1991; Beekmann et al., 1994; Muramatsu et al., 2008). Inputs of O_3 in stratosphere and/or free troposphere should be highly responsible for the ^{17}O -enrichment of O_3 in April.

Another important finding is that the significant deviations in $\Delta^{17}\text{O}$ between daytime and nighttime (1.2‰ on average) larger than the standard error of the ambient $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ measurement (0.6‰ on average), indicating that the $\Delta^{17}\text{O}$ values of O_3 varied diurnally: higher in daytime and lower in nighttime. The formation of inversion layer during nighttime was highly responsible for the deviations. That is, the contribution of O_3 produced locally in low altitude relatively increased during nighttime due to the formation of the temperature inversion layer, while O_3 with higher $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values in free troposphere increased during daytime because the inversion layer disappeared due to warming by solar radiation. Increase in the $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ values from +35‰ to +40‰ in accordance with the altitudes from 0 to 10 km (Lyons 2001) supported this hypothesis. The observed diurnal variation of $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ at ground surface impacts using $\Delta^{17}\text{O}$ values to constrain atmospheric chemical paths, such as the $\text{SO}_3^{2-} + \text{O}_3$ oxidation to produce sulfate and $\text{NO}_2 + \text{O}_3 + \text{H}_2\text{O}$ oxidation to produce nitrate. With this diurnal variation, more precise

contribution fractions of the O₃ oxidation pathway can be quantified different from daytime and nighttime. Additionally, by considering this diurnal variation of $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$, the three-dimensional GEOS-Chem chemical transport model might obtain more accurate $\Delta^{17}\text{O}$ values of atmospheric sulfate and nitrate, which are produced through the O₃ oxidation pathway.

585 The $\delta^{18}\text{O}$ values of O₃ in the terminal positions ($\delta^{18}\text{O}_\theta$) were ranged from +128.5‰ to +166.2‰ with a mean value and a standard variation of $+147.6 \pm 11.7\%$ (Table 3). The mean value were somewhat higher than those determined using the cryogenic measurement, $+136.5 \pm 7.6\%$ for Krankowsky *et al.* (1995) and $+123.4 \pm 10.0\%$ for Johnston and Thiemens (1997), respectively. This discrepancy is likely that our method provides an isotopic measurement of the O-atom in the

590 terminal positions of O₃ that is transferred during the reaction R1, different from the cryogenic measurement suffer from interference from the low collection efficiency and atmospheric xenon (Brenninkmeijer *et al.*, 2003). Additionally, the $\delta^{18}\text{O}$ values of O₃ in the terminal positions obtained in this study were somewhat higher than those of the single nitrite-coated filter method as well, $+126.3 \pm 11.9\%$ and $+130.4 \pm 12.9\%$ for Vicars and Savarino, (2014). While our multi-step nitrite-

595 coated filter pack method accompanied significant kinetic isotope fractionation during the collections on the filters, we obtained reliable $\delta^{18}\text{O}$ values of tropospheric O₃ in this method as well, by using Eq. (27) for correcting the isotope fractionations. The values of isotope enrichment factor (ϵ) obtained in this study were $-12.6 \pm 8.4\%$ (1σ) in daytime and $-10.7 \pm 7.8\%$ (1σ) in nighttime, respectively (Table 3), indicating that kinetic isotope fractionation during the reaction R1 was

600 significant. The kinetic fractionation of isotopes associated with insufficient collection in past studies could be responsible for the discrepancy in the $\delta^{18}\text{O}$ values. The discrepancy possibly associated with the contribution of nitrate blank using the single nitrite-coated filter method as well. In order to clarify the reasons for the discrepancies, we must increase the amount of data on the $\delta^{18}\text{O}$ values of tropospheric O_3 . Besides, we must check the accuracy of determining $\delta^{18}\text{O}$ of O_3 605 generated using the ozone generator with constant values of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$.

4. CONCLUSIONS

We herein described a new analytical and data correction scheme for measuring the oxygen isotopic compositions of tropospheric O_3 using multi-step nitrite-coated filter pack system. This 610 method offers several advantages over previous measurements, such as (i) the nitrate blank quantities on each filter can be estimated and excluded from the intercept of the linear correlation between the reciprocal of quantities and $\Delta^{17}\text{O}$ of NO_3^- on the filters (Fig. 4); (ii) the analytical precision (standard error of average value) of $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ had been improved from 2.6‰ (Vicars et al., 2012; Vicars and Savarino, 2014; Savarino et al., 2016) to 0.6‰; and (iii) provide a method for 615 calibration of $\delta^{18}\text{O}$ value of O_3 in the terminal positions using the equations of mass balance and Rayleigh fractionation due to the kinetic isotope fractionation.

The results obtained in this study indicate that the multi-step nitrite-coated filter pack system technique is a sufficiently robust and reliable method for determining accurate and precise oxygen

isotopic composition of atmospheric O₃, which enabled us to detect variations in $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$
620 between daytime and nighttime (ca. 1.2‰) for the first time in this study. Additionally, we also
detected significant ¹⁷O-enrichment of O₃ in April. Future research using the multi-step nitrite-
coated filter pack system would provide us with a fully robust theoretical framework to investigate
the potential diurnal, seasonal, and spatial features of ozone isotopic composition in the atmosphere.

625 **Acknowledgements**

We are grateful to Ryo Shingubara, Takashi Sanbuichi, Rei Nakane, Dong Ding, and other
present and past members of the Biogeochemistry Group, Nagoya University, for their valuable
support throughout this study. This work was supported by a grant-in-aid for scientific research
from the Ministry of Education, Culture, Sports, Science and Technology of Japan under grant
630 number 26241006.

635

Table 1. The $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of NO_3^- from which produced through the reaction between O_3 in the terminal positions and NO_2^- at the initial and contribution of nitrate blank have been corrected, together with the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of O_3 in the terminal positions ($\delta^{18}\text{O}_0$ and $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) from those obtained during the experiments of ozone generator and an additional collection of ambient
 645 ozone. The $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values are present by average \pm standard error.

Experiment name	NO_3^-			O_3 (terminal)	
	^a $10^3 \delta^{18}\text{O}_m$	^a $10^3 \Delta^{17}\text{O}_m$	^b $10^3 \Delta^{17}\text{O}_c$	^c $10^3 \delta^{18}\text{O}$	^d $10^3 \Delta^{17}\text{O}$
ozone generator					
Exp. A	+43.5 to +50.4	+12.2 to +15.2	$+15.2 \pm 0.2$	$+158.6 \pm 3.9$	$+45.7 \pm 0.6$
Exp. B	+45.5 to +53.6	+11.8 to +14.2	$+15.1 \pm 0.2$	$+164.0 \pm 2.8$	$+45.2 \pm 0.7$
^e SD			0.12	3.9	0.4
duplicate collection					
Exp. C-1	+49.2 to +53.3	+11.6 to +12.8	$+12.7 \pm 0.2$	$+150.8 \pm 2.9$	$+38.2 \pm 0.7$
Exp. C-2	+49.8 to +54.0	+11.1 to +12.4	$+12.8 \pm 0.1$	$+146.3 \pm 1.0$	$+38.3 \pm 0.3$
^e SD			0.01	3.2	0.04

^a The range of measured $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of NO_3^- on the nitrite-coated filters.

^b Corrected $\Delta^{17}\text{O}$ values of NO_3^- obtained as the intercept of the linear relationship between reciprocal of the measured quantities NO_3^- and $\Delta^{17}\text{O}$ of NO_3^- on each filter of the multi-step nitrite-
 650 coated filter system.

^c Calculated $\delta^{18}\text{O}$ values of O_3 in the terminal positions using Eq. (27).

^d Calculated $\Delta^{17}\text{O}$ values of O_3 in the terminal positions using $\Delta^{17}\text{O}(\text{NO}_3^-)_c$ values and Eq. (2).

^e Standard deviations (1σ) calculated using the average value obtained during each experiment.

655 Table 2. Isotopic measurements for the ozone generation using the gas adsorption method. The $\Delta^{17}\text{O}$ values are present by average \pm standard error.

Expt. No.	Initial O_2	Final O_2		NO_3^-		O_3 (calc.)
	$10^6 \Delta^{17}\text{O}$	mmol ^a	$10^6 \Delta^{17}\text{O}$	μmol	$10^3 \Delta^{17}\text{O}^b$	$10^3 \Delta^{17}\text{O}_{\text{term}}^c$
1	-365.3 ± 1.6	19.2	-1423.6 ± 5.1	879.2	$+15.0 \pm 0.3$	$+45.9 \pm 0.3$
2	-364.2 ± 2.2	19.3	-1482.9 ± 7.5	936.7	$+15.2 \pm 0.2$	$+45.9 \pm 0.5$
3	-363.3 ± 2.6	20.3	-1475.2 ± 4.7	989.0	$+14.9 \pm 0.1$	$+45.4 \pm 0.3$

^a The total volumes (cm^3) of final O_2 measured using a flowmeter and then its number of moles calculated by ideal gas law ($pV = nRT$; $p = 1\text{atm}$, $T = 293\text{K}$).

660 ^b Measured $\Delta^{17}\text{O}$ values of NO_3^- in the aqueous NO_2^- solution.

^c Calculated for O_3 in the terminal positions using Eq. (34).

665

Table 3. The oxygen isotopic compositions of ambient O₃ collected using multi-step nitrite-coated filter pack system. The $\delta^{18}\text{O}$, ϵ , and $\Delta^{17}\text{O}$ values are present by average \pm standard error.

sample collection start point ^a	Average O ₃ conc. (ppb) ^b	$10^3 \Delta^{17}\text{O}(\text{NO}_3)_c^c$	$10^3 \delta^{18}\text{O}_0^d$	$10^3 \epsilon^e$	$10^3 \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}^f$
16/9/17 D	33.0	+12.2 \pm 0.1	+134.9 \pm 0.7	-24.2 \pm 1.7	+36.5 \pm 0.3
16/9/17 N	n.d.	+11.8 \pm 0.1	+128.5 \pm 1.1	-18.4 \pm 10.3	+35.5 \pm 0.4
16/10/17 D	24.0	+12.6 \pm 0.1	+159.5 \pm 3.1	-2.2 \pm 2.9	+37.8 \pm 0.4
16/10/17 N	n.d.	+12.5 \pm 0.1	+154.1 \pm 1.7	-1.0 \pm 4.1	+37.5 \pm 0.4
3/11/17 D	25.4	+13.0 \pm 0.2	+148.2 \pm 2.4	-10.1 \pm 3.4	+39.0 \pm 0.7
3/11/17 N	16.4	+12.6 \pm 0.4	+145.6 \pm 7.8	-2.5 \pm 2.6	+37.8 \pm 1.3
12/12/17 D	22.7	+12.3 \pm 0.1	+138.3 \pm 2.9	-3.5 \pm 8.5	+37.0 \pm 0.3
12/12/17 N	17.0	+12.0 \pm 0.2	+138.5 \pm 1.0	-2.9 \pm 1.2	+36.1 \pm 0.5
29/12/17 D	25.1	+12.6 \pm 0.2	+166.2 \pm 2.5	-21.8 \pm 5.5	+37.9 \pm 0.7
29/12/17 N	21.0	+12.4 \pm 0.3	+160.7 \pm 2.4	-10.2 \pm 5.9	+37.2 \pm 0.8
17/2/18 D	31.5	+12.5 \pm 0.2	+132.2 \pm 3.0	-9.2 \pm 6.5	+37.6 \pm 0.7
17/2/18 N	29.2	+12.2 \pm 0.1	+140.6 \pm 6.2	-8.8 \pm 10.5	+36.7 \pm 0.4
9/3/18 D	36.0	+12.7 \pm 0.3	+164.4 \pm 6.8	-23.6 \pm 22.1	+38.2 \pm 0.9
9/3/18 N	29.4	+12.1 \pm 0.3	+147.5 \pm 6.2	-22.7 \pm 14.2	+36.4 \pm 0.8
24/4/18 D	49.7	+13.2 \pm 0.3	+163.4 \pm 5.9	-8.7 \pm 10.3	+39.7 \pm 1.0
24/4/18 N	44.8	+12.7 \pm 0.3	+150.1 \pm 2.8	-18.3 \pm 4.9	+38.2 \pm 0.8
30/5/18 D	45.0	+12.9 \pm 0.1	+144.7 \pm 3.9	-10.3 \pm 5.1	+38.8 \pm 0.3
30/5/18 N	22.2	+12.0 \pm 0.3	+138.8 \pm 2.7	-10.6 \pm 10.7	+36.0 \pm 0.8
Mean values ^g	31.2 \pm 10.3	+12.5 \pm 0.4	+147.6 \pm 11.7	-11.6 \pm 8.0	+37.4 \pm 1.1

n.d.: no data

675 ^a D and N are the collection period of daytime and nighttime, respectively.

^b The average concentrations of O₃ during each sampling period determined by Ministry of the Environment Government of Japan at Atmospheric Environmental Regional Observation System (<http://soramame.taiki.go.jp>).

^c $\Delta^{17}\text{O}$ values of NO₃⁻ from which changes in $\Delta^{17}\text{O}$ due to the concentration of nitrate blank had
680 been corrected.

^d Calculated $\delta^{18}\text{O}$ values of O₃ in the terminal positions using Eq. (27).

^e Calculated ε values of O₃ on the filters during the reaction R1 using Eq. (28).

^f Calculated $\Delta^{17}\text{O}$ values of O₃ in the terminal positions using $\Delta^{17}\text{O}(\text{NO}_3^-)_c$ values and Eq. (2).

^g Mean values calculated using the average value obtained during each sampling period.

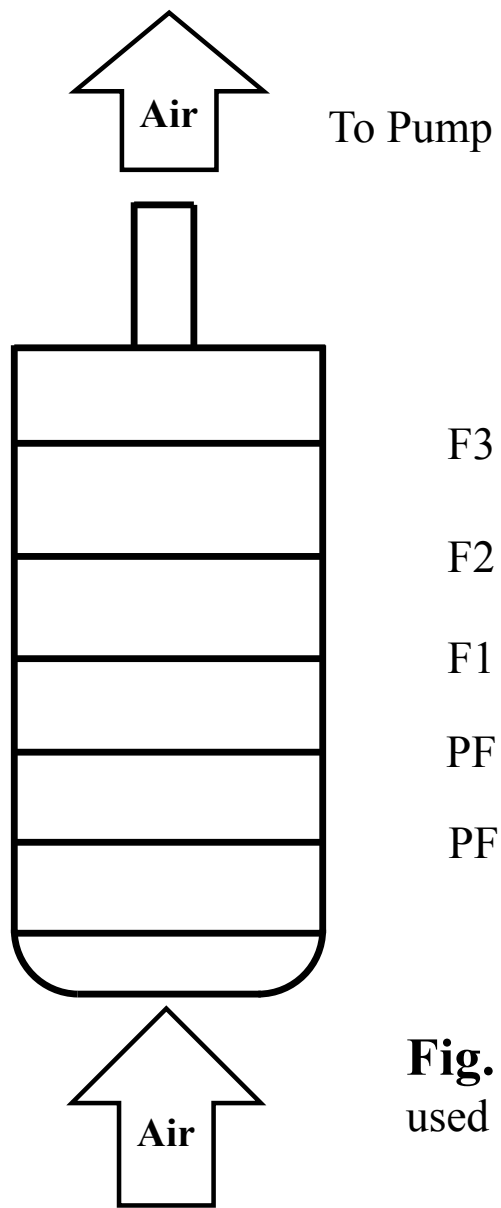


Fig. 1. A schematic diagram showing the multi-step nitrite-coated filter pack system used in this study. PF: Nylon filters; F1, F2 and F3: NaNO_2 impregnated filters.

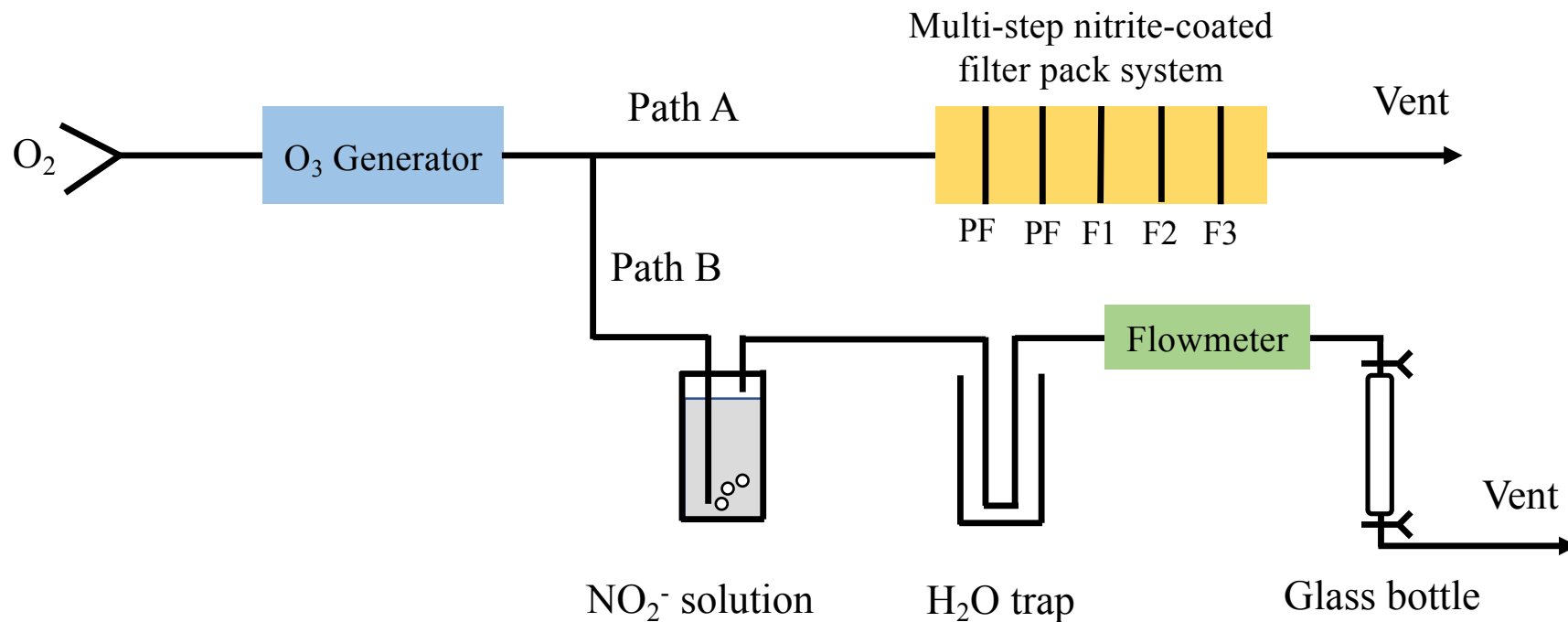


Fig. 2. A schematic diagram showing the flow paths of the experiments using the ozone generator. While the $\Delta^{17}O$ values of O_3 produced by the ozone generator were determined from the $\Delta^{17}O$ values of NO_3^- produced on the multi-step nitrite-coated filter pack system developed in this study in path A, they were determined from the changes in the $\Delta^{17}O$ values of O_2 in the path B as well.

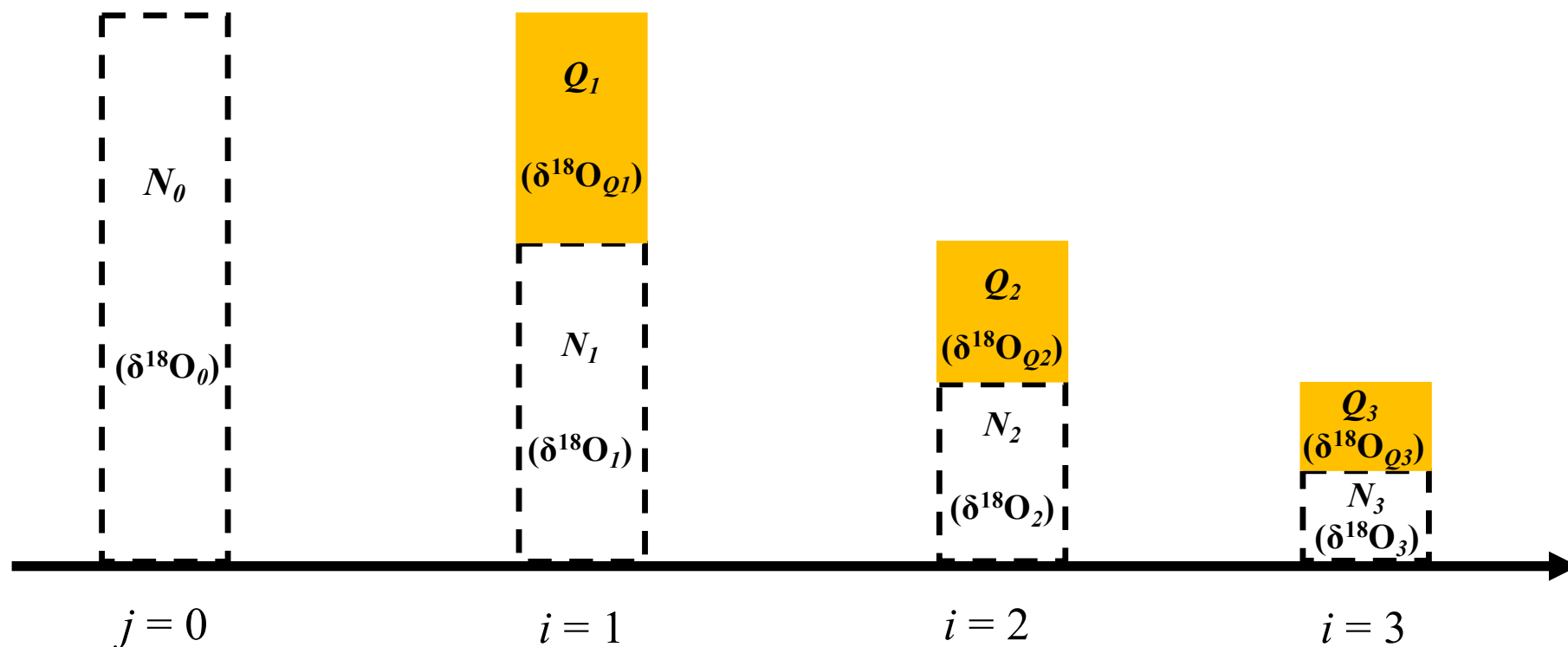


Fig. 3. The conceptual diagram showing the quantities atmospheric O₃ prior to sampling (N_0), together with those passed through the nitrite-coated filter i (N_i ; $i = 1, 2$, and 3). The quantities of O₃-derived O-atoms which reacted with NO₂⁻ at the filter i of the nitrite-coated filters (Q_i) are shown by the yellow sbars as well. The $\delta^{18}\text{O}$ of O₃ that passed through the nitrite-coated filter i ($\delta^{18}\text{O}_i$) could be different from the initial ($\delta^{18}\text{O}_0$) due to the kinetic isotope fractionation during the reaction R1.

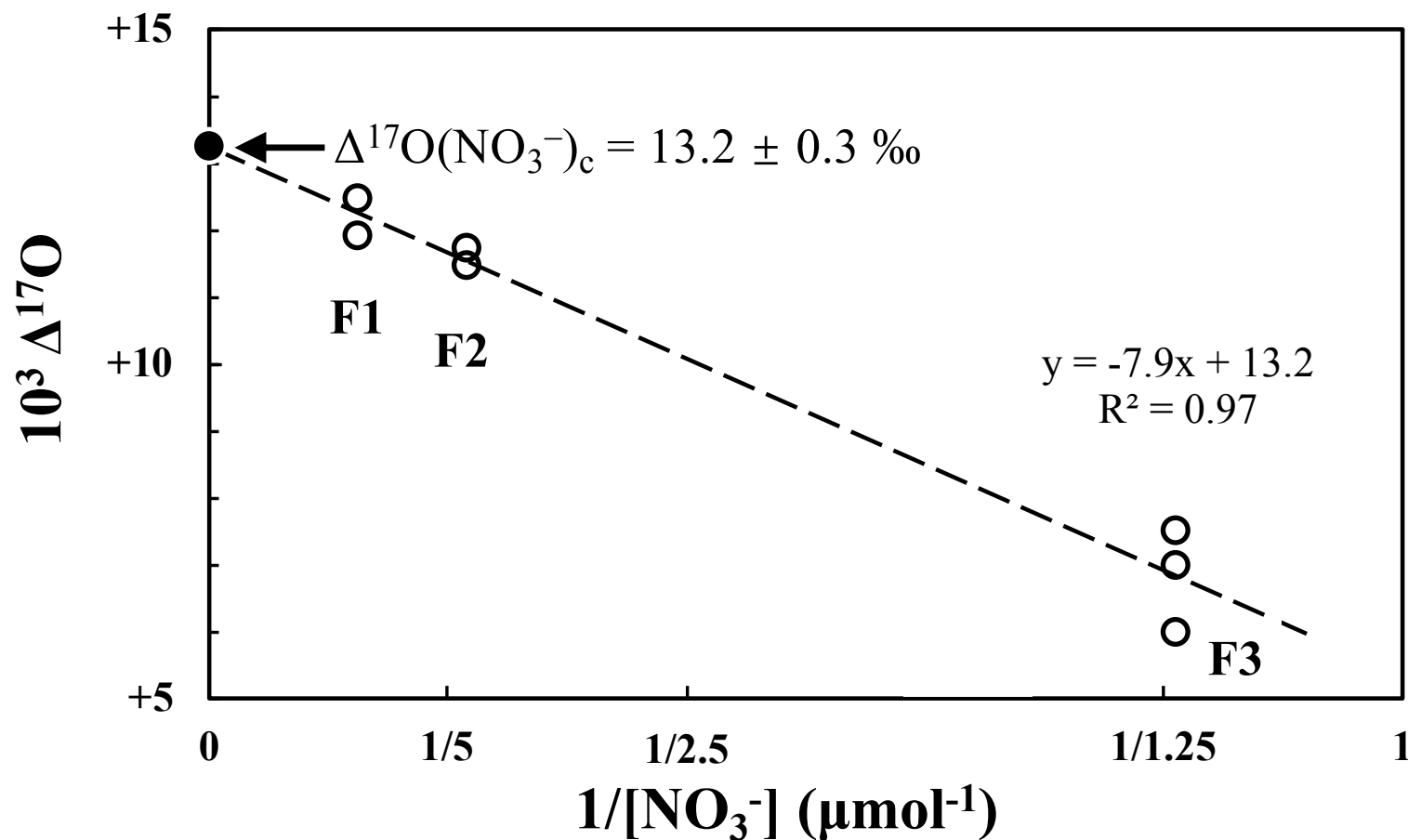


Fig. 4. An example of the relationship between $\Delta^{17}\text{O}$ of NO_3^- and the reciprocal of NO_3^- quantities on the nitrite-coated filters (F1, F2 and F3) obtained during the ambient ozone collection (daytime sample of April 2018). Open circles represent the relationship between the measured quantities of NO_3^- (m) and the measured $\Delta^{17}\text{O}$ values of NO_3^- ($\Delta^{17}\text{O}(\text{NO}_3^-)_m$) on the nitrate-coated filters (F1, F2 and F3). Closed circle represents the corrected $\Delta^{17}\text{O}$ value of NO_3^- ($\Delta^{17}\text{O}(\text{NO}_3^-)_c$) from which the changes in $\Delta^{17}\text{O}$ values due to nitrate blank contribution have been subtracted.

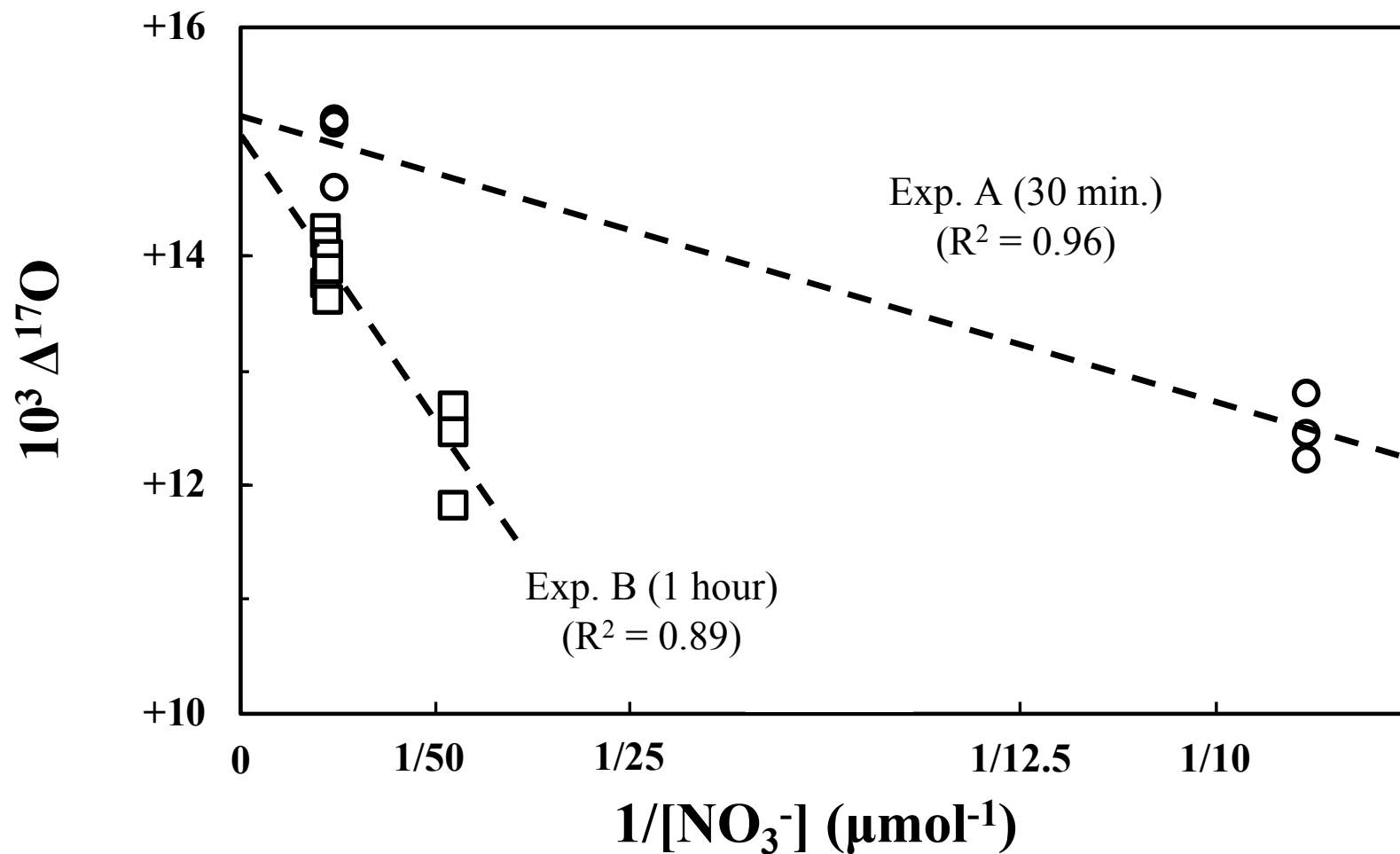


Fig. 5. Relationship between $\Delta^{17}\text{O}$ of NO_3^- and the reciprocal of NO_3^- quantities on each filter obtained through the ozone generator experiments (Exps. A and B). The circles represent Exp. A (30 min.) and the squares represent Exp. B (1 hour). The dotted lines represent the least squares fitting to each experiment.

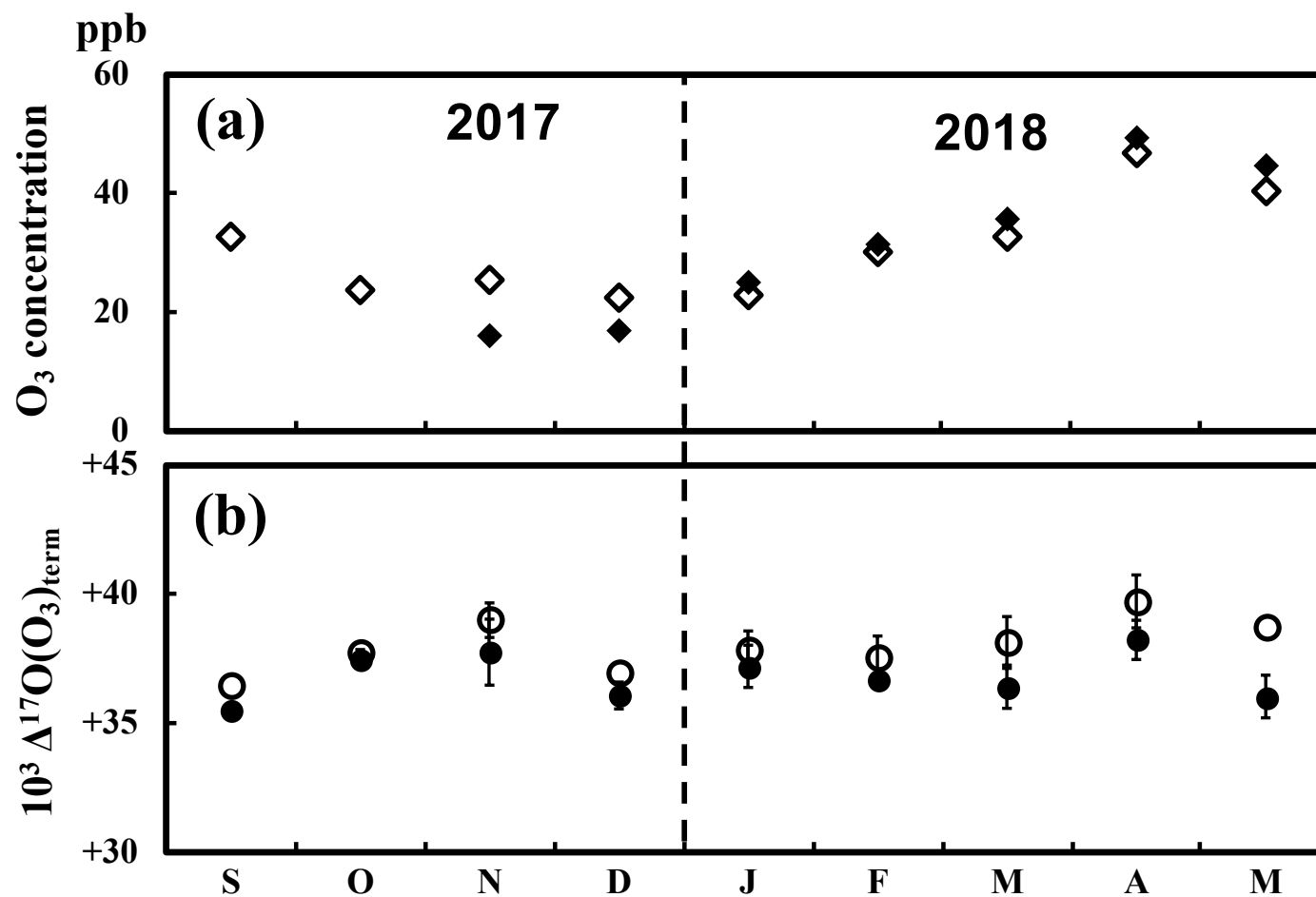


Fig. 6. Temporal variations in the concentrations (a) and $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ (b) of tropospheric O_3 in the terminal positions ($\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$) determined using the multi-step nitrite-coated filter pack system. Open and closed diamonds represent the ambient O_3 concentrations in daytime and nighttime, respectively. Open and closed circles represent $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ in daytime and nighttime, respectively. Vertical error bars represent the uncertainty (standard error) of the measurements.