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# Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign

J. Savarino<sup>1,2</sup>, W. C. Vicars<sup>1,2,a</sup>, M. Legrand<sup>1,2</sup>, S. Preunkert<sup>1,2</sup>, B. Jourdain<sup>1,2</sup>, M. M. Frey<sup>3</sup>, A. Kukui<sup>4,5</sup>, N. Caillon<sup>1,2</sup>, and J. Gil Roca<sup>4,5</sup>

<sup>1</sup>Université Grenoble Alpes, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), 38000 Grenoble, France

<sup>2</sup>CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), 38000 Grenoble, France

<sup>3</sup>British Antarctic Survey, Natural Environment Research Council, Cambridge, UK

<sup>4</sup>Laboratoire Atmosphère, Milieux et Observations Spatiales (LATMOS), UMR8190, CNRS-Université de Versailles Saint Quentin, Université Pierre et Marie Curie, Paris, France

<sup>5</sup>Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), UMR6115 CNRS-Université d'Orléans, 45071 Orléans CEDEX 2, France

<sup>a</sup>now at: Technical Services Program, Air Pollution Control Division, Colorado Department of Public Health and Environment, Denver, CO, USA

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Correspondence to: J. Savarino (jsavarino@ujf-grenoble.fr)

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## Abstract

Variations in the stable oxygen isotope composition of atmospheric nitrate act as novel tools for studying oxidative processes taking place in the troposphere. They provide both qualitative and quantitative constraints on the pathways determining the fate of atmospheric nitrogen oxides ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ). The unique and distinctive  $^{17}\text{O}$ -excess ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of ozone, which is transferred to  $\text{NO}_x$  via oxidation, is a particularly useful isotopic fingerprint in studies of  $\text{NO}_x$  transformations. Constraining the propagation of  $^{17}\text{O}$ -excess within the  $\text{NO}_x$  cycle is critical in polar areas where there exists the possibility of extending atmospheric investigations to the glacial/interglacial time scale using deep ice core records of nitrate. Here we present measurements of the comprehensive isotopic composition of atmospheric nitrate collected at Dome C (East Antarctic plateau) during the austral summer of 2011/12. Nitrate isotope analysis has been here combined for the first time with key precursors involved in nitrate production ( $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{RO}_2$ , etc.) and direct observations of the transferrable  $\Delta^{17}\text{O}$  of surface ozone, which was measured at Dome C throughout 2012 using our recently developed analytical approach. Assuming that nitrate is mainly produced in Antarctica in summer through the  $\text{OH} + \text{NO}_2$  pathway and using concurrent measurements of  $\text{OH}$  and  $\text{NO}_2$ , we calculated a  $\Delta^{17}\text{O}$  signature for nitrate in the order of  $(21\text{--}22 \pm 3)\text{‰}$ . These values are lower than the measured values that ranged between 27 and 31 ‰. This discrepancy between expected and observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values suggests the existence of an unknown process that contributes significantly to the atmospheric nitrate budget over this east Antarctic region.

## 1 Introduction

The search for ice core proxies related to past change of oxidative properties of the atmosphere is motivated by the need to model simulations of ozone and  $\text{OH}$  changes over preindustrial–industrial and glacial–interglacial timescales. Early ice

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was to reconcile observations of  $\Delta^{17}\text{O}$  for atmospheric nitrate at Dome C with quantitative predictions based on nitrate isotope mass balance and atmospheric chemistry parameters, a unique opportunity offered by the OPALE campaign.

## 2 Methods

### 2.1 Site description and scientific context

Dome C is situated 3233 m a.s.l. on the East Antarctic Plateau (75°06' S, 123°23' E), approximately 1100 km from the coastal research station Dumont d'Urville and 560 km from the Vostok station. Deep ice cores were extracted at Dome C in the framework of the European Project for Ice Coring in Antarctica (EPICA) covering approximately 800 000 yr (EPICA-community-members, 2004) and Vostok covering the last 420 000 years (Petit et al., 1999). In parallel, studies aiming to understand the meteorological, chemical, and physical factors governing the variability of trace constituents preserved in the ice were initiated. This was done for aerosol in the framework of the French environmental observation service CESOA (Etude du cycle atmosphérique du Soufre en relation avec le climat aux moyennes et hautes latitudes Sud, <http://cesoa.ore.fr>) dedicated to the study of the sulfur cycle (Jourdain et al., 2008; Preunkert et al., 2008).

Although the Antarctic plateau is extraordinarily dry, cold, and far removed from sources of anthropogenic emissions, first atmospheric measurements of oxidants conducted in 1998–1999 during the ISCAT (Investigation of Sulfur Chemistry in the Antarctic Troposphere) field campaign revealed a high level of photochemical activity. For example, the average summertime OH concentration ( $2 \times 10^6 \text{ cm}^{-3}$ ) over the South Pole was found to be similar to that of the tropical marine boundary layer (MBL) (Mauldin et al., 2001). Unexpectedly high levels of nitric oxide (NO) were also detected, with concentrations one to two orders of magnitude higher than that typically observed in other remote regions (Davis et al., 2001). Model simulations revealed that the large OH

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extracted in 40 mL of ultra-pure water via centrifugation using Millipore Centricon™ filter units. Nitrate concentration was then determined for each filter extract solution using a colorimetric technique (Frey et al., 2009).

### 2.3 Ozone collection

The nitrite-coated filter technique for ozone isotope analysis has been described in detail in (Vicars et al., 2012; Vicars and Savarino, 2014). The principle of ozone collection underlying this technique is the filter-based chemical trapping of ozone via aqueous phase reaction with nitrite (Adon et al., 2010; Geyh et al., 1997; Koutrakis et al., 1993; Krzyzanowski, 2004):



By coupling this routine ozone measurement technique with recent analytical developments in the  $\Delta^{17}\text{O}$  analysis of nanomole quantities of nitrate (Kaiser et al., 2007), the  $^{17}\text{O}$ -excess transferred by one of the two  $\text{O}_3$  terminal atoms through bimolecular chemical reactions, denoted  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$ , as well as ozone's bulk  $\Delta^{17}\text{O}$  value, denoted  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  ( $= 2/3 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$  since all  $^{17}\text{O}$ -excess is located at the two  $\text{O}_3$  terminal atoms (Bhattacharya et al., 2008; Janssen and Tuzson, 2006), can be inferred from the oxygen isotopic composition of the nitrate produced via R1 within the coated filter matrix.

Ambient ozone collections were performed using an active air sampler consisting of 1/4" Teflon™ (PFA) tubing connecting three main sampler components: (i) a standard low-volume vacuum pump (Welch™, Model 2522C-02) equipped with a volume counter and needle valve (or flow meter) for flow rate regulation, (ii) a closed PFA filter holder assembly (Saville™) containing a pre-coated 47 mm glass fiber sampling substrate (Whatman™, GF/A type), and (iii) an open-faced PFA filter holder assembly containing a 47 mm PTFE membrane filter (Zylon™, 5 μm pore size) for the removal of particulate species upstream of the coated filter. Glass fiber sampling substrates were

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coated prior to sample collection with 1 mL of a nitrite-based ozone sampling solution (0.1 M NaNO<sub>2</sub>, 0.05 M K<sub>2</sub>CO<sub>3</sub>, 0.1 M glycerol) (Koutrakis et al., 1993), allowed to dry at 75 °C for approximately 10 min, and then stored frozen in the dark in individual plastic PetriSlide™ containers (Millipore™). Samples were collected by loading pre-coated filters into the sampling filter holder, which was then connected to the prefilter (upstream) and needle valve/pump (downstream) and covered in aluminum foil to limit light exposure, a step that is necessary to limit the blank production rate during sample collection (Vicars et al., 2012). Air was then pumped through the sampling system at a target flow rate of 3.0 L min<sup>-1</sup>.

Sampling was conducted during the OPALE campaign (December 2011–January 2012) from a climate-controlled shelter, and a total of 28 samples were collected. However, due to difficulties in the application of our analytical technique to the unique environmental conditions encountered in Antarctica, the results obtained from these samples were inconclusive (i.e. unrealistic variability) due to the lack of light protection of the filter holder (Vicars et al., 2012, 2013). Sampling and isotopic analysis of ozone was therefore repeated in 2012, and a complete annual record of Δ<sup>17</sup>O(O<sub>3</sub>) was obtained (*n* = 60). Procedural filter blanks were also collected at regular intervals and were subjected to all of the same preparation, storage, handling, and analytical procedures as field samples. After sample collection, filter samples and procedural blanks were returned to their containers, which were covered in aluminum foil and stored at –20 °C before processing and analysis.

Filter samples were extracted in 18 mL of deionized water (18.2 MΩ, hereafter referred to as “MQ water”). In order to remove the excess (i.e., unreacted) nitrite reagent from the sample extracts, the solutions were treated with 1 mL of a 1 M sulfamic acid solution and then neutralized with a corresponding addition of high-purity sodium hydroxide (Granger and Sigman, 2009; Vicars et al., 2012). Extract solutions were then filtered via centrifugation using Millipore Centricon™ assemblies. The nitrate extracted from the coated filter samples was then subjected to isotopic analysis, as described in the following section.

## 2.4 Isotopic analysis

The comprehensive isotopic composition of nitrate ( $^{15}\text{N}/^{14}\text{N}$ ,  $^{17}\text{O}/^{16}\text{O}$ ,  $^{18}\text{O}/^{16}\text{O}$ ) was measured on a Finnigan<sup>TM</sup> MAT253 isotope ratio mass spectrometer (IRMS), equipped with a GasBench II<sup>TM</sup> and coupled to an in-house built nitrate interface (Morin et al., 2009). Nitrate in both the nitrite-coated filter and aerosol sample extracts was prepared for isotopic analysis by conversion to  $\text{N}_2\text{O}$  via the bacterial denitrifier method (Casciotti et al., 2002; Kaiser et al., 2007; Michalski et al., 2002; Sigman et al., 2001). The detailed analytical procedure has been described elsewhere (see Morin et al., 2009) and is here briefly presented.

Denitrifying bacteria (*Pseudomonas aureofaciens*) were cultured in nitrate-amended soy broth and incubated for 5 days in stoppered glass bottles. Bacterial cultures, after concentration by centrifugation and re-suspension, were dispensed as 2 mL aliquots into 20 mL glass vials, which were then crimped and purged with helium for 3 h. Approximately 100 nmol of sample nitrate was then injected into the purged vials and conversion of the sample nitrate to nitrous oxide ( $\text{N}_2\text{O}$ ) via bacterial denitrification was allowed to proceed overnight. The  $\text{N}_2\text{O}$  sample was then cryo-focused in a liquid nitrogen trap and introduced into a gold furnace where it was thermally decomposed at 900 °C into  $\text{O}_2$  and  $\text{N}_2$ . Following separation via gas chromatography, the  $\text{O}_2$  and  $\text{N}_2$  sample gases were directed into the ionization chamber of the IRMS. All analytical steps were simultaneously performed on nitrate isotopic standards and their equimolar mixtures (International Atomic Energy Agency USGS 32, USGS 34, and USGS 35), which were prepared in an identical background matrix as the samples. Individual analyses were normalized through comparison with these three nitrate reference materials (Coplen, 2011; Werner and Brand, 2001). All isotopic enrichment values for nitrate are reported relative to VSMOW and air  $\text{N}_2$  for oxygen and nitrogen, respectively. The overall accuracy of the method is estimated as the standard deviation of the residuals from the linear regression between the measured reference materials and

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A time series showing the year-round record of  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  at Dome C in 2012 is presented in Fig. 3.  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  averaged  $24.9 \pm 1.9\text{‰}$  over 2012, corresponding to  $\Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$  values of  $37.4 \pm 1.9\text{‰}$ . As shown in Fig. 4, these  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values are consistent with those observed in Grenoble (France), as well as with measurements conducted along a latitudinal transect from  $50^\circ\text{S}$  to  $50^\circ\text{N}$  in the Atlantic Ocean (Vicars and Savarino, 2014). Although the  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  seasonal cycle reveals some interesting features, like the winter maximum, probably in response of the permanent winter darkness and stratospheric air mass intrusions, a complete description is beyond the scope of the present paper. What should be kept in mind here is the pretty stable  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  value close to  $26\text{‰}$  that can be considered as representative for the OPALE campaign hold in November–January.

### 3.2 Nitrate isotope mass balance

The availability of a large database of trace chemical species measurements at Dome C during a portion of the OPALE field campaign (December 2011) offers a unique opportunity to compare observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values in the atmosphere to estimated ones calculated from concurrent observations. As discussed at length in recent studies (for example, by Morin et al., 2011 and Vicars et al., 2013), the  $^{17}\text{O}$ -excess transfer functions associated with the various nitrate production pathways (i.e.,  $\Delta^{17}\text{O}(\text{NO}_3^-)_i$  values) can be estimated as a function of the  $\Delta^{17}\text{O}$  of nitrate precursor gases (i.e.,  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{OH}$ , etc.) using mass balance calculations that trace the origin of oxygen atoms transferred during the chemical transformation of  $\text{NO}_x$  in the atmosphere. All atmospheric nitrate production channels involve either  $\text{NO}_2$  or a  $\text{NO}_x$  reservoir species derived from  $\text{NO}_2$  (e.g.,  $\text{N}_2\text{O}_5$ ). The first step in determining the  $\Delta^{17}\text{O}$  signature of each pathway is therefore a quantitative assessment of the steady state  $\Delta^{17}\text{O}$  value of  $\text{NO}_2$ , which is typically calculated as a function of the  $\Delta^{17}\text{O}$  value of  $\text{O}_3$  and the reaction dynamics involved in the conversion of  $\text{NO}$  to  $\text{NO}_2$ . As Dome C in summer is





leading to the following  $^{17}\text{O}$ -excess mass balance (Michalski et al., 2003 ; Morin et al., 2011):

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

In order to predict the  $\Delta^{17}\text{O}$  value of the nitrate produced through Reaction (R5) by mass balance, the isotopic composition of tropospheric OH must be known. The OH radical participates in a rapid isotopic exchange with atmospheric water vapor, which represents a very large oxygen reservoir relative to OH, with a  $\Delta^{17}\text{O}$  that is negligible compared to ozone or nitrate (Luz and Barkan, 2010). This exchange tends to erase the  $^{17}\text{O}$ -excess of OH under humidity and temperature conditions typical of the mid-latitudes (Dubey et al., 1997); therefore, the  $\Delta^{17}\text{O}$  of OH is normally assumed to be zero in modeling studies applied to these regions. As discussed by Morin et al. (2007), this assumption of  $\Delta^{17}\text{O}(\text{OH}) = 0$  is not valid under the low humidity conditions encountered in the polar atmosphere. The degree of isotopic equilibration between OH and  $\text{H}_2\text{O}$  can be determined as a function of the relative rates of the isotope exchange reaction and the main OH sink reactions:

$$\beta = \frac{L}{L + k_{\text{H}_2\text{O}+\text{OH}}[\text{H}_2\text{O}]} \quad (4)$$

where  $L$  represents the total chemical loss rate of OH.  $\beta$  is the factor relating the initial  $\Delta^{17}\text{O}$  transferred to OH upon its formation, denoted  $\Delta^{17}\text{O}(\text{OH})_{\text{prod.}}$ , to its steady state  $\Delta^{17}\text{O}$  value (Morin et al., 2007):

$$\Delta^{17}\text{O}(\text{OH}) = \beta \times \Delta^{17}\text{O}(\text{OH})_{\text{prod.}} \quad (5)$$

In plain words, Eqs. (4) and (5) predict that when the isotopic exchange reaction dominates over OH chemical losses (i.e.,  $\beta \ll 1$ ), the steady state  $\Delta^{17}\text{O}$  value of OH will be equal to that of water (i.e.,  $\Delta^{17}\text{O} \approx 0\text{‰}$ ). Conversely, when water vapor concentrations are low and the rate of chemical loss is large relative to the rate of the isotopic

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nificant sources of OH at Dome C during the period of seasonal snowpack emissions (Kukui et al., 2014). However, the measurement of HONO (around  $\text{pmol mol}^{-1}$ ) during OPALE, probably biased by  $\text{HO}_2\text{NO}_2$  interference (Legrand et al., 2014) is incompatible with the  $\text{HO}_x$  ( $= \text{OH} + \text{HO}_2/\text{RO}_2$ ) radical budget. Best agreement is achieved when HONO at Dome C is assumed to originate from snow emissions with the emission strength evaluated by Legrand et al. (2014). Using a 1-D model, Kukui et al. (2014) show that the concentrations of HONO corresponding to about 20–30 % of measured HONO are consistent with those calculated from the budget analysis of OH radicals with the concentrations of  $\text{NO}_2$  either calculated from NO measurements assuming PSS or observed by Frey et al. (2014). Therefore, the production of OH by HONO photolysis is adjusted consequently and the 0-D box model (Kukui et al., 2014) is used to calculate all other production rates of OH. Note that even lowering HONO to 20–30 % of the measured values, this species remains the major primary source of radicals at Dome C. Applying the isotope  $^{17}\text{O}$ -excess transfer (Morin et al., 2011) and the  $\text{OH}_{\text{prod.}}$  isotope mass balance,  $\Delta^{17}\text{O}(\text{OH})_{\text{prod.}}$  on average equals  $5 \pm 2\%$  ( $1 \sigma$ ). Because the major process leading to the emission of HONO from the snowpack is the photolysis of nitrate, which possesses a  $\Delta^{17}\text{O}$  value of approximately 32‰, both in the snow “skin layer” (Erbland et al., 2013) and in the top 10 cm of snow (Frey et al., 2009), we have assumed that  $\Delta^{17}\text{O}(\text{HONO})_{\text{atm}} = \Delta^{17}\text{O}(\text{NO}_3^-)_{\text{snow}}$  as both oxygen atoms of HONO can be tracked back to the nitrate. An example of the isotope mass balance calculation is given in Table 1. Figure 7 shows the diurnally-integrated average of the  $\Delta^{17}\text{O}(\text{OH})$ .  $\Delta^{17}\text{O}(\text{OH})$  varies in a narrow range, between 1 and 3‰. An estimation of the  $\Delta^{17}\text{O}$  signature for the  $\text{NO}_2 + \text{OH}$  channel,  $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{R2}}$ , that accounts for the  $^{17}\text{O}$ -excess carried by the OH radical results in values ranging between 20 and 23‰. Averaging over the same time period as the nitrate atmospheric sampling, diurnally-integrated average  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values of  $21\text{--}22\% \pm 3\%$  can be estimated for December (Table 2). These values are 6–8‰ lower than the observed atmospheric values for  $\Delta^{17}\text{O}(\text{NO}_3^-)$  (27–30‰ during OPALE, Fig. 2 and Table 2). The source of discrepancy between ob-

served and modeled  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is presently unknown. A critical evaluation may offer nevertheless some clues.

## 4 Discussion

### 4.1 Alternative sources of $\text{NO}_2$

5 A possible explanation for the underestimation of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  involves the potential  
role of reactive halogen chemistry in the troposphere over the Antarctic plateau (Bloss  
et al., 2010; Morin et al., 2008). Reactive halogen oxides ( $X\text{O} = \text{BrO}, \text{ClO}, \text{IO}, \text{etc.}$ )  
are produced through the reaction of halogen radicals ( $X$ ) with ozone, a pathway that  
10 plays an important role in the catalytic process responsible for ozone depletion events  
(ODEs) observed in the Arctic boundary layer since the 1980s (Fan and Jacob, 1992;  
Simpson et al., 2007):



In terms of the chemical budget of  $\text{NO}_x$ , the impact of  $X\text{O}$  can occur via two chemi-  
cal mechanisms (see Sect. 4.2 for the second mechanism involving the formation of  
15 halogen nitrate,  $X\text{ONO}_2$ ). First,  $X\text{O}$  can oxidize  $\text{NO}$  to  $\text{NO}_2$ , a pathway that competes  
with the  $\text{NO} + \text{O}_3$  and  $\text{NO} + \text{HO}_2/\text{RO}_2$  reactions in terms of  $\text{NO}$  oxidation:



For conditions typical of the Antarctic boundary layer,  $1 \text{ pmol mol}^{-1}$  of  $X\text{O}$  has roughly  
the same oxidizing power as  $4 \text{ nmol mol}^{-1}$  of ozone in terms of  $\text{NO}$  oxidation (Atkinson  
20 et al., 2007). Therefore, when halogen oxides are present at relevant levels, the R7  
reaction can result in concentrations of  $\text{NO}_2$  that are higher than that predicted from the  
balance between  $\text{NO}_2$  destruction via photolysis and production through the reaction

of NO with O<sub>3</sub> or HO<sub>2</sub>/RO<sub>2</sub> (i.e., the extended Leighton mechanism):

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_{\text{NO}+\text{O}_3}[\text{O}_3] + k_{\text{NO}+\text{HO}_2}[\text{HO}_2] + k_{\text{NO}+\text{RO}_2}[\text{RO}_2] + k_{\text{NO}+\text{XO}}[\text{XO}]}{j_{\text{NO}_2}} \quad (6)$$

The interaction of XO in the NO<sub>x</sub> cycle at Dome C would have important implications for the Δ<sup>17</sup>O of atmospheric nitrate. The production of halogen oxide radicals proceeds through a direct transfer of a terminal oxygen atom from ozone to the XO product (Zhang et al., 1997). Therefore, it is expected that the Δ<sup>17</sup>O of XO is equal to Δ<sup>17</sup>O(O<sub>3</sub>)<sub>term.</sub>, which means that the reaction of NO with XO is roughly equivalent to the NO + O<sub>3</sub> reaction in terms of Δ<sup>17</sup>O transfer to NO<sub>2</sub> (note that the NO + XO transfer is greater than NO + O<sub>3</sub> as in the later case, part of the central O<sub>3</sub> atom participates in the reaction). The participation of XO species in the oxidation of NO thus leads to a greater Δ<sup>17</sup>O transfer to NO<sub>2</sub> by effectively increasing the value of α. However, on the Antarctic plateau, BrO did not exceed 2–3 pmol mol<sup>-1</sup> at most during OPALE campaign (Frey et al., 2014). Including BrO chemistry would only increase α by 2% (due to the specific form of α ≡ 1/(1+x)) of which is too low to significantly influence Δ<sup>17</sup>O(NO<sub>2</sub>) and ultimately Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>). In the absence of measurements of other halogens we cannot completely rule out a role of the halogen chemistry there. However, even with α = 1, its maximum but unrealistic value due to the high concentration of HO<sub>2</sub>, Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) would reach the range of 23–25‰, in better agreement with the observations but still significantly lower. Similarly, in the event of a non isotopic steady state of NO<sub>2</sub> (Michalski et al., 2014), it is very unlikely that Δ<sup>17</sup>O(NO<sub>2</sub>) could reach values greater than its primary snow nitrate source (i.e. Δ<sup>17</sup>O(NO<sub>2</sub>) > Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>)<sub>snow</sub> = 30–35‰ in summer at Dome C, (Erland et al., 2013; Frey et al., 2009), still leaving the predicted Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) underestimated with respect to atmospheric observations.

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## 4.2 Alternative oxidation pathways of NO<sub>2</sub>

Considering Reaction (R5) as the main source of HNO<sub>3</sub>, an alternative approach is to consider that OH bears a higher Δ<sup>17</sup>O than the estimate calculated previously. Assuming a β of one, which seems again unrealistic, will increase Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) by 1‰ at most (Table 2), still insufficient to explained atmospheric observations as NO + HO<sub>2</sub> remain a major source of OH, independently of the assumed β.

Alternatively, if measured HONO concentrations are considered instead of those assumed to constrain by the HO<sub>x</sub> budget (i.e. 4 times lower than measured), average Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) values of 23–24‰ are calculated (Table 2), again systematically lower than the observed range of 27–30‰. However, given the significant uncertainty surrounding the isotopic composition of HONO and its relative contribution to total OH production at Dome C, it is not possible to make a firm conclusion in this regard.

Therefore, neither the common sources of NO<sub>2</sub> nor the daytime formation of HNO<sub>3</sub> seems to be able to explain the high Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) values of atmospheric nitrate observed at Dome C in summer. When this observation is taken together with the high NO<sub>2</sub>/NO ratio observed by Frey et al. during two summer seasons at Dome C (Frey et al., 2013, 2014), clearly our current understanding of the NO<sub>x</sub> chemistry on the Antarctic plateau seems to be incomplete.

There are several other processes that possibly account for the disagreement between the measurements and mass balance calculations. Indeed, in addition to its impact on NO<sub>x</sub> cycling through the R7 pathway, an increasing body of evidence points towards reactive halogen chemistry as a major NO<sub>x</sub> sink and source of nitrate via the production and subsequent hydrolysis of XNO<sub>3</sub> species (Sander et al., 1999; Savarino et al., 2013; Vogt et al., 1996):





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it would act to increase the  $\Delta^{17}\text{O}$  value of nitrate in the boundary layer relative to the local  $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{R5}}$  oxidation signature. However, considering the propensity of nitric acid to stick on snow (Crowley et al., 2010), the snowpack to act as a sink rather than a source of nitric acid (Dibb, 2004; Erbland et al., 2013) and the fast  $\text{NO}_x$  recycling that should take place within the snowpack, it is very unlikely that  $\Delta^{17}\text{O}(\text{NO}_3^-)$  could be explained by a direct nitric acid emissions from snow, which has been ultimately shown to be limited (Slusher et al., 2010; Erbland et al., 2013; Berhanu et al., 2014).

A critical analysis of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  shows in fact that such high values correspond mainly to the nighttime chemistry of  $\text{NO}_x$  (Michalski et al., 2003; Morin et al., 2008). Nighttime chemistry involves species like  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  in the process of forming  $\text{HNO}_3$  and again efficiently by-pass the OH pathway. It is conceivable that below the photic zone, within the snowpack,  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  could be produced when  $\text{O}_3$  and  $\text{NO}_2$  are transported at depth but there is no reason to think that such dark  $\text{NO}_x$  chemistry could in a way or in another survive the photic zone transition and thus influences the overlying atmosphere.

Stratospheric nitrate deposited to the surface snow during winter, which has been observed to possess  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values in the range of 35–41 ‰ (Erbland et al., 2013) and possibly more, may act to buffer the  $\Delta^{17}\text{O}$  of the atmospheric nitrate reservoir via evaporation late into the spring and summer. However, this seems again unlikely given the rapidity of  $\text{NO}_x$  cycling and oxidative loss at Dome C during this time (Frey et al., 2013; Legrand et al., 2009).

While it is presently difficult to determine the precise nature of the process(es) leading to the relatively large  $^{17}\text{O}$ -excess values observed for atmospheric nitrate at Dome C, the correlation observed between the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values of atmospheric nitrate (see Sect. 3.1) provides at least one direct line of evidence that the high  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values observed during spring and early summer could be associated with snowpack emissions of  $\text{NO}_x$ . Considering only samples collected at Dome C between October and December, both those reported here and those collected in 2009 and described by Erbland et al. (2013), a strong anticorrelation ( $r = -0.90$ ) is observed between the

$\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values of atmospheric nitrate (Fig. 8). In other words, the atmospheric nitrate sampled in early spring, which is heavily depleted in  $^{15}\text{N}$  due its formation from snowpack  $\text{NO}_x$  emissions, possessed consistently higher  $\Delta^{17}\text{O}$  values than the nitrate sampled directly after this period of maximum snow photochemistry. This finding suggests that the mechanism producing enhanced  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values observed during this time is tightly coupled in time and space with the intensity of  $\text{NO}_x$  emissions from the snowpack, an observation very similar to that of Morin et al. (2012), who detected a similar relationship between  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  for atmospheric nitrate in the springtime boundary layer over Barrow, Alaska ( $71^\circ\text{N}$ ). The authors of this study attributed the observed correlation to the coupling of snowpack  $\text{NO}_x$  emissions and reactive halogen chemistry, suggesting that these two processes were interrelated and mutually strengthening. In the case of the OPALE 2011–2012 data, the correlation between  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  could arise from any of the potential pathways previously discussed. For example, as proposed by Morin et al. (2012), the R8 and R9 pathways may be enhanced under periods of intense snowpack emissions. Alternatively, a correlation could result from an increased contribution to total OH production from the photolysis of HONO, which is co-emitted with  $\text{NO}_x$  via nitrate photochemistry (Grannas et al., 2007) and may induce a larger  $^{17}\text{O}$ -excess in OH as compared to the conventional  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  pathway. Furthermore, the hydrolysis of  $\text{NO}_2$  in snow, should it contribute significantly to nitrate production at Dome C, is likely amplified during periods when concentrations  $\text{NO}_2$  are high in the snowpack interstitial air due to nitrate/nitrite photochemistry. Therefore, while the processes responsible for driving the formation of atmospheric nitrate at Dome C during summer cannot be unambiguously identified, the isotopic results presented here clearly indicate that snowpack emissions result in enhanced  $\Delta^{17}\text{O}$  transfer to nitrate. Our understanding of  $\text{NO}_x$  chemistry above the snow surface at Dome C is therefore incomplete.

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## 5 Conclusions

Constraining the propagation of ozone's  $^{17}\text{O}$ -excess signature within the  $\text{NO}_x$  cycle is critical in polar areas where the opportunity is offered to extend atmospheric investigations based on  $\Delta^{17}\text{O}$  measurements to the glacial/interglacial time scale using deep ice core records of nitrate. However, the factors governing the present-day isotopic composition of atmospheric nitrate over the Antarctic plateau remain poorly understood, primarily due to the complex nature of the boundary layer photochemistry initiated during spring by  $\text{NO}_x$  emissions from the snowpack.

An isotopic mass balance performed for atmospheric nitrate during December 2011, informed by in situ oxidant concentration measurements conducted within the framework of the OPALE field study, suggests the existence of an unexpected process bypassing the commonly accepted daytime chemistry of  $\text{NO}_2$  (i.e.  $\text{NO}_2 + \text{OH}$ ) that contributes significantly to the atmospheric nitrate budget over Dome C. The strong negative correlation observed between the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values of nitrate between October and December suggests that this unknown process is enhanced during periods of intense emissions from the snowpack. Potential explanations for this observation include: (i) an increased  $\Delta^{17}\text{O}$  transfer from OH due to its formation from the photolysis of HONO released from the snowpack, (ii) heterogeneous hydrolysis of  $\text{NO}_2$  due to the high concentrations of  $\text{NO}_2$  in the snowpack interstitial air, and (iii) the co-emission of reactive halogen species that act as an intermediate in the transfer of  $\Delta^{17}\text{O}$  from ozone to nitrate. Further research is needed to solve the many inconsistencies (e.g. high  $\text{NO}_2/\text{NO}$  ratio, high concentration of  $\text{NO}_2$ , unresolved HONO atmospheric concentration, interference such as  $\text{HO}_2\text{NO}_2$ , isotope mass balance) observed during the OPALE experiments.

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**Table 1.** Rate of production and sink of OH and mass balance calculation of  $\Delta^{17}\text{O}$ .

Conditions for 19 Dec 2011, 3:45 p.m. OH = 3.96 molecules cm <sup>-3</sup>	<sup>a</sup> Median rate in 10 <sup>5</sup> molecules cm <sup>-3</sup> s <sup>-1</sup>	$\Delta^{17}\text{O}_i^c$ in ‰
<b>Net sources of OH</b>		
P1 HONO + <i>hν</i> → OH + NO	5.1 <sup>b</sup>	32
P2 H <sub>2</sub> O <sub>2</sub> + <i>hν</i> → 2OH	1.7	2
P3 O <sub>3</sub> + <i>hν</i> + H <sub>2</sub> O → 2OH	0.6	20
P4 CH <sub>3</sub> OOH + <i>hν</i> → HO <sub>2</sub> + OH	0.3	0
<b>Recycling RO<sub>2</sub> → OH</b>		
P5 NO + HO <sub>2</sub> → NO <sub>2</sub> + OH	7.7	0
P6 HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	0.4	0
<b>Net sink of OH</b>		
L1 CO + OH → HO <sub>2</sub> + CO <sub>2</sub>	6.3	
L2 CH <sub>4</sub> + OH → CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	2.6	
L2 HCHO + OH → HO <sub>2</sub> + CO	0.8	
L4 CH <sub>3</sub> CHO + OH → CH <sub>3</sub> CO <sub>3</sub>	0.9	
L5 O <sub>3</sub> + OH → HO <sub>2</sub> + O <sub>2</sub>	0.6	
L6 H <sub>2</sub> + OH + O <sub>2</sub> → HO <sub>2</sub> + H <sub>2</sub> O	0.60	
L7 CH <sub>3</sub> OOH + OH → CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	0.5	
L8 H <sub>2</sub> O <sub>2</sub> + OH → HO <sub>2</sub> + H <sub>2</sub> O	0.3	
<b>Net OH losses</b>		
L9 NO <sub>2</sub> + OH → HNO <sub>3</sub>	3.9	
L10 NO + OH → HONO	0.6	
L11 OH + RO <sub>2</sub> → products	0.5	
L12 OH + RO <sub>2</sub> NO <sub>2</sub> → products	0.6	
L13 OH + HONO → NO <sub>2</sub> + H <sub>2</sub> O	0.2	
L14 OH + HNO <sub>3</sub> → H <sub>2</sub> O + NO <sub>3</sub>	0.0	
<b>Isotope exchange</b>		
E <sub>1</sub> HQ + H <sub>2</sub> O ⇌ HO + H <sub>2</sub> Q	24.3	
<b>NO<sub>2</sub> main source</b>		
N1 NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	27.0	37
<b><sup>17</sup>O-excess NO<sub>2</sub></b>		
$\alpha = (N1 / (N1 + P5))$	0.78	
$\Delta^{17}\text{O}(\text{NO}_2)$		29
<b><sup>17</sup>O-excess OH</b>		
$\Delta^{17}\text{O}(\text{OH})_{\text{prod}} = (\sum P_i \times \Delta^{17}\text{O}_i) / \sum P_i$		5.8
$\beta = \sum L_i / (\sum L_i + E_1)$	0.43	
$\Delta^{17}\text{O}(\text{OH})$		2.5

<sup>a</sup>: Production rates obtained from a 0-D box model (see Kukui et al., 2014 for details).

<sup>b</sup>: HONO production rate divided by a factor 4 to balance the HO<sub>2</sub> radical budget (see Kukui et al., 2014; Legrand et al., 2014 for justification).

<sup>c</sup>: HONO is assumed to be formed by the photodissociation of nitrate in snow.  $\Delta^{17}\text{O}(\text{NO}_3)_{\text{snow}}$  is therefore assigned to HONO. The rest of the <sup>17</sup>O-excess transfer (i.e. P<sub>2</sub> to P<sub>6</sub> and N<sub>1</sub>) follows the rules established in (Morin et al., 2011) and a  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} = 26\%$ .

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**Table 2.** Comparison of measured and calculated  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values.

Sampling Period	Measured	Calculated			
		$\alpha$ constrained by observations $\Delta^{17}\text{O}(\text{OH})^*$ based on $\text{HO}_x$ budget	$\alpha = 1$ $\Delta^{17}\text{O}(\text{OH})^*$ based $\text{HO}_x$ budget	$\alpha$ constrained by observations $\beta = 1$	$\alpha$ constrained by observations $\Delta^{17}\text{O}(\text{OH})$ based on observed HONO
10 Dec–16 Dec	<b>29.6</b>	21.9	25.6	22.6	27.0
16 Dec–23 Dec	<b>29.0</b>	21.0	25.6	21.7	26.3
23 Dec–30 Dec	<b>27.8</b>	21.6	25.4	22.0	25.7
30 Dec–2 Jan	<b>27.3</b>	21.5	25.3	22.4	24.9

\* HONO production rate divided by a factor 4 to balance the  $\text{HO}_x$  radical budget (see Kukui et al. (2014) and Legrand et al. (2014) for justification).

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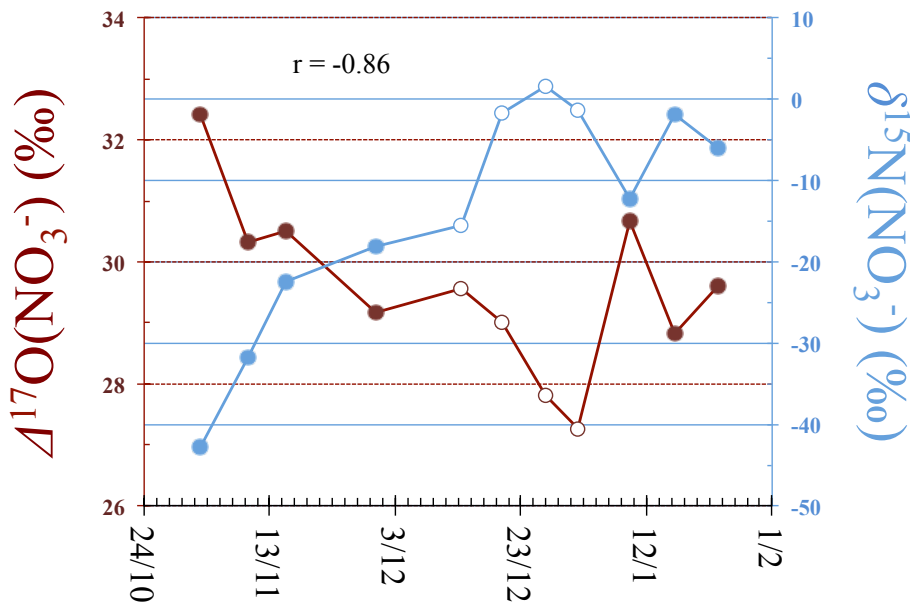
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**Figure 2.**  $\Delta^{17}\text{O}$  (primary y axis) and  $\delta^{15}\text{N}$  (secondary y axis) of atmospheric nitrate collected between October 2011 and January 2012. The samples collected during the intensive measurement period of the OPALE campaign (December 2011) are indicated with open symbols.

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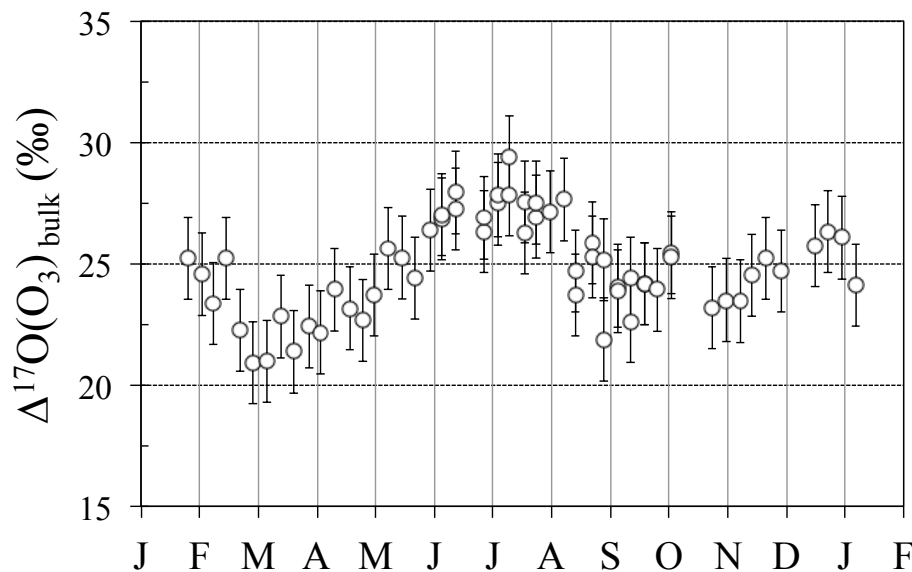
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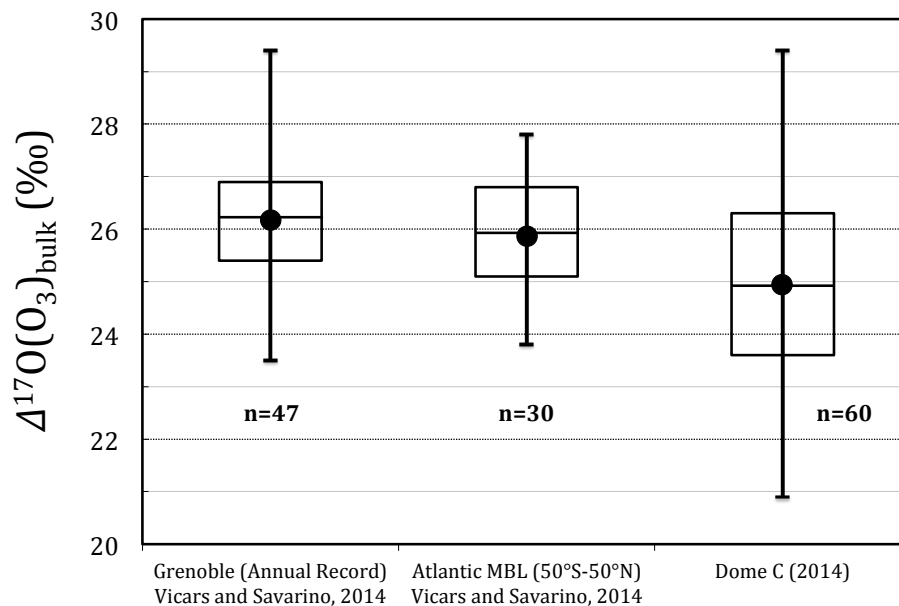


**Figure 3.**  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values for the 60 ambient air samplings done at Dome C throughout 2012. Vertical error bars refer to the total uncertainty estimated for the technique ( $\pm 1.7\text{‰}$ ).

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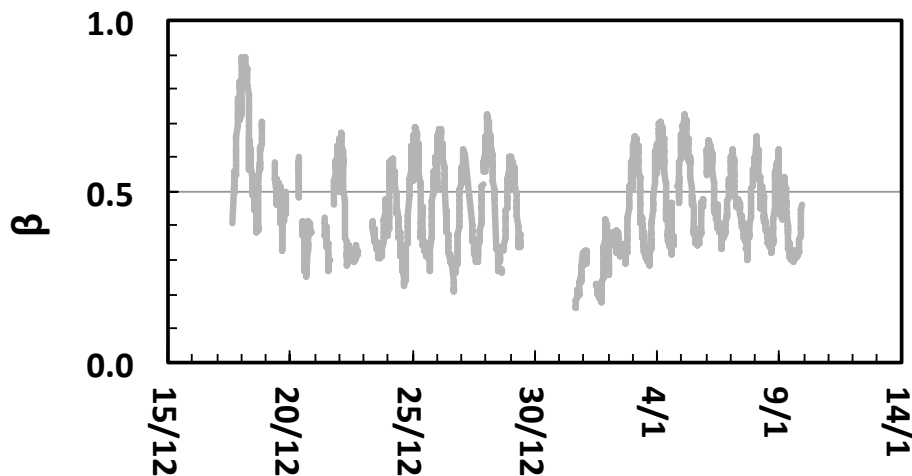
**Figure 4.** Comparison of  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$  values obtained at Dome C with those previously reported by Vicars and Savarino (2014) at other sites. The box plot indicates the interquartile range (box) and the median (line), maximum, and minimum values. The mean value is denoted by a circle.

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**Figure 6.** December 2011 time-series for  $\beta$ , the fraction of the  $^{17}\text{O}$ -excess originally associated with the OH radical that is preserved against isotopic exchange with water.

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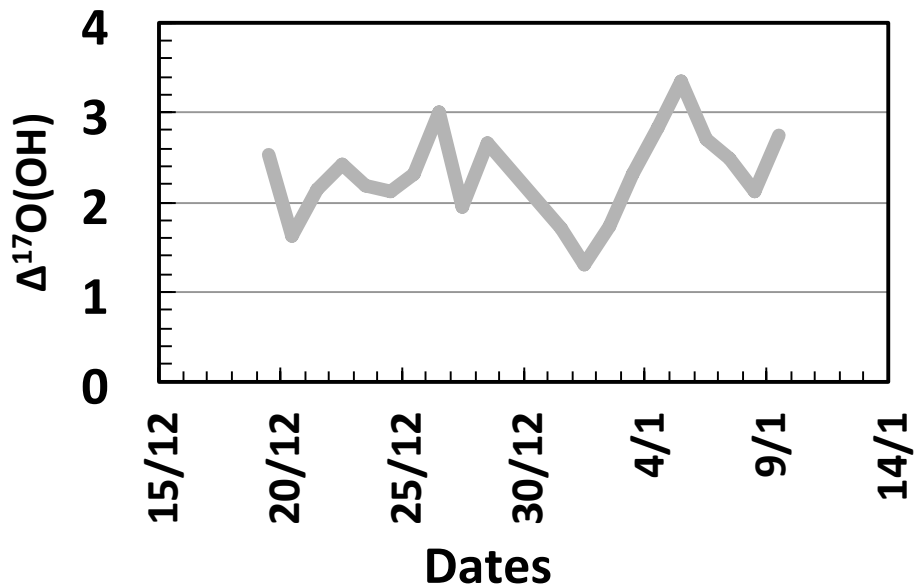


Figure 7. Same as Fig. 5 but for  $\Delta^{17}\text{O}$  of OH.

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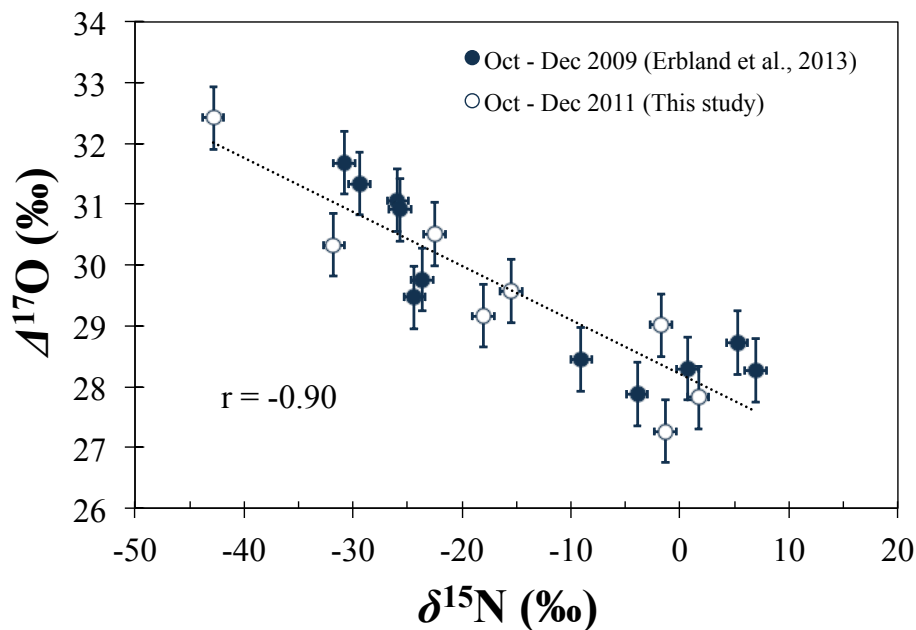
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**Figure 8.** Relationship observed between the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values of atmospheric nitrate present at Dome C between October and December during both the 2009 and 2011 summer campaigns. Error bars indicate the typical analytical uncertainties associated with the measurements.

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