Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastal Antarctica

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Abstract

Triple oxygen isotopic compositions ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of atmospheric sulfate (SO_4^{2-}) and nitrate (NO_3^-) in the atmosphere reflect the relative contribution of oxidation pathways involved in their formation processes, which potentially provides information to reveal missing reactions in atmospheric chemistry models. However, there remain many theoretical assumptions for the controlling factors of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values in those model estimation. To test one of those assumption that $\Delta^{17}O$ values of ozone have a flat value and does not influence the seasonality of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values, we performed the first simultaneous measurement of $\Delta^{17}O$ values of atmospheric sulfate, nitrate, and ozone collected at Dumont d'Urville station (66°40'S, 140°01'E) throughout 2011. $\Delta^{17}O$ values of sulfate and nitrate exhibited seasonal variation characterized by minima in the austral summer and maxima in winter, within the ranges of 0.9–3.4 ‰ and 23.0–41.9 ‰, respectively. In contrast, $\Delta^{17}O$ values of ozone showed no significant seasonal variation, with values of 26 ± 1 ‰ throughout the year. These contrasting seasonal trends suggest that seasonality in $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are not the result of changes in $\Delta^{17}O(O_3)$ but the changes in oxidation chemistry. The summer/winter trends for $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are caused by sunlight-driven changes in the relative contribution of O_3 oxidation to the oxidation by HO_X, RO_X, and H_2O_2. In addition to that general trend, by comparing $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values to ozone mixing ratios, we found $\Delta^{17}O(SO_4^{2-})$ values observed in spring (September to November) were lower than in fall (March to May), while there is no significant spring/fall difference in $\Delta^{17}O(NO_3^-)$ values. The relatively lower sensitivity of $\Delta^{17}O(SO_4^{2-})$ values to the ozone mixing ratio in spring compared to fall is possibly explained by (i) increased contribution of SO_2 oxidations by OH and H_2O_2 caused by NO_X emission from snowpack and/or (ii) SO_2 oxidation by hypohalous acids (HOX = HOCl + HOBr) in the aqueous phase.

1 Introduction

Triple oxygen isotopic compositions ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of atmospheric sulfate and nitrate have shown potential to probe the relative importance of various oxidation pathways involved in their formations (e.g., Michalski et al., 2003; Lee and Thiemens, 2001). Atmospheric ozone (O_3) possesses high $\Delta^{17}O$ values of approximately 26 ‰ (Krankowsky et al., 1995; Johnston and Thiemens, 1997; Vicars et al., 2012, 2014), contrary to most of the oxygen bearing compounds such as O_2 and H_2O, which have $\Delta^{17}O$ values of approximately 0 ‰ (Barkan and Luz, 2003, 2005). Oxygen atoms of O_3 are directly or indirectly transferred to sulfate and nitrate through various oxidation pathways of their precursors, SO_2 and NO_X (= NO + NO_2), respectively. Therefore, O_3 oxidation produces sulfate and nitrate possessing high $\Delta^{17}O$ values, whereas oxidation by OH, RO_2 and H_2O_2 produces sulfate and nitrate with low $\Delta^{17}O$ values. In general, the $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values can be prognosticated using the given $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values for each reaction pathways and the estimates of relative contribution of each oxidation pathways by atmospheric chemistry/transport models (e.g., Alexander et al., 2009; Morin et al., 2011; Sofen et al., 2011). Considering the higher HO_X levels in summer due to enhanced photochemical activity relative to winter, $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are expected to show the specific seasonal trend with summer minima and winter maxima in the mid to high latitude regions. By comparing those expected values to observations, missing processes for sulfate and nitrate formation in the models have been proposed. For example, McCabe et al. (2006) performed an year-round observation of $\Delta^{17}O(SO_4^{2-})$ values at Alert, Canada, showing lower $\Delta^{17}O(SO_4^{2-})$ values during winter compared to the calculated values using a model of Feitcher et al. (1996); they suggest a twofold overestimate of O_3 oxidation in sulfate formation during winter in the Northern hemisphere, and pointed out 10-18% contribution of metal catalyzed O_2 oxidation in aqueous phase. An observation of $\Delta^{17}O(NO_3^-)$ values in Alert by Morin et al. (2008) revealed significantly higher values during spring compared to the calculated values, which is expected to be a result of NO_2 oxidation by BrO. Savarino et al. (2013) also had shown significantly higher $\Delta^{17}O(NO_3^-)$ values at the marine boundary layer compared to an estimate of chemical transport model by Alexander et al. (2009), while the mismatch was fixed by considering a contribution of BrO in nitrate formation. The $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are thus used to examine the lack of oxidation schemes in the models. However, the observational data of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ to constrain these models are still not enough to demonstrate theoretical assumptions of the controlling factors of $\Delta^{17}O$ signatures in these model estimation (e.g., Morin et al., 2011).

One of the important parameters which have to be confirmed by observations is $\Delta^{17}O$ value of ozone, because of the possibility that $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are influenced not only by changes in oxidation chemistry but also variations in $\Delta^{17}O(O_3)$ values. Indeed, various $\Delta^{17}O(O_3)$ values ranging 25-35 ‰ are used for model calculations to reproduce the observed variations in $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values (Alexander et al., 2009; Morin et al., 2011; Sofen et al., 2011). Those varied $\Delta^{17}O(O_3)$ values were assumed based on the observations using the cryogenic collection method (Johnston and Thiemens, 1997; Krankowsky et al., 1995), which showed highly varied values of 6-54 ‰. However, the recent observations of $\Delta^{17}O(O_3)$ values using the nitrite-coated filter method, which was developed by Vicars et al. (2012), and applied at Grenoble, R/V Polarstern Campaign (Vicars et al., 2014) and Dome C (Savarino et al., 2016), had shown the insignificant spatial and temporal variability with values ranging 23-27 ‰. This result suggests that the variations observed in $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are not the result of changes in $\Delta^{17}O(O_3)$ values, but mainly explained by the changes in oxidation pathways. To test this hypothesis, it is necessary to investigate the spatial and temporal variability of $\Delta^{17}O(O_3)$ values, which is expected to have the stable value, simultaneously with variations in $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values.

Antarctica is a suitable site to test this hypothesis, because of the clear seasonality in solar radiation, which is one of the main factors influencing $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values through the changes in photochemical oxidants variations. In fact, several studies have been reported the clear seasonal variations in $\Delta^{17}O(NO_3^-)$ values at coastal and inland Antarctica, Dumont d'Urville and Dome C, showing an austral summer minimum and a winter maximum (Erbland et al., 2013; Frey et al., 2009; Savarino et al., 2007). This trend is mainly explained by increased NO_X oxidation by OH and RO_2 under solar radiation in summer, relative to winter when NO_X oxidation is dominated by the reaction transferring the oxygen atoms from O_3 to nitrate in dark polar winter, when assuming the values are mainly controlled by oxidation chemistry. The similar trend following solar cycle is expected for $\Delta^{17}O(SO_4^{2-})$ values, which is mainly controlled by the relative importance of SO_2 oxidation by OH, H_2O_2 and O_3. The first attempt of the monthly scale observation of $\Delta^{17}O(SO_4^{2-})$ values at Dome C showed the increasing trend from January to June (summer to winter) and decreasing trend from October to next January (spring to summer), despite the unexpected decline during mid-winter, July-August (Hill-Falkenthal et al., 2013). Nevertheless, the variability of $\Delta^{17}O(SO_4^{2-})$ value throughout the year is larger than those which have ever been observed on the earth (Lee and Thiemens, 2001; Li et al., 2013; McCabe et al., 2006). It is thus ideal to examine if at Antarctica, the $\Delta^{17}O(O_3)$ values show a flat value throughout a year in contrast to those seasonal variability in $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values, for demonstrating that the seasonality of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values is a direct consequence of changes in chemistry and not the variation in $\Delta^{17}O(O_3)$ values.

In this study, we present the first simultaneous observations of $\Delta^{17}O$ values of sulfate, nitrate and ozone at the coastal Antarctic site, Dumont d'Urville Station (DDU) throughout 2011, to answer the key question about the controlling factors of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values as well as to provide a set of data that can be used to constrain chemistry/transport model scheme in the future study. The series of oxidants observations such as O_3 (Legrand et al., 2009, 2016a), HO_X (Kukui et al., 2012, 2014) and NO_X (Grilli et al., 2013) have demonstrated that due to the katabatic winds, air masses on the East Antarctic Plateau enriched in oxidants produced via reactive nitrogen emission from surface snow and subsequent interactive reactions between HO_X, NO_X and RO_2, are frequently exported to DDU. They also suggested the influence of bromine chemistry is much less significant in East Antarctica compared to West coastal site such as Halley and Neumayer. However, besides the framework of that project, model-aided analyses of $\Delta^{17}O(SO_4^{2-})$ observations by Chen et al. (2016) pointed the significant contribution (33-50%) of SO_2 oxidation by hypohalous acids on total sulfate production in remote marine boundary layer including Southern Ocean, indicating the possibility of its influence in coastal Antarctic site. Hence, we secondary aimed to reveal any features of oxidation mechanisms of their precursors based on seasonality of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values at this specific site.

2 Samples and analytical methods

2.1 Sampling site and aerosol sample collection

2.1.1 Sampling site

Samples were collected at DDU (66°40'S, 140°01'E; 40 m above the sea level), located on a small island, 1 km off the coast of Antarctica. The climate of DDU is described in Konig-Langlo et al. (1998). Compared with other parts of Antarctica, DDU is temperate, with temperatures ranging from −30 to 5°C throughout the year. Most parts of the island are free of snow, and the sea ice disappears completely during summer. Recent observations of surface ozone and the OH radical (Legrand et al., 2016a; Kukui et al., 2012) revealed that at DDU, O_3 and OH levels are approximately 2 and 10 times higher, respectively, compared to the Palmer station (Jefferson et al., 1998), due to the transportation of air masses influenced by the snowpack emission of reactive nitrogen species on the East Antarctic Plateau and the subsequent oxidants productions.

2.1.2 Aerosol sample collection

Aerosol samples were collected using a high-volume air sampler (HVAS; General Metal Works GL 2000H Hi Vol TSP; Tisch Environmental, Cleves, OH, USA). Coarse (> 1 μm) and fine (< 1 μm) particles were collected separately, using a four-stage cascade impactor and a backup glass fiber filter, respectively. The slotted 12.7 cm × 17.8 cm glass fiber filters were mounted on the cascade impactor, while 20.3 cm × 25.4 cm glass fiber filters were used for backup. The HVAS was placed on a platform, 1 m above ground, 50 m from the coast, and 20 m away from the closest building. Aerosol collection was carried out at weekly intervals, with flow rates of ~1.5 m^3/min, yielding an average pumped air volume of 15000 m^3 per sample. Samples collected between January 2011 and January 2012 were used for this study. Once per month, a field blank was checked by mounting filters onto the filter holder, and running the cascade impactor for 1 min.

After each collection period, the filters were removed from the cascade impactor inside a clean chemical hood; they were wrapped in aluminum foil and stored in plastic bags at −20°C. The four filters on the impactor stage were grouped together as “coarse” particle samples, while the backup filters were kept as “fine” particle samples. Samples were transported back to University Grenoble Alpes (France) for chemical and isotopic analyses, while frozen.

2.1.3 Quantification of ionic species

The soluble compounds in the aerosols were extracted with ultra-pure water (Millipore filter, 18 MΩcm; EMD Millipore, MA, USA), according to the process described in Savarino et al. (2007); more than 98% of the initial water volume was recovered. Field blank filters were processed in the same way.

Small aliquots of these sample solutions were taken for quantification of ionic species. Anions (Cl^-, NO_3^-, SO_4^{2-}) and sodium (Na^+) concentrations were analyzed using ion chromatography systems described in Savarino et al. (2007) and Jourdain and Legrand (2002), respectively.

Atmospheric concentrations of these ionic species were calculated using the aerosol loading for each filter, the mean filter blank values, and the air volume pumped through the filter. The air volume was corrected to standard temperature and pressure (T = 273.15 K, p = 101325 Pa) based on meteorological data from DDU provided by Meteo France. The uncertainties for atmospheric concentrations were calculated by propagating the typical uncertainty of the ion chromatography analysis (5%) and standard deviation (1σ) of filter blank values .

2.2 Oxygen isotopic analyses of sulfate and nitrate in aerosols

2.2.1 Definition of triple oxygen isotopic compositions

Given the two isotope ratios, notated as ^{17}R (= $^{17}O/^{16}O$) and ^{18}R (= $^{18}O/^{16}O$), stable oxygen isotope ratios are conventionally scaled using a delta (δ) notation:

$$\delta\,^{x}O = \frac{^{x}R_{\mathrm{sample}}}{^{x}R_{\mathrm{VSMOW}}} - 1 \tag{1}$$

where R_{VSMOW} denotes the isotope ratio of the standard material, Vienna Standard Mean Ocean Water (VSMOW); and x is 17 or 18. Despite the robust relationship of the mass-dependent law ($\delta^{17}O = 0.52 \times \delta^{18}O$) in most of the oxygen-containing species, (e.g., O_2 and H_2O), atmospheric ozone does not follow mass-dependent fractionation and possesses a significant positive $\Delta^{17}O$ (= $\delta^{17}O - 0.52 \times \delta^{18}O$), inherited from mass-independent fractionation associated with its formation process (Gao and Marcus, 2001). Since non-zero $\Delta^{17}O$ values can be observed in various atmospheric species bearing oxygen atoms inherited from O_3 (e.g., sulfate and nitrate), the $\Delta^{17}O$ signature is a powerful tracer, used to investigate the relative contribution of O_3 to oxidation processes.

2.2.2 Oxygen isotopic analysis of sulfate and data correction

All $\Delta^{17}O$ values of sulfate were measured with an isotope ratio mass spectrometer (IRMS) (MAT253; Thermo Fisher Scientific, Bremen, Germany), coupled with an in-house measurement system at Tokyo Institute of Technology. The measurement system for $\Delta^{17}O(SO_4^{2-})$ follows Savarino et al. (2001), with modifications described in several studies

(Schauer et al., 2012; Geng et al., 2013). Briefly, 1 μmol of sulfate is separated from other ions using ion chromatography and chemically converted to silver sulfate (Ag_2SO_4). This Ag_2SO_4 powder is transported in a custom-made quartz cup, which is dropped into a furnace at 1000°C within a high temperature conversion elemental analyzer (TC/EA; Thermo Fisher Scientific, Bremen, Germany) and thermally decomposed into O_2 and SO_2. Gas products from this sample pyrolysis are carried by ultrahigh-purity He (>99.99995 % purity; Japan Air Gases Co., Tokyo, Japan), which is first purified using a molecular sieve (5Å) held at −196°C (Hattori et al., 2015). The gas products O_2 and SO_2 are carried through a cleanup trap (trap 1) held at −196°C to trap SO_2 and trace SO_3, while O_2 continues to another molecular sieve (5Å) in a 1/16 inch o. d. tubing trap (trap 2) held at −196°C to trap O_2 separately from the other gas products. The O_2 is purified using a gas chromatograph, with a CP-Molsieve (5Å) column (0.32 mm i.d., 30 m length, 10 μm film; Agilent Technologies Inc., Santa Clara, CA, USA) held at 40°C, before being introduced to the IRMS system to measure m/z = 32, 33, and 34. The inter-laboratory calibrated standards (Sulf-α, β and ε; Schauer et al., 2012) were used to assess the accuracy of our measurements; our values were in good agreement with published ones (Fig. 1). As discussed by Schauer et al. (2012), this method results in the oxygen isotope exchange between the O_2 products and the quartz cups as well as the quartz reactor, which shifts $\delta^{17}O$, $\delta^{18}O$, and thus $\Delta^{17}O$ measurements. The shift in $\Delta^{17}O(SO_4^{2-})$ value is corrected by estimating the magnitude of the oxygen isotope exchange with quartz materials, whose $\Delta^{17}O$ value is assumed to be approximately 0 ‰ (Matsuhisa et al., 1978). The intercept of −0.03 in Fig. 1 also supports this assumption. Since $\delta^{17}O$ and $\delta^{18}O$ values of each quartz materials used in this study are not known, the corrected $\delta^{17}O$ and $\delta^{18}O$ values of SO_4^{2-} shown in Supplementary materials are unreliable, and therefore we don't discuss these values. Note that those $\delta^{17}O$ and $\delta^{18}O$ values of SO_4^{2-} are relative values to our O_2 reference gas. The precision of $\Delta^{17}O$ is typically better than ±0.2 ‰ based on replicate analyses of the standards.

Since sea salt sulfate aerosols (ss-SO_4^{2-}) are of little importance to atmospheric sulfur oxidation processes (i.e., $\Delta^{17}O$(ss-SO_4^{2-}) = 0‰), both total sulfate concentrations and $\Delta^{17}O$ values were corrected for their ss-SO_4^{2-} component to obtain their non-sea salt sulfate (nss-SO_4^{2-}) content, using Eq. (2) and (3) below.

$$[\mathrm{nss}-\mathrm{SO_4^{2-}}] = [\mathrm{total}-\mathrm{SO_4^{2-}}] - k \times [\mathrm{Na^+}] \tag{2}$$

$$\Delta^{17}\mathrm{O}(\mathrm{nss}-\mathrm{SO_4^{2-}}) = \frac{[\mathrm{total}-\mathrm{SO_4^{2-}}]}{[\mathrm{nss}-\mathrm{SO_4^{2-}}]} \times \Delta^{17}\mathrm{O}(\mathrm{total}-\mathrm{SO_4^{2-}}) \tag{3}$$

where "total" is the quantity measured by ion chromatography, corresponding to the sum of ss- and nss-SO_4^{2-} components; and k is the mass ratio of $[SO_4^{2-}]/[Na^+]$ in sea water (0.25; Holland et al., 1986). To take into account sea salt chemical fractionation processes that affect the Antarctic region in winter, when temperatures drop below −8°C in the presence of sea-ice (Wagenbach et al., 1998), we used a k value of 0.13±0.04, estimated from the average at winter DDU previously by Jourdain and Legrand (2002) as well as confirmed by our own dataset; this was applied to samples collected from May to October. Note that the sea salt fractionation is a chemical fractionation and is different from an isotopic fractionation. Eq. (3) is the isotope mass balance equation between ss- and nss-SO_4^{2-}, with $\Delta^{17}O$(ss-SO_4^{2-}) = 0 ‰. The total uncertainties for $\Delta^{17}O$(nss-SO_4^{2-}) values were calculated using the precision of $\Delta^{17}O$ measurement and the uncertainty of k value, resulting in the uncertainty of ±1.9 ‰ at maximum. The propagated error for both [nss-SO_4^{2-}] and $\Delta^{17}O$(nss-SO_4^{2-}) values are shown in Supplementary material.

The measurement of $\Delta^{17}O(SO_4^{2-})$ value were performed only for the fine mode samples, because sulfate in the coarse mode samples consists of more than 80% ss-SO_4^{2-}. The influence of ornithogenic soil emission on Na^+ and SO_4^{2-} concentration was not taken into account, since it mainly affects supermicron (coarse) aerosols (Jourdain and Legrand, 2002).

2.2.3 Oxygen isotopic analysis of nitrate

The $\Delta^{17}O$ value of nitrate was measured simultaneously with $\delta^{18}O$ and $\delta^{15}N$ values using a bacterial denitrifier method (Casciotti et al., 2002), coupled with IRMS measurement using our in-house peripheral system at University Grenoble Alpes (Morin et al., 2009). All nitrates in our samples were converted to N_2O via bacterial denitrification. This N_2O was introduced to the measurement system, separated from CO_2, H_2O and other volatile organic compounds, and pre-concentrated in a cold trap. The trapped N_2O was converted into O_2 and N_2 by pyrolysis at 900°C, using a gold tube furnace, followed by separation of O_2 and N_2 via a 10 m Molsieve (5Å) gas chromatography column, before being introduced to the IRMS system. Measurements were performed simultaneously for samples equivalent to 100 nmol nitrate, as well as a subset of international nitrate reference materials (US Geological Survey 32, 34, and 35, as well as their mixtures) for correction and calibration of $\Delta^{17}O$ and $\delta^{18}O$ values relative to VSMOW and $\delta^{15}N$ values relative to air N_2. Analytical uncertainty was estimated based on the standard deviation of the residuals from a linear regression between the measured reference materials and their expected values. The uncertainties (1σ) for $\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$ were 0.4 ‰ and 0.3 ‰, respectively.

2.3 Sampling and analytical methods of oxygen isotopic composition of ozone

The sampling and isotopic analysis of surface ozone were performed by coupling the nitrite-coated filter method with nitrate isotopic measurements described in Vicars et al. (2012, 2014). The principle of ozone collection underlying this technique is the filter-based chemical trapping of ozone via its reaction with nitrite:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad . \qquad \text{(R1)}$$

During R1, one of the three oxygen atoms of nitrate is transferred from one of the two terminal oxygen atoms of ozone, while the other two oxygen atoms are derived from the reagent nitrite. Since the $\Delta^{17}O$ signature of ozone is located only on the terminal atoms of ozone (Bhattacharya et al., 2008; Janssen and Tuzson, 2006), simple mass balance implies that $\Delta^{17}O(O_3)_{term}$ is 2/3 of $\Delta^{17}O(O_3)_{bulk}$. Thus, $\Delta^{17}O(O_3)_{term}$ values can be inferred using the simple mass-balance of Eq. (4):

$$\Delta^{17}O(O_3)_{term.} = 3 \times \Delta^{17}O(NO_3^-) - 2 \times \Delta^{17}O(NaNO_2), \qquad (4)$$

where $\Delta^{17}O(NaNO_2)$ of the reagent is confirmed to be zero (Vicars et al., 2012). Therefore, the $\Delta^{17}O$ value of ozone can be determined from the oxygen isotopic composition of nitrate produced on the coated filter via R1, determined by the same measurement system described above.

Ozone sampling was carried out by pumping ambient air, using a low-volume vacuum pump (Model 2522C-02; Welch, IL, USA), through a glass fiber filter (Ø 47 mm, GF/A type; Whatman, UK), pre-coated with a mixture of $NaNO_2$, K_2CO_3 and glycerol. Sampling was conducted once per week from May 2011 to April 2012, with 24–48 h sampling intervals. After sampling, filter samples and procedural blanks were extracted in 18MΩ water. Any unreacted nitrite reagent was removed using the reaction with sulfamic acid, neutralized later with NaOH solutions (Granger and Sigman, 2009; Vicars et al., 2012). The sample solutions were stored in the dark at −20°C, and transported back to Grenoble. After nitrate concentration analysis using a colorimetric technique (Frey et al., 2009), the isotopic analysis of nitrate (i.e., ozone) was performed using the same protocol as the nitrate isotope analysis. In addition to the isotope measurements of ozone, we aligned the mixing ratio of surface ozone to the weekly average using data reported in Legrand et al. (2016a) to fit the time resolution of our aerosol sampling.

2.4 Complementary analyses

To investigate relationships between the origins of the air masses and the $\Delta^{17}O$ signatures of sulfate and nitrate, transport pathways of sampled air masses were analyzed using the NOAA's HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (Stein et al., 2015). The model was used with NCEP-NCAR reanalysis data fields using a regular 2.5° × 2.5° longitude-latitude grid. Five-day backward trajectories for air masses arriving at the DDU at an altitude of 40 m above sea level were computed twice per day for each day during sampling periods.

The sea ice area fraction around the Antarctic continent was derived from the Advanced Microwave Scanning Radiometer on-board NASA's Earth Observing System Aqua satellite using the ARTIST sea ice algorithm (Kaleschke et al., 2001). The contact times of these air masses with the Antarctic continent and sea ice were calculated using five-day backward trajectories and sea ice area fractions.

3 Results

3.1 Sulfate

Seasonal variations in atmospheric concentrations and $\Delta^{17}O$ values of SO_4^{2-} are shown in Fig. 2a. Atmospheric concentrations of nss-SO_4^{2-} showed a clear seasonal trend. The [nss-SO_4^{2-}] had a maximum of up to ~280 ng m^{-3} from January to February, corresponding to the austral summer period, but decreased to a background level (~10 ng m^{-3}) during May to August, winter period, before increasing as summer returned. This trend in [nss-SO_4^{2-}] at coastal Antarctic sites results from enhanced marine biogenic activity, emitting dimethyl sulfide (DMS) in circum-Antarctic regions in summer, as has often been reported previously (e.g., Wagenbach et al., 1998; Minikin et al., 1998; Jourdain and Legrand, 2002;

Preunkert et al., 2008). As Antarctica is surrounded by ocean, DMS is the major source of atmospheric non-sea salt sulfur (Minikin et al., 1998; Jourdain and Legrand, 2002). Interestingly, a sample from 18–25 July had an anomalously high value of 46 ng m^{-3}, four times the monthly mean level for July (~12 ng m^{-3}).

The Δ^{17}O(nss-SO_4^{2-}) values showed the reverse trend, with a summer minimum and a winter maximum. The Δ^{17}O(nss-SO_4^{2-}) value increased from 1.0 ‰ observed in January to a maximum of 3.4 ‰ at the end of June, decreasing to 0.9 ‰ in December. The annual weighted mean value of Δ^{17}O(nss-SO_4^{2-}) was 1.4 ± 0.1 ‰. Higher values (greater than 2 ‰) were generally observed during April to July, but the anomalous peak from 18–25 July was characterized by a low Δ^{17}O(nss-SO_4^{2-}) value of 0.9 ‰. Consequently, the monthly mean value had a maximum in July (2.6 ± 0.6 ‰), when the 18–25 July data were excluded.

3.2 Nitrate

Seasonal variations in atmospheric concentrations and Δ^{17}O values for nitrate are shown in Fig. 2b. Nitrate concentrations increased to 55 ng m^{-3} in January but gradually decreased to less than 10 ng m^{-3} in March to May. In July, a significant peak of 28 ng m^{-3} was observed, followed by a seasonal increase as summer returned. The Δ^{17}O(NO_3^-) values showed a simple seasonal variation, with a summer minimum and a winter maximum. Δ^{17}O(NO_3^-) increased from 27 ‰ in January to over 40 ‰ in July, decreasing moderately to a minimum value of 23 ‰ in December. These trends in nitrate concentrations and Δ^{17}O(NO_3^-) values are consistent with those observed at this site 10 years ago (Savarino et al., 2007).

3.3 Ozone

Daily averaged ozone mixing ratios are presented in Fig. 2c; these exhibit a distinct seasonal variation, with a summer minimum and a winter maximum. The minimum ozone mixing ratio was observed in January, having a value lower than 10 ppbv, while the maximum was observed during July to August, having a value higher than 35 ppbv. From November to December, sudden increases in ozone levels to values over 30 ppbv were observed a few times, consistent with seasonal trends for ozone at DDU (Legrand et al., 2009). The $\Delta^{17}O(O_3)_{bulk}$ values showed an insignificant variation, with a summer maximum of 28 ‰ and a winter minimum of 23 ‰, and an annual mean $\Delta^{17}O(O_3)_{bulk}$ value of 26 ± 1 ‰.

4 Discussion

4.1 Δ^{17}O values and atmospheric formation pathways of sulfate and nitrate

Atmospheric sulfate and nitrate are produced from the oxidation of their precursor, SO_2 and NO_X, by various oxidants. Therefore, $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values for sulfate and nitrate produced via each oxidation pathways are determined by the Δ^{17}O values of their precursors and the Δ^{17}O values of oxidants, which provides oxygen atom to the products in different transferring factors. To interpret the our data, we estimated the $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values produced via each oxidation pathways. The $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values for the oxidation by O_3 were estimated using the mean $\Delta^{17}O(O_3)$ value (i.e., 26 ‰) observed in this study. Each oxidation pathways and corresponding Δ^{17}O values of products sulfate and nitrate are summarized in Table 1.

4.1.1 Δ^{17}O values of sulfate

Since SO_2 quickly exchanges its oxygen atoms with abundant water vapor in the atmosphere, the $\Delta^{17}O(SO_2)$ value is assumed to be 0 ‰ (Holt et al., 1983). Thus, the $\Delta^{17}O(SO_4^{2-})$ value is dependent only on the oxidation pathway of SO_2 to SO_4^{2-}. SO_2 oxidation by OH ($\Delta^{17}O(OH)$ = ~0 ‰) in the gas phase produces sulfuric acid (H_2SO_4) which possesses the $\Delta^{17}O(SO_4^{2-})$ value of approximately 0‰.

$$SO_2 + OH \xrightarrow{O_2,H_2O,M} H_2SO_4 \tag{R2}$$

SO_2 can also dissolve into the aqueous phase on aerosol surfaces, where it can be oxidized by O_3, H_2O_2 or metal-catalyzed oxidation by O_2, to form sulfate (Seinfeld and Pandis, 2006). Given that $\Delta^{17}O(O_3)_{bulk}$ values of approximately 26 ‰ have been observed, the $\Delta^{17}O(SO_4^{2-})$ value of sulfate produced by ozone should be around 6.5 ‰, based on a Δ^{17}O signature transfer factor of 0.25 (Savarino et al., 2000).

$$SO_3^{2-} + O_3 \longrightarrow SO_4^{2-} + O_2 \tag{R3}$$

Give the $\Delta^{17}O(H_2O_2)$ values of 1.6 ‰ on average (Savarino et al., 1999), the $\Delta^{17}O(SO_4^{2-})$ of sulfate produced by H_2O_2 is estimated to be 0.8 ‰, using a transfer factor of 0.5 (Savarino et al., 2000).

$$HSO_3^{2-} + H_2O_2 \longrightarrow HSO_4^- + H_2O \tag{R4}$$

The $\Delta^{17}O(O_2)$ value was measured to be −0.3 ‰ (Barkan and Luz, 2003), producing sulfate with a $\Delta^{17}O(SO_4^{2-})$ value of almost 0 ‰ (Savarino et al., 2000).

$$SO_3^{2-} + O_2 \xrightarrow{Fe,Mn} SO_4^{2-} \tag{R5}$$

Additionally, aqueous phase SO_2 oxidation by hypohalous acids (HOX = HOCl, HOBr) has been proposed as one of the major reactions in marine boundary layer (Vogt et al., 1996; von Glasow et al., 2002). Details are discussed in section 4.3.

Thus, $\Delta^{17}O(SO_4^{2-})$ of nss-SO_4^{2-} results from a subtle balance between various oxidation reactions each one transferring a specific amount of $\Delta^{17}O$ signature to sulfate.

4.1.2 $\Delta^{17}O$ values of nitrate

The $\Delta^{17}O(NO_3^-)$ value is dependent on both the $\Delta^{17}O(NO_2)$ value and the oxidation pathways of NO_2 to NO_3^-. The $\Delta^{17}O(NO_2)$ is determined by the relative contribution of NO oxidation pathways during the following photochemical cycle.

$$\mathrm{NO_2} \xrightarrow{\mathrm{hv}} \mathrm{NO} + \mathrm{O(^1D)} \tag{R6}$$

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2} \tag{R7}$$

$$\mathrm{NO} + \mathrm{RO_2} \longrightarrow \mathrm{NO_2} + \mathrm{RO} \tag{R8}$$

Since all non-zero $\Delta^{17}O$ of ozone is positioned in the terminal oxygen atoms (Bhattacharya et al., 2008), which preferentially react with NO (Savarino et al., 2008), NO_2 formed by ozone exhibits a higher isotopic value than the bulk $\Delta^{17}O(O_3)$. On the other hand, NO + RO_2 reaction produces the nitrate with lower $\Delta^{17}O(NO_3^-)$ value because $\Delta^{17}O(RO_2)$ is approximately 0 ‰ (Morin et al., 2007). NO_2 is then converted into nitrate through one of the following reactions.

$$\mathrm{NO_2} + \mathrm{OH} \xrightarrow{\mathrm{M}} \mathrm{HNO_3} \tag{R9}$$

$$\mathrm{NO_2} + \mathrm{O_3} \longrightarrow \mathrm{NO_3} \tag{R10}$$

$$\mathrm{NO_3} \xrightarrow{\mathrm{hv}} \mathrm{NO_2} + \mathrm{O(^1D)} \tag{R11}$$

$$\mathrm{NO_3} + \mathrm{RH} \longrightarrow \mathrm{HNO_3} + \text{products} \tag{R12}$$

$$\mathrm{NO_3} + \mathrm{NO_2} \overset{\mathrm{M}}{\Longleftrightarrow} \mathrm{N_2O_5} \xrightarrow{\mathrm{H_2O}} \mathrm{2HNO_3} \tag{R13}$$

It has been pointed out that BrO plays a significant role in both NO and NO_2 oxidation in marine boundary layer (Savarino et al., 2013) through the following reactions;

$$\mathrm{NO} + \mathrm{BrO} \longrightarrow \mathrm{NO_2} + \mathrm{Br}\ , \tag{R14}$$

$$\mathrm{NO_2} + \mathrm{BrO} \longrightarrow \mathrm{BrONO_2} \xrightarrow{\mathrm{H_2O}} \mathrm{HNO_3} + \mathrm{HOBr}\ , \tag{R15}$$

while they are thought to have little importance (2% at maximum) on the Antarctic Plateau during the austral summer, due to low BrO levels up to 2-3 pmol/mol (Frey et al., 2015; Savarino et al., 2016). The oxidation by BrO may also produce NO_2 and nitrate with high $\Delta^{17}O$ values (Morin et al., 2007), because BrO is thought to possess the terminal oxygen atom of ozone (Bhattacharya et al., 2008).

Following the principle that two of the three oxygen atoms in NO_3^- come from NO_2 and one arises through conversion of NO_2 to NO_3^-, the $\Delta^{17}O(NO_3^-)$ value of nitrate produced by each pathway can be expressed as Eq. (5).

$$\Delta^{17}\mathrm{O(NO_3^-)} = \frac{2}{3} \times \Delta^{17}\mathrm{O(NO_2)} + \frac{1}{3} \times \Delta^{17}\mathrm{O(Oxidant)} \tag{5}$$

For a given value of $\Delta^{17}O(NO_2)$, the NO_2 + OH pathway produces the lowest $\Delta^{17}O(NO_3^-)$ value, while the NO_3 + RH pathway or $BrONO_2$ hydrolysis produce the highest $\Delta^{17}O(NO_3^-)$ values.

4.2 General trend of seasonal variations in $\Delta^{17}O$ values of sulfate and nitrate

The $\Delta^{17}O$ signatures of atmospheric sulfate and nitrate originate from the oxygen transfers from ozone, via oxidation of their precursors. Thus, changes in $\Delta^{17}O(O_3)$ values likely affect both $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values. However, given the small seasonal variability of the $\Delta^{17}O(O_3)_{bulk}$ (ca. 5 ‰), and assuming that all oxygen atoms transferred to NO_X are from the terminal oxygen of ozone, the expected variability of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ should not exceed 1.3 ‰ and 7.5 ‰, respectively. Clearly, these upper limits do not explain the 2.5 ‰ and 19 ‰ seasonal variability observed in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ at DDU, respectively. Furthermore, the seasonal variation in $\Delta^{17}O(O_3)$ values, with a summer maximum and a winter minimum, is the reverse pattern to $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values, with summer minima and winter maxima. These inconsistencies suggest that variability in $\Delta^{17}O(O_3)$ values is not the major factor influencing the seasonal variations in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values.

Meanwhile, $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are dependent on the relative importance of various oxidation pathways involved in their formation as described in the previous sections. Since the relative importance of these oxidation pathways is sensitive to the relative concentrations of oxidants in the atmosphere, and there is seasonal variation for ozone mixing ratios at a continental scale (Crawford et al., 2001; Legrand et al., 2009), the mixing ratio of ozone is expected to correlate with $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values. Indeed, $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values, as well as ozone mixing ratios, all display similar seasonal variations, as shown in Fig. 2. The seasonal variation in the ozone mixing ratios at DDU is generally explained by accumulation of ozone in winter, and its photochemical destruction in summer (Legrand et al., 2009; 2016a), which induces the production of HO_X, RO_X, and H_2O_2 in the summer period. Therefore, we propose that seasonal variations in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ result from a shift in oxidation pathways from O_3 to HO_X, RO_X, and H_2O_2. Decreases in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are caused by the combining effect of decrease in the ozone concentration and decrease in the transfer efficiency of $\Delta^{17}O(O_3)$ to the final products. Thus, the changes in relative concentrations of O_3 vs. HO_X, RO_X, and H_2O_2, along with the changes in sunlight level, are the main factors controlling the seasonal variations of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values.

A similar seasonal variation in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values has been observed at Dome C, an inland Antarctic site (Hill-Falkenthal et al., 2013). However, the $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values observed at Dome C significantly declined in July and August, in contrast to our observations that showed only a single significant decline in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values during the period of 18–25 July. This low $\Delta^{17}O(nss\text{-}SO_4^{2-})$ sample is also characterized by high $nss\text{-}SO_4^{2-}$ concentration (Fig. 2a). We don't have any evidence of contamination from station activities or laboratory works. The preliminary result of sulfur isotope analysis of sulfate in the same sample, showing $\delta^{34}S$ value of 17.6 ‰ (to be published), suggests that this sulfate results from marine biogenic sulfur (i.e., DMS) which possesses $\delta^{34}S$ values ranging 16–20 ‰ (Oduro et al., 2012; Amrani et al., 2013). However, the results of the back trajectory analyses exhibit that DDU was under continental outflow condition over this period, as well as throughout July (Fig. 3). It is hence difficult to identify the origin of this low $\Delta^{17}O(nss\text{-}SO_4^{2-})$ value during 18–25 July. Nevertheless, this point doesn't change the interpretation that $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values are generally lower in summer and higher in winter. Thus, this sample was excluded from consideration for the following discussion and does not impair our further interpretation.

For sulfate, the relative contribution of O_3 oxidation for sulfate formation ($f(nss\text{-}SO_4^{2-})_{O3}$) was calculated. Since positive $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values result from only H_2O_2 and O_3 oxidation and the other pathways result in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ of approximately 0 ‰, we calculated the maximum and the minimum $f(nss\text{-}SO_4^{2-})_{O3}$ by assuming no contribution of H_2O_2 oxidation, and assuming the contribution from only H_2O_2 and O_3 oxidation, respectively, using the simple mass balance equation. Consequently, the mean summer (Jan., Feb., and Dec.) $\Delta^{17}O(nss\text{-}SO_4^{2-})$ value of 1.2 ‰ is corresponding to $f(nss\text{-}SO_4^{2-})_{O3}$ of 0.07-0.18, whereas the mean winter (Jun. - Aug.) $\Delta^{17}O(nss\text{-}SO_4^{2-})$ value of 2.4 ‰ is corresponding to $f(nss\text{-}SO_4^{2-})_{O3}$ of 0.28-0.37. The relative contribution of O_3 oxidation is thus 2 to 4 folds higher in winter than in summer. However, it is important to mention that DMS levels are quite low at DDU in winter (Preunkert et al. 2007); the sulfate collected at DDU is likely produced at a lower latitude region under more sunlight. Thus, the observed $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values in winter may not solely reflect oxidation chemistry in the local atmosphere at DDU. The sulfur sources need to be constrained for the interpretation of winter data. Also for nitrate, it is believed that during Antarctic winter period, the atmospheric nitrate results mainly from the deposition of polar stratospheric clouds (Santacesaria et al., 2001; Savarino et al, 2007) and $\Delta^{17}O(NO_3^-)$ values are not representative of the oxidation chemistry of the atmosphere at this site. On the other hand, since a mean summer $\Delta^{17}O(NO_3^-)$ value of 27.1 ‰ requires the contribution of NO_2+OH pathway ($f(NO_3^-)_{OH}$), the maximum and minimum $f(NO_3^-)_{OH}$ value was calculated by assuming no contribution of N_2O_5 hydrolysis, and by assuming no contribution of NO_3+RH and $BrONO_2$ hydrolysis pathways, respectively. As a result, $f(NO_3^-)_{OH}$ value corresponding to the summer $\Delta^{17}O(NO_3^-)$ value of 27.1 ‰ is expected to range 0.28-0.52. However, this is in contradiction to an expectation that the termination reaction is only NO_2+OH pathway under permanent sunlight. For further constraints on oxidation chemistry, a coupled stratosphere/troposphere chemical transport model will be necessary, which is beyond the scope of this paper.

4.3 Sensitivity of sulfate and nitrate $\Delta^{17}O$ values to the ozone mixing ratio

To examine the response of $\Delta^{17}O$ values to the changes in oxidant concentration, we compared $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values to ozone mixing ratio (Figure 4), which was only one oxidant observed in year-round scale at the same time. In Fig. 4, $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are generally co-varied with ozone mixing ratios, suggesting that a change in the ozone mixing ratio is one of the main factors controlling $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values. Note that as mentioned in section 4.2, in winter, $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are not directly linked to ozone mixing ratios at DDU.

Excluding winter data (June to August), the regression lines for sulfate and nitrate have slopes, intercepts and correlation coefficients (R^2) of 0.07, −0.01 and 0.50, and 0.55, 18.2 and 0.80, respectively (Fig. 4). These slopes indicate how sensitive $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are to ozone mixing ratios. Meanwhile, the intercepts indicate $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values when assuming ozone was not involved in the oxidation of SO_2 and NO_2. If this was true, it would imply that the seasonal cycles of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ are controlled largely by the last stage of oxidation and not by the $\Delta^{17}O$ values of their precursors. In the case of sulfate, this is likely to be true, given that $\Delta^{17}O(SO_2)$ = 0 ‰ year-round, because of oxygen isotopic exchange between SO_2 and water vapor. Therefore, the intercept for sulfate of approximately 0 ‰ is consistent with $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values for sulfate produced via the SO_2 + OH pathway. Meanwhile, the intercept of approximately 18 ‰ for nitrate (Fig. 4b) corresponds to a $\Delta^{17}O(NO_2)$ value of 27 ‰, assuming all nitrate is produced via the NO_2 + OH pathway. This $\Delta^{17}O(NO_2)$ value is in a good agreement with the value of 26 ‰ calculated for conditions at 80°N, under the assumption that $\Delta^{17}O(OH)$ = 0 ‰ (Morin et al, 2011). Using the calculation processes of Morin et al. (2011), we calculated $\Delta^{17}O(NO_2)$ to be 26.5 ‰, consistent with the intercept value. In this calculation, we employed DDU conditions for summer, with a mean temperature of about 0°C, $\Delta^{17}O(O_3)$ = 26 ‰, mixing ratios of O_3 and RO_2 of 5.6×10^{11} molecules cm^{-3} and 3.3×10^{8} molecules cm^{-3}, respectively (Legrand et al., 2009; Kukui et al., 2012). Thus, the plot of $\Delta^{17}O(NO_3^-)$ values as a function of ozone mixing ratios has potential to be used for estimating $\Delta^{17}O(NO_2)$ values, which they have never been measured.

The sensitivity of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values to ozone mixing ratios in spring (September to November) seems to be lower than in fall (March to May) (Fig. 4). Fixing the intercept to −0.01, the slopes between $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values and ozone mixing ratios for spring and fall were 0.063 ± 0.004 and 0.084 ± 0.005, respectively, showing a clear difference over their range of deviation. In contrast to $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values, the slopes between $\Delta^{17}O(NO_3^-)$ values and ozone mixing ratios for an intercept fixed to 18.2 show less difference between spring and fall, with the values of 0.54 ± 0.02 and 0.57 ± 0.01, respectively. However, $\Delta^{17}O(nss\text{-}SO_4^{2-})$ is also sensitive to HO_X, RO_X, and H_2O_2. If the relative abundance of O_3 vs. HO_X, RO_X, and H_2O_2 are regulated only by changes in solar irradiation as discussed in section 4.2, then the slopes between $\Delta^{17}O$ values for sulfate and nitrate against ozone mixing ratios should be the same for spring and fall. The different slopes observed for sulfate in spring and fall indicate the effects of various oxidation processes, decreasing $\Delta^{17}O(nss\text{-}SO_4^{2-})$ in spring and/or increasing $\Delta^{17}O(nss\text{-}SO_4^{2-})$ in fall. There are several processes that could explain such a spring/fall difference.

One possible explanation involves the influence of NO_X emissions from snowpack covering the East Antarctic Plateau (Davis et al., 2001; Crawford et al., 2001; Chen et al., 2001). The Antarctic atmosphere is strongly affected by NO_X emissions from snowpack, starting at the beginning of spring with the return of the sunlight. These snow NO_X emissions subsequently enhance both O_3 and OH productions, with OH in greater proportion than O_3. This is particularly true at DDU in summer, where katabatic air from the East Antarctic Plateau causes the ozone mixing ratio to be in the range of 10–40 ppbv (Legrand et al., 2009; 2016a), with a mean OH concentration of 2.1×10^6 molecules cm^{-3} (Kukui et al., 2012). In contrast, Palmer Station is exposed to oceanic air, producing ozone mixing ratios within the range of 9–20 ppbv, with a mean OH concentration of about 1.0×10^5 molecules cm^{-3} (Jefferson et al., 1998). These observations suggest that NO_X emissions increase oxidants at DDU, compared with the Palmer Station, about 2-fold for O_3 and more than 10-fold for OH. Chemical transport models over the Antarctic continent show that NO_X emitted from snow during summer increase O_3 and OH by a factor of 2 and 7, respectively, compared with estimations not including snow NO_X emissions (Zatko et al., 2016). Additionally, ^{15}N depletion in nitrate starts from the beginning of September (See Supplement), which is consistent with previous measurement at DDU (Savarino et al., 2007), supporting that the snow NO_X emission happens in early spring at DDU. Thus, by snow NO_X emission, OH production is enhanced more efficiently than O_3 production in spring, possibly resulting in lower Δ^{17}O(nss-SO_4^{2-}) spring values.

Another possible explanation is that hypohalous acids (HOX = HOCl, HOBr) act as important oxidants of SO_2 via the aqueous phase reaction (R16 and R17) in the marine boundary layer (Fogelman et al., 1989; von Glasow, 2002):

$$\mathrm{HOX} + \mathrm{SO_3^{2-}} \rightarrow \mathrm{OH^-} + \mathrm{XSO_3^{2-}} \quad , \qquad \text{(R16)}$$

$$\mathrm{XSO_3^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{X^-} + 2\mathrm{H^+} \quad . \qquad \text{(R17)}$$

This reaction is expected to produce sulfate with Δ^{17}O = 0 ‰, as all oxygen atoms of sulfate originate from water (Fogelman et al., 1989; Troy and Margerum, 1991: Yiin and Margerum, 1988), leading to lower Δ^{17}O(nss-SO_4^{2-}) values in the atmosphere. Indeed, unexpectedly low Δ^{17}O(nss-SO_4^{2-}) values have been observed in marine aerosols, which is possibly explained by a contribution of HOX oxidation of 33%–50% to total sulfate production in the marine boundary layer (Chen et al., 2016). Chen et al. (2016) estimated that a minimum concentration of gaseous HOX of 0.1 pptv could account for half of the sulfate production in the marine boundary layer. At DDU, year-round observations of gaseous inorganic bromine species ($[Br_y^*] = [HBr] + [HOBr] + 0.9[Br_2] + 0.4[BrO] + [BrNO_2] + [BrONO_2] + [Br]$) revealed that maximum concentrations are observed in September, with values of 13.0 ± 6.5 ng m^{-3} (~ 3.6 pptv) (Legrand et al., 2016b). Even if only one third of the Br_y^* corresponds to HOBr, as estimated using the model calculations by Legrand et al. (2016b) under summer conditions, then it is expected that HOX at DDU in spring is > 1 pptv; thus, HOX could play a significant role in sulfate production in spring. Likewise, Br_y^* concentration at DDU is at minimum in May, with values of 3.4 ± 1.0 ng m^{-3} (Legrand et al., 2016b), corresponding to less than one third of spring values. This would lead to a lower contribution of HOX to sulfate production in fall, compared with spring. Hence, sulfate production via aqueous oxidation by HOX may explain the lower Δ^{17}O(SO_4^{2-}) in spring, relative to fall.

A change in pH of the aqueous phase on the aerosol surfaces may also explain the spring/fall difference in Δ^{17}O(nss-SO_4^{2-}). Given that SO_2 oxidation by ozone in the aqueous phase is favored at high pH (>5.5) (Seinfeld and Pandis, 2006), if the pH of aerosol droplets is higher in fall than in spring, then the relative importance of the $SO_2 + O_3$ reaction resulting in higher Δ^{17}O values would increase in fall. However, ion concentration analyses of aerosols collected at DDU exhibited higher alkalinity in spring than in fall (Jourdain and Legrand, 2002; Legrand et al., 2016b), which is inconsistent with this explanation. Hence, this process can be excluded from further consideration.

It should be noted that smaller difference was observed between spring and fall $\Delta^{17}O(NO_3^-)$ values, which would be also affected by the above two processes. Snow NO_X emission would decrease $\Delta^{17}O(NO_3^-)$ through depression of the contribution of O_3 oxidation relative to the other oxidation pathways by HO_X and RO_X, while halogen chemistry would lead to high $\Delta^{17}O(NO_3^-)$ values through an oxygen atom transfer from O_3 to BrO and consequently to nitrate (Morin et al., 2007; Savarino et al., 2013). Although it is difficult to identify the precise processes involved, observations of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values at an inland site (e.g., Concordia Station) would enable us to determine which process causes the spring/fall difference in the oxidation chemistry in the DDU atmosphere. If snow NO_X emission is the source of low $\Delta^{17}O(nss\text{-}SO_4^{2-})$ at DDU in spring, then $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ at an inland site would also exhibit lower values in spring than in fall.

4.4 Air mass origin analysis

Using observations of several oxidants at DDU and Concordia Station (e.g., Legrand et al., 2009, 2016a; Kukui et al, 2012, 2014; Grilli et al., 2013), it has been suggested that the oxidative capacity of the atmosphere at DDU is influenced by air masses transported from the East Antarctic Plateau during katabatic wind outflows. The NO_X emission from snowpack in inland Antarctica stimulates the ozone, HO_X, RO_X, and H_2O_2 production through the enhanced NO_X cycle. Thus, the atmosphere at DDU is enriched in all of those photochemical oxidants, when air masses are from inland regions, compared to when air masses are from the ocean (Legrand et al., 2009). Therefore, we expected that $\Delta^{17}O$ values for sulfate and nitrate also depend on air mass origin.

In Fig. 5, the $\Delta^{17}O$ values for sulfate and nitrate are given as a function of the time that air masses were over the continent during the five-days travel prior to arriving at DDU. Summer data show that the contact times of air masses with the continent varied between 20 and 120 h (i.e., continental air and oceanic air are well mixed). Similarly, their $\Delta^{17}O$ values show insignificant variation, having low values of around 1‰ and 25‰ for sulfate and nitrate, respectively. This trend reflects two different phenomena, decreased $\Delta^{17}O$ values in summer because of the high contribution of photo-oxidants to atmospheric chemistry, and increased import of oceanic air. In contrast, plots for other seasons show that the $\Delta^{17}O$ values exhibit high variation, although most of the air masses originate from the continent. It is important to note that this non-correlation does not mean that there is no link between $\Delta^{17}O$ values and air mass origin. The influence of air mass transport on oxidative capacity has been demonstrated in daily observations of oxidants (e.g., Legrand et al., 2009). Given that air masses at this site are from a variety of directions, and are mixed together, this makes interpretation of weekly averaged analyses more complicated. Hence, no significant correlation between $\Delta^{17}O$ values and air mass origin in weekly data could reflect a real lack of correlation or a too broad time resolution for these data.

5 Summary

To develop an understanding of the factors influencing $\Delta^{17}O$ values of atmospheric sulfate and nitrate, seasonal variations of $\Delta^{17}O$ values of atmospheric sulfate, nitrate and ozone were analyzed using the aerosol samples collected at DDU throughout 2011. Both $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values exhibited clear seasonal variations, with summer minima and winter maxima. In contrast, $\Delta^{17}O$ values of ozone showed limited variability throughout the year, indicating that $\Delta^{17}O(O_3)$ values do not significantly influence summer/winter trends in $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values. We hence, for the first time, demonstrated that $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are direct results of local oxidation chemistry of their precursors. The summer/winter trends of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values are likely to reflect sunlight-driven changes in the relative importance of oxidation pathways; oxidation by HO_X, RO_X and H_2O_2 are increased during summer when the solar radiation enhances the production of those oxidants, whereas the relative contribution of oxidation reaction transferring oxygen atoms of O_3 to sulfate and nitrate is increased during winter period. Interestingly, by comparing $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ values to ozone mixing ratios, we found that the $\Delta^{17}O(nss\text{-}SO_4^{2-})$ values in spring months were lower than in fall months despite of similar ozone levels for spring and fall, whereas there was no clear difference between $\Delta^{17}O(NO_3^-)$ values. Possible explanations for the spring/fall differences for sulfate include: (i) low relative contribution of O_3 oxidation in spring induced by reactive nitrogen emissions from snowpack at inland sites being transported to coastal sites; and (ii) effects of SO_2 oxidation by hypohalous acids (HOCl, HOBr), enhanced in spring by interaction of sea salt particles with photo-oxidants. Further observations of $\Delta^{17}O(nss\text{-}SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ in aerosols collected at Antarctic inland sites will help us to identify the processes causing such different sulfate and nitrate formation in spring and fall. Nevertheless, the dataset of this study can be dedicated to atmospheric chemical transport models to better constraints on unique local oxidation chemistry at DDU.

Author contributions

S. Ishino, S. Hattori and J. Savarino designed the research. M. Legrand, B. Jourdain and S. Preunkert provided qualified complementary data, organized the Antarctic field campaign, and collected samples. S. Ishino, S. Hattori, J. Savarino, A. Barbero and N. Caillon performed experiments. S. Ishino, S. Hattori, J. Savarino, K. Kuribayashi, and N. Yoshida analyzed data. S. Ishino, S. Hattori and J. Savarino prepared the manuscript, with contributions from all other co-authors.

Data availability

The data used for the figures and the interpretations are shown in Supplement materials.

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Table 1: Summary of $\Delta^{17}O$ values of sulfate and nitrate produced via each reaction pathways with oxidants. $\Delta^{17}O$ values of sulfate are calculated based on Savarino et al. (2000). $\Delta^{17}O$ values of nitrate refer to estimate of box model by Morin et al. (2011). $\Delta^{17}O$ value of nitrate produced by $BrONO_2$ hydrolysis is assumed to be equal to the value for NO_3 + RH pathway.

	Oxidation pathway	**$\Delta^{17}O$ (oxidant) (‰)**	**Transferring factor**	**$\Delta^{17}O$ (product) (‰)**
SO_4^{2-}	$SO_2 + OH$	0 [a]	-	0
	$SO_3^{2-} + O_3$ (aq.)	26 [b]	$0.25 \times \Delta^{17}O(O_3)_{bulk}$	6.5
	$HSO_3^- + H_2O_2$ (aq.)	1.6 [c]	$0.50 \times \Delta^{17}O(H_2O_2)$	0.8
	$SO_3^{2-} + O_2$ (cat. Fe, Mn)	−0.3 [d]	$0.25 \times \Delta^{17}O(O_2)$	−0.1
	$SO_3^{2-} + HOX + H_2O$	39 (HOX)[e], 0 (H_2O)[f]	-	0
NO_3^-	$NO_2 + OH$	0	$2/3 \times \Delta^{17}O(NO_2)$	17.3-25.1
	N_2O_5 hydrolysis	26 (O_3), 0 (H_2O)	$2/3 \times \Delta^{17}O(NO_2) + 1/6 \times \Delta^{17}O(O_3)_{term}$	31.0-35.2
	NO_3 + RH	26 (O_3)	$2/3 \times \Delta^{17}O(NO_2) + 1/3 \times \Delta^{17}O(O_3)_{term}$	38.0-42.7
	$BrONO_2$ hydrolysis	39 (BrO)[e]	$2/3 \times \Delta^{17}O(NO_2) + 1/3 \times \Delta^{17}O(O_3)_{term}$	38.0-42.7

[a] Holt et al. (1983); [b] Vicars et al. (2014); [c] Savarino et al. (1999); [d] Barkan and Luz (2003); [e] assumed based on Bhattacharya (2008); [f] Barkan and Luz (2005)

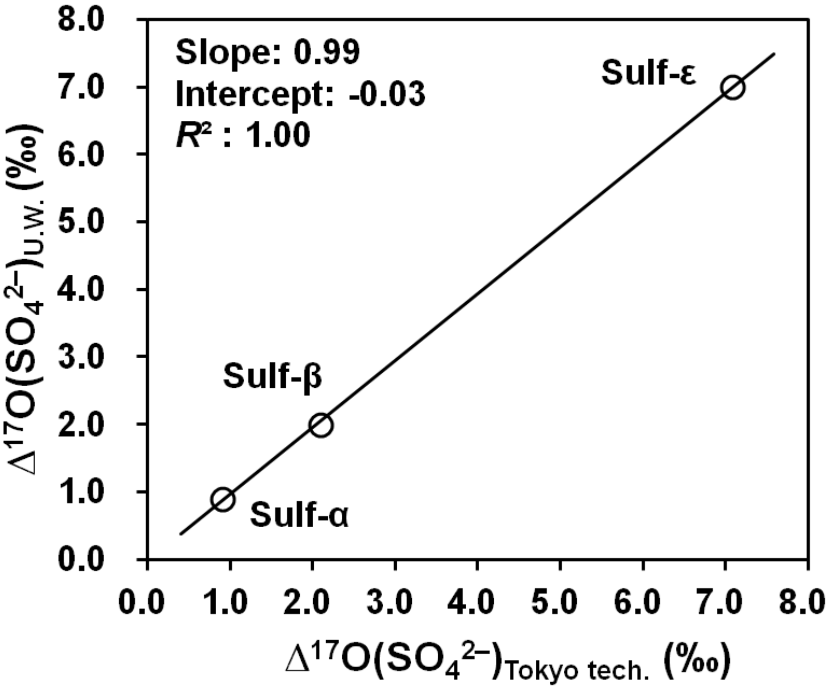


Figure 1: Comparison of Δ^{17}O values of sulfate for standard materials measured at the University of Washington (U.W.) and Tokyo Institute of Technology (Tokyo tech.).

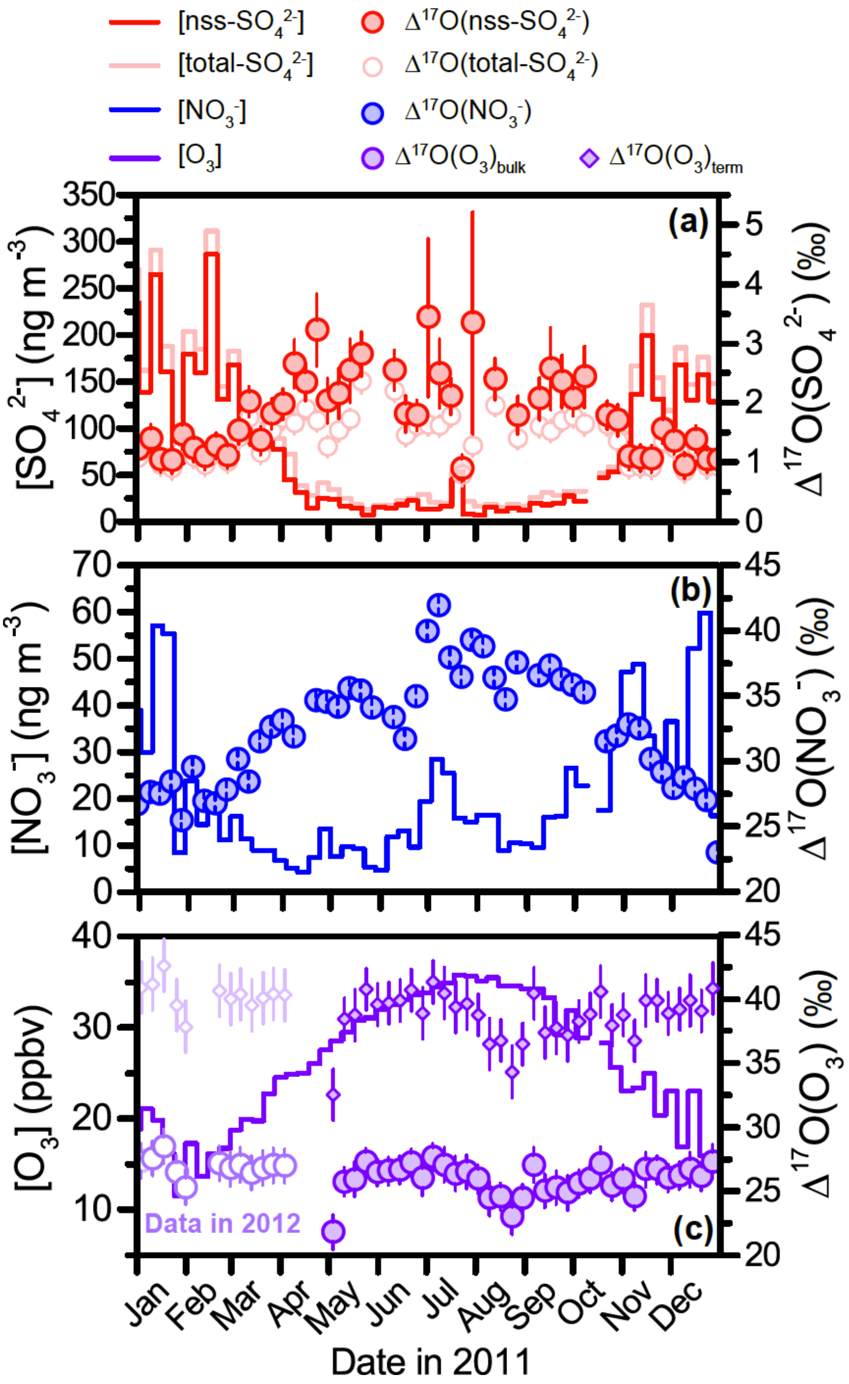
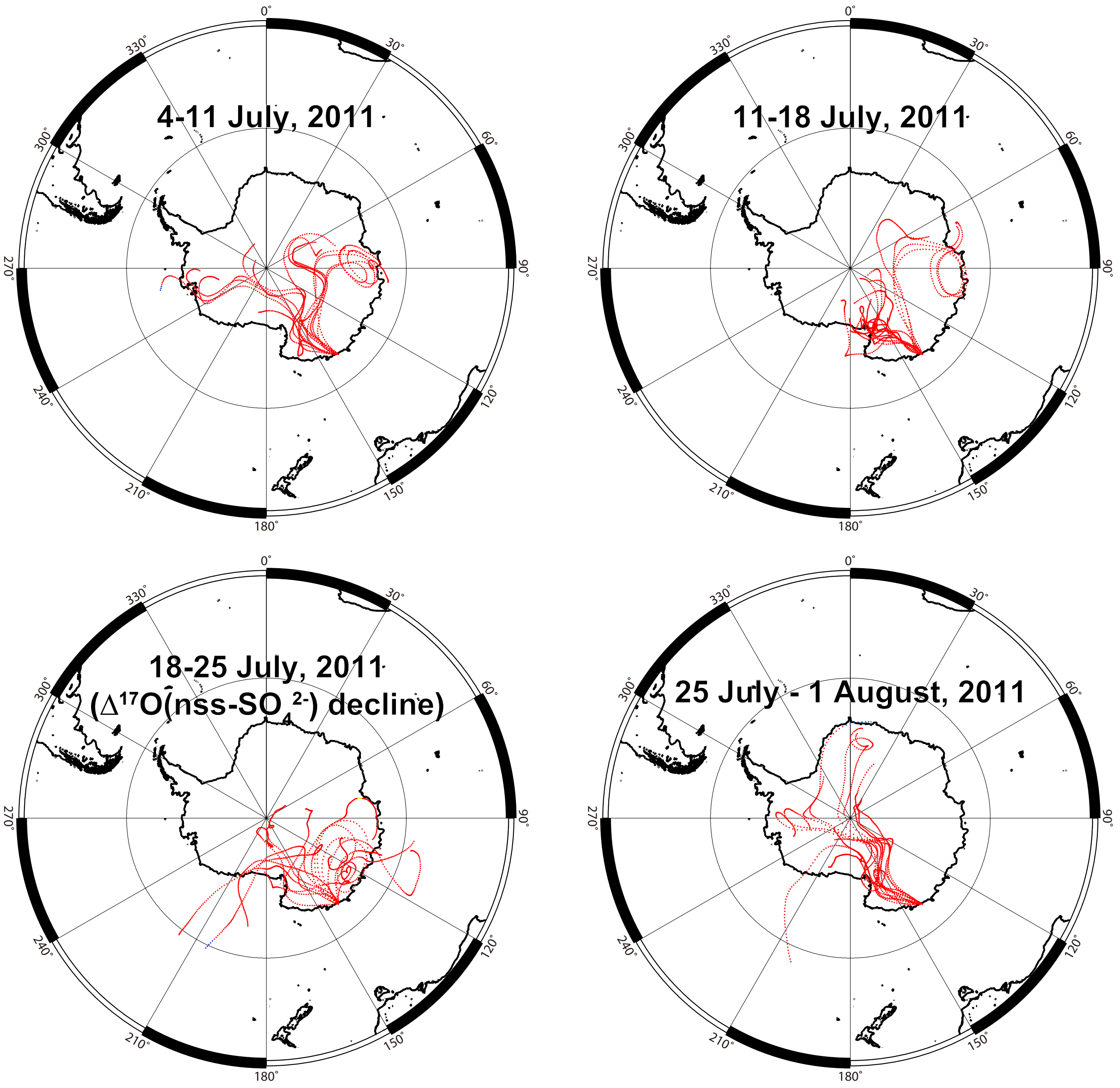


Figure 2: Seasonal variations of concentrations (solid line) and Δ^{17}O values (circles) of sulfate (red), nitrate (blue), and ozone (purple) at Dumont d'Urville Station during 2011. Δ^{17}O values of ozone are shown as bulk (circle) and terminal (square) values. Δ^{17}O values of ozone include samples collected from January to April 2012.



4-11 July, 2011

11-18 July, 2011

18-25 July, 2011 ($\Delta^{17}O(nss\text{-}SO_4^{2-})$ decline)

25 July - 1 August, 2011

Figure 3: Air mass pathways arriving at Dumont d'Urville Station during sampling periods in July 2011.

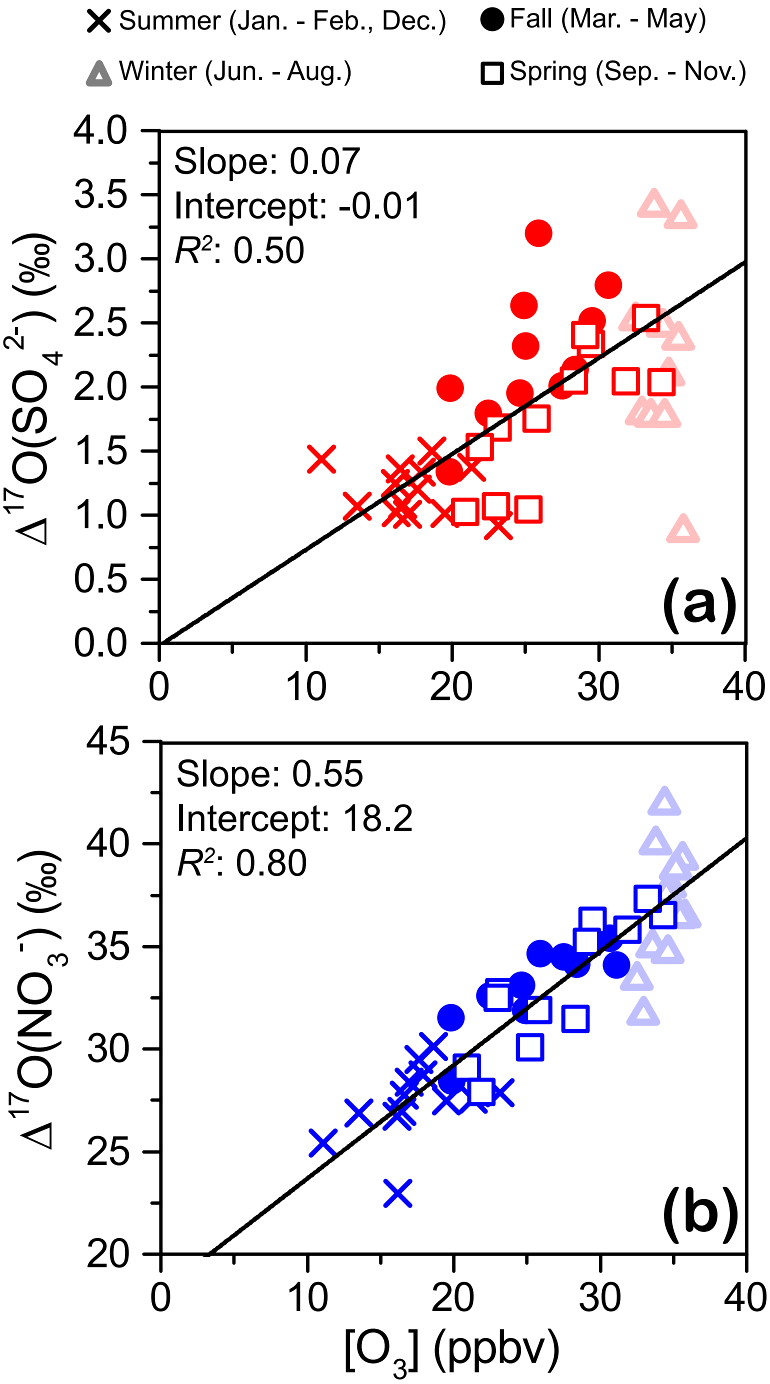


Figure 4: $\Delta^{17}O$ values of (a) sulfate, and (b) nitrate as a function of ozone mixing ratios $[O_3]$. Winter values were not taken into account in the calculation of slopes and intercepts.

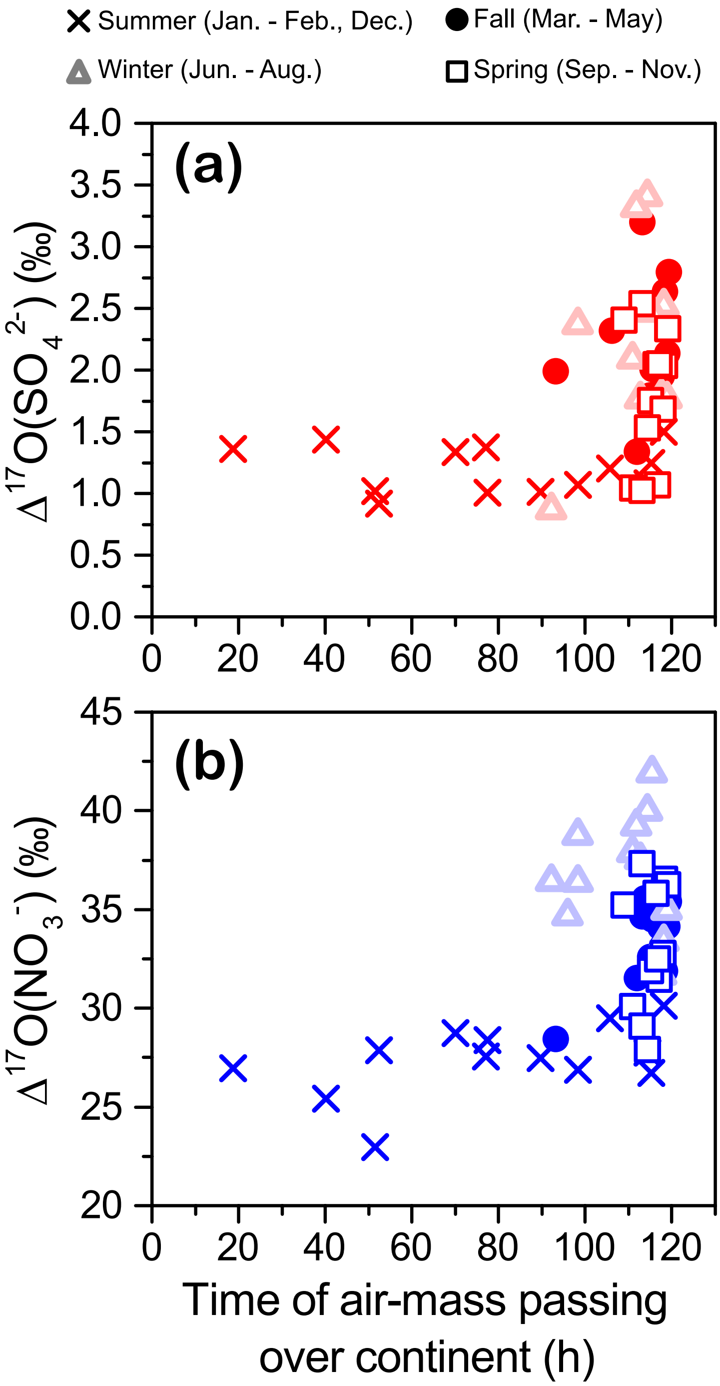


Figure 5: Relationship between Δ^{17}O values of (a) sulfate, and (b) nitrate, with the time taken for air masses to pass over the Antarctic continent (i.e., air mass contact time with surface snow).