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

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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}O -excess ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of ozone, which is transferred to NO_x via oxidation, is a particularly useful isotopic fingerprint in studies of NO_x transformations. Constraining the propagation of ^{17}O -excess within the 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 (NO_x , O_3 , OH , HO_2 , 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 OH and 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 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}O -excess transferred by one of the two 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}O -excess is located at the two 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 NaNO₂, 0.05 M K₂CO₃, 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⁻¹.

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 Δ¹⁷O(O₃) 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 FinniganTM MAT253 isotope ratio mass spectrometer (IRMS), equipped with a GasBench IITM 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 N_2O 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 (N_2O) via bacterial denitrification was allowed to proceed overnight. The N_2O 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 O_2 and N_2 . Following separation via gas chromatography, the O_2 and 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 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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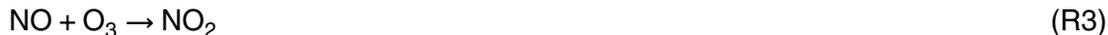
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permanently under sunlight, photochemical inter-conversion of NO_x is permanent:



5 At photochemical steady state (i.e. Reactions R2–R4 being faster than NO_2 net sink reactions), an assumption that can be reasonably applied throughout the day at Dome C during summer, we have (Morin et al., 2011):

$$\Delta^{17}\text{O}(\text{NO}_2) = \alpha \times (1.18 \times \Delta^{17}(\text{O}_3)_{\text{bulk}} + 6.6) \quad (1)$$

10 where the term in bracket represents the laboratory deduced anomaly transfer function of the $\text{NO} + \text{O}_3$ reaction (Savarino et al., 2008), $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ the ^{17}O -excess of the bulk O_3 and α represents the fraction of the atmospheric NO_2 reservoir that has been produced through oxidation by O_3 rather than HO_2/RO_2 at photochemical equilibrium (Alexander et al., 2009; Michalski et al., 2003; Morin et al., 2011; Röckmann et al., 2001):

$$15 \alpha = \frac{k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3]}{k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3] + k_{\text{NO}+\text{HO}_2}[\text{NO}][\text{HO}_2]^*} \quad (2)$$

with $[\text{HO}_2]^* = [\text{HO}_2] + [\text{RO}_2]$.

It is important to note here that Eqs. (1) and (2) although established under the NO_x steady-state approximation, are independent of NO_2 concentration for which a bias in measurement cannot be ruled out. Indeed, as discussed by Frey et al. (2013, 2014), bias in NO_2 measurements is suspected partly because it remains difficult to explain the observed ratio of NO_2/NO which is systematically higher (up to a factor of 7) than predicted by calculations made by assuming photochemical steady state considering the NO_2 photolysis and reaction of NO with O_3 , HO_2/RO_2 and BrO . Equation (2) also assumes that $[\text{HO}_2]^*$ is predominantly formed by the reaction $\text{H} + \text{O}_2$

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exchange, then $\Delta^{17}\text{O}(\text{OH}) = \Delta^{17}\text{O}(\text{OH})_{\text{prod.}}$. Kukui et al. (2014), using a Master Chemical Mechanism box model, constrained by the OPALE meteorological conditions and concurrent chemical observations, give the rate of the OH chemical sources and sinks. NO_2 as measured by Frey et al. (2014) represents at most only ca. 10 % (equivalent of ca. 1 ‰) of the total sink of OH, which is predominantly dominated by reactions with CO , CH_4 , aldehydes and to a lesser extent by reactions with O_3 , H_2 , and NO . Thus, the possible overestimation of NO_2 concentration has only a minor effect on β calculation and is well embedded within the total uncertainty of such calculation. To assess the value of $\Delta^{17}\text{O}(\text{OH})$, we have computed β for the conditions found during the OPALE campaign using the same 0-D box model that is used to evaluate the budget of OH and RO_2 during the OPALE campaign (see Kukui et al., 2014 and Table 1) and used the exchange kinetic rates given in Dubey et al. (1997). The absolute water vapor concentration is deduced from relative humidity and temperature measurements using Bolton, (1980) (i.e. $P_{\text{water}} = 6.112 \times e^{\frac{(17.67 \times (T-273))}{T-29.5}}$, with P_{water} in hPa and T in K). The results of this calculation (Fig. 6), indicate that β varies between 0.70 ± 0.10 (1σ) and 0.30 ± 0.10 from midnight to noon for conditions prevailing during the OPALE campaign, suggesting that on daily average basis approximately 43 % of the $\Delta^{17}\text{O}$ value originally present in OH is preserved from exchange with H_2O , consistent with estimates for an Arctic site described by Morin et al. (2007).

The value of $\Delta^{17}\text{O}(\text{OH})_{\text{prod.}}$ is more difficult to assess because of the interplay of HO_x family and the different sources involved in OH formation. In the rich NO_x atmosphere at Dome C in summer, the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction forming OH is a minor reaction pathway. When multiple pathways are involved in the production of OH, $\Delta^{17}\text{O}(\text{OH})_{\text{prod.}}$ can be estimated by a simple isotope mass balance equation where $\Delta^{17}\text{O}(\text{OH})_{\text{prod.}} = \sum_i P_i \times \Delta^{17}\text{O}_i$ with P_i the relative production rate of the i th reaction pathway with respect to the total production rate and $\Delta^{17}\text{O}_i$ its associated ^{17}O -excess (Morin et al., 2011). Observations at Dome C during the OPALE campaign indicate that the photolysis of HONO and the $\text{HO}_2 + \text{NO}$ reaction may represent the most sig-

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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 pmol mol^{-1}) during OPALE, probably biased by HO_2NO_2 interference (Legrand et al., 2014) is incompatible with the 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 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}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 $5 \pm 2\%$ (1σ). 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}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-

of NO with O₃ or HO₂/RO₂ (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_x cycle at Dome C would have important implications for the Δ¹⁷O 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 Δ¹⁷O of XO is equal to Δ¹⁷O(O₃)_{term.}, which means that the reaction of NO with XO is roughly equivalent to the NO + O₃ reaction in terms of Δ¹⁷O transfer to NO₂ (note that the NO + XO transfer is greater than NO + O₃ as in the later case, part of the central O₃ atom participates in the reaction). The participation of XO species in the oxidation of NO thus leads to a greater Δ¹⁷O transfer to NO₂ by effectively increasing the value of α. However, on the Antarctic plateau, BrO did not exceed 2–3 pmol mol⁻¹ 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 Δ¹⁷O(NO₂) and ultimately Δ¹⁷O(NO₃⁻). 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 HO₂, Δ¹⁷O(NO₃⁻) 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 NO₂ (Michalski et al., 2014), it is very unlikely that Δ¹⁷O(NO₂) could reach values greater than its primary snow nitrate source (i.e. Δ¹⁷O(NO₂) > Δ¹⁷O(NO₃⁻)_{SNOW} = 30–35‰ in summer at Dome C, (Erland et al., 2013; Frey et al., 2009), still leaving the predicted Δ¹⁷O(NO₃⁻) underestimated with respect to atmospheric observations.

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4.2 Alternative oxidation pathways of NO₂

Considering Reaction (R5) as the main source of HNO₃, an alternative approach is to consider that OH bears a higher Δ¹⁷O than the estimate calculated previously. Assuming a β of one, which seems again unrealistic, will increase Δ¹⁷O(NO₃⁻) by 1‰ at most (Table 2), still insufficient to explained atmospheric observations as NO + HO₂ 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_x budget (i.e. 4 times lower than measured), average Δ¹⁷O(NO₃⁻) 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 NO₂ nor the daytime formation of HNO₃ seems to be able to explain the high Δ¹⁷O(NO₃⁻) values of atmospheric nitrate observed at Dome C in summer. When this observation is taken together with the high NO₂/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_x 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_x cycling through the R7 pathway, an increasing body of evidence points towards reactive halogen chemistry as a major NO_x sink and source of nitrate via the production and subsequent hydrolysis of XNO₃ species (Sander et al., 1999; Savarino et al., 2013; Vogt et al., 1996):



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A critical analysis of the CHABLIS data led Bauguitte et al. (2012) to conclude that the Reactions (R8) and (R9) pathway exerted predominant control over the chemical loss rate of NO_x during the campaign, despite the significant uncertainties involved in the parameterization of the uptake processes (Finlayson-Pitts, 2009). This implies that $X\text{NO}_3$ uptake may also represent a significant source of nitrate at Dome C should halogen oxide radicals ($X\text{O}$) be present at the required concentration. Experimental (Gane et al., 2001) and theoretical (McNamara and Hillier, 2001) studies suggest that the oxygen atom initially associated with $X\text{O}$ combines with the N atom of NO_2 to form nitrate, thus transferring the isotopic signature of both $X\text{O}$ and NO_2 . The specific $\Delta^{17}\text{O}$ value induced by $X\text{NO}_3$ hydrolysis can thus be expressed as follows (Morin et al., 2007):

$$\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{R6}} = \frac{2}{3}\Delta^{17}\text{O}(\text{NO}_2) + \frac{1}{3}\Delta^{17}\text{O}(\text{O}_3)_{\text{term}} \quad (7)$$

efficiently bypassing the OH^{17}O -excess budget. Through consideration of the increased $\Delta^{17}\text{O}$ transfer associated with Reaction (R8), the observations of $\Delta^{17}\text{O}(\text{NO}_3^-)$ during December can be reconciled with the values calculated by mass-balance if approximately 10–20 % of total nitrate production is assumed to occur via $X\text{NO}_3$ hydrolysis. However, no sufficient halogen concentration has been observed on the Antarctic plateau to sustain such chemical pathway but we note that chlorine chemistry has never been probed on the Antarctic plateau.

There is increasing body of evidence that heterogeneous hydrolysis of NO_2 can be a possible source of HONO and HNO_3 in acidic conditions (Finlayson-Pitts, 2009), with the potential to explain the difference between the calculated and measured atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ values. This mechanism would represent a source of nitrate with a $\Delta^{17}\text{O}$ value roughly equivalent to the nitrate originally present in the surface snow (i.e., 30–35‰), a signature significantly higher than that induced by Reaction (R5). If this production mechanism is active at the air–snow interface at Dome C and results in the slow emission of nitrate to the atmosphere via physical release after its formation,

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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 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 NO_x (Michalski et al., 2003; Morin et al., 2008). Nighttime chemistry involves species like N_2O_5 and NO_3 in the process of forming HNO_3 and again efficiently by-pass the OH pathway. It is conceivable that below the photic zone, within the snowpack, N_2O_5 and NO_3 could be produced when O_3 and NO_2 are transported at depth but there is no reason to think that such dark 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 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}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 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}N due its formation from snowpack 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 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°N). The authors of this study attributed the observed correlation to the coupling of snowpack 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 NO_x via nitrate photochemistry (Grannas et al., 2007) and may induce a larger ^{17}O -excess in OH as compared to the conventional $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ pathway. Furthermore, the hydrolysis of NO_2 in snow, should it contribute significantly to nitrate production at Dome C, is likely amplified during periods when concentrations 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 NO_x chemistry above the snow surface at Dome C is therefore incomplete.

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Constraining the propagation of ozone's ^{17}O -excess signature within the 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 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 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 NO_2 due to the high concentrations of 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 NO_2/NO ratio, high concentration of NO_2 , unresolved HONO atmospheric concentration, interference such as HO_2NO_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 ⁻³	^a Median rate in 10 ⁵ molecules cm ⁻³ s ⁻¹	$\Delta^{17}\text{O}_i^c$ in ‰
Net sources of OH		
P1 HONO + <i>hν</i> → OH + NO	5.1 ^b	32
P2 H ₂ O ₂ + <i>hν</i> → 2OH	1.7	2
P3 O ₃ + <i>hν</i> + H ₂ O → 2OH	0.6	20
P4 CH ₃ OOH + <i>hν</i> → HO ₂ + OH	0.3	0
Recycling RO₂ → OH		
P5 NO + HO ₂ → NO ₂ + OH	7.7	0
P6 HO ₂ + O ₃ → OH + 2O ₂	0.4	0
Net sink of OH		
L1 CO + OH → HO ₂ + CO ₂	6.3	
L2 CH ₄ + OH → CH ₃ O ₂ + H ₂ O	2.6	
L2 HCHO + OH → HO ₂ + CO	0.8	
L4 CH ₃ CHO + OH → CH ₃ CO ₃	0.9	
L5 O ₃ + OH → HO ₂ + O ₂	0.6	
L6 H ₂ + OH + O ₂ → HO ₂ + H ₂ O	0.60	
L7 CH ₃ OOH + OH → CH ₃ O ₂ + H ₂ O	0.5	
L8 H ₂ O ₂ + OH → HO ₂ + H ₂ O	0.3	
Net OH losses		
L9 NO ₂ + OH → HNO ₃	3.9	
L10 NO + OH → HONO	0.6	
L11 OH + RO ₂ → products	0.5	
L12 OH + RO ₂ NO ₂ → products	0.6	
L13 OH + HONO → NO ₂ + H ₂ O	0.2	
L14 OH + HNO ₃ → H ₂ O + NO ₃	0.0	
Isotope exchange		
E ₁ HQ + H ₂ O ⇌ HO + H ₂ Q	24.3	
NO₂ main source		
N1 NO + O ₃ → NO ₂ + O ₂	27.0	37
¹⁷O-excess NO₂		
$\alpha = (N1 / (N1 + P5))$	0.78	
$\Delta^{17}\text{O}(\text{NO}_2)$		29
¹⁷O-excess OH		
$\Delta^{17}\text{O}(\text{OH})_{\text{prod}} = (\sum P_i \times \Delta^{17}\text{O}_i) / \sum P_i$		5.8
$\beta = \sum L_i / (\sum L_i + E_1)$	0.43	
$\Delta^{17}\text{O}(\text{OH})$		2.5

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

^b: HONO production rate divided by a factor 4 to balance the HO₂ radical budget (see Kukui et al., 2014; Legrand et al., 2014 for justification).

^c: 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 ¹⁷O-excess transfer (i.e. P₂ to P₆ and N₁) 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			
		α constrained by observations $\Delta^{17}\text{O}(\text{OH})^*$ based on HO_x budget	$\alpha = 1$ $\Delta^{17}\text{O}(\text{OH})^*$ based HO_x budget	α constrained by observations $\beta = 1$	α constrained by observations $\Delta^{17}\text{O}(\text{OH})$ based on observed HONO
10 Dec–16 Dec	29.6	21.9	25.6	22.6	27.0
16 Dec–23 Dec	29.0	21.0	25.6	21.7	26.3
23 Dec–30 Dec	27.8	21.6	25.4	22.0	25.7
30 Dec–2 Jan	27.3	21.5	25.3	22.4	24.9

* HONO production rate divided by a factor 4 to balance the HO_x radical budget (see Kukui et al. (2014) and Legrand et al. (2014) for justification).

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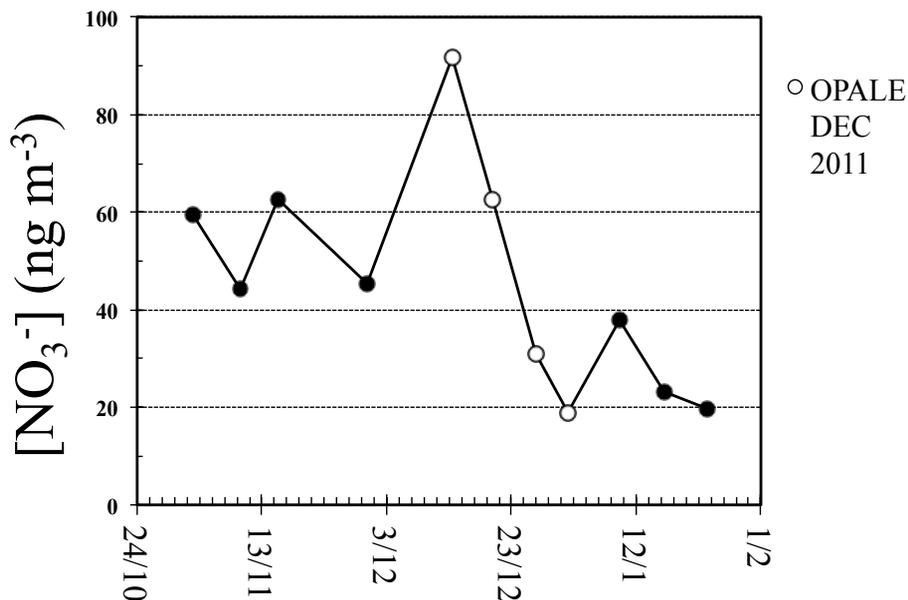


Figure 1. Atmospheric nitrate concentrations observed between October 2011 and January 2012. The samples collected during the intensive measurement period of the OPALE campaign (December 2011) are indicated with open circles.

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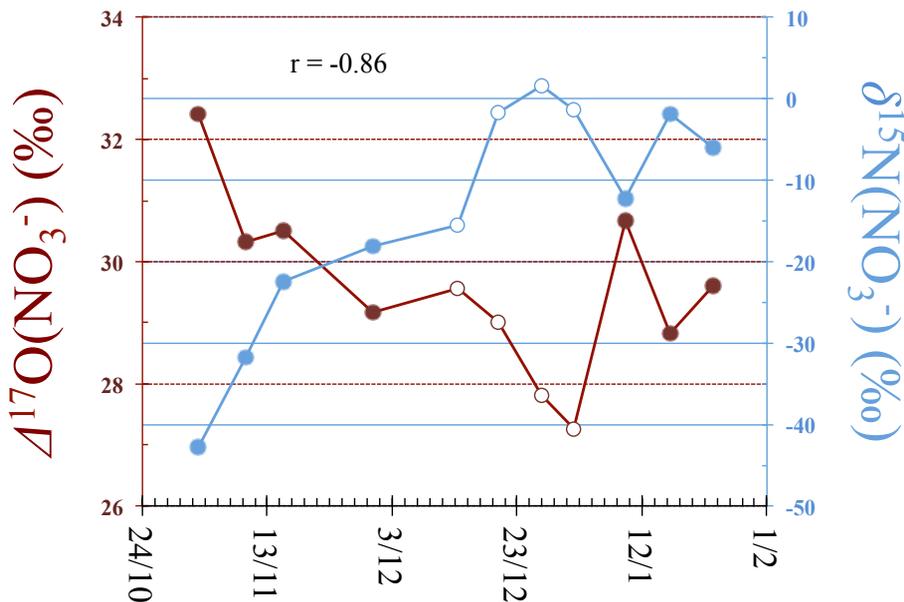


Figure 2. $\Delta^{17}\text{O}$ (primary y axis) and $\delta^{15}\text{N}$ (secondary y axis) of atmospheric nitrate collected between October 2011 and January 2012. The samples collected during the intensive measurement period of the OPALE campaign (December 2011) are indicated with open symbols.

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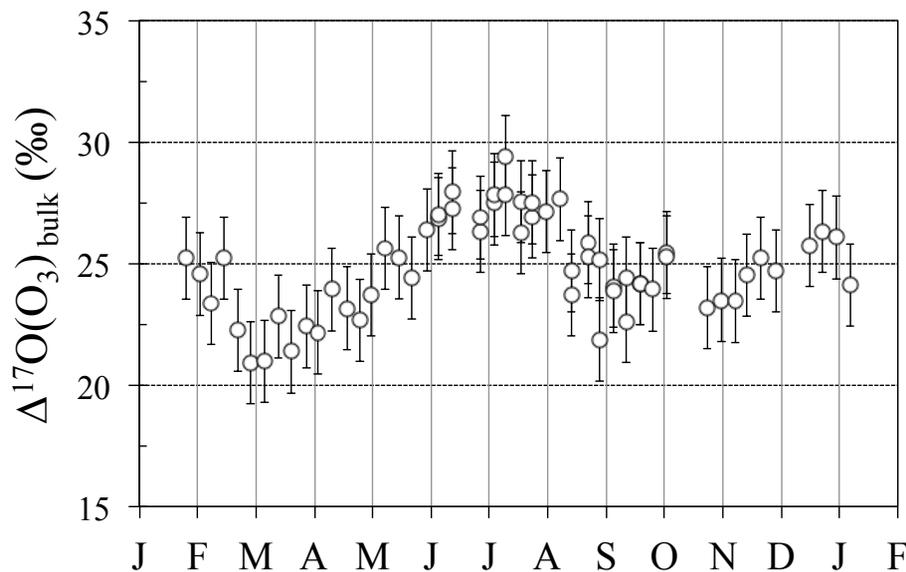


Figure 3. $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ values for the 60 ambient air samplings done at Dome C throughout 2012. Vertical error bars refer to the total uncertainty estimated for the technique ($\pm 1.7\text{‰}$).

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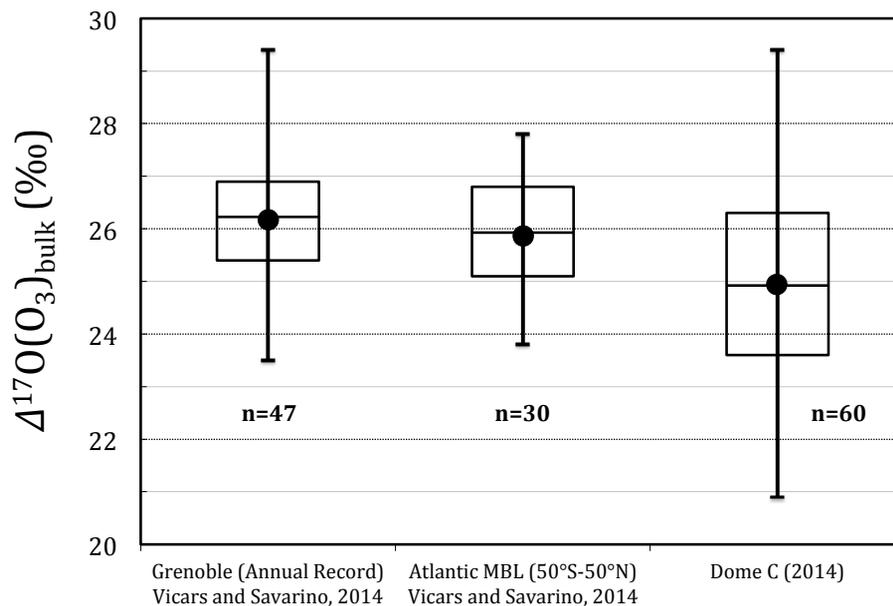


Figure 4. Comparison of $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ values obtained at Dome C with those previously reported by Vicars and Savarino (2014) at other sites. The box plot indicates the interquartile range (box) and the median (line), maximum, and minimum values. The mean value is denoted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

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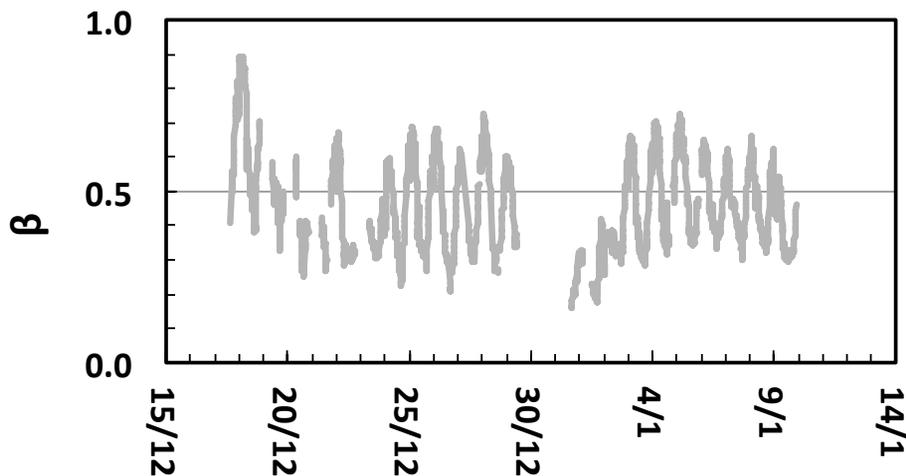


Figure 6. December 2011 time-series for β , the fraction of the ^{17}O -excess originally associated with the OH radical that is preserved against isotopic exchange with water.

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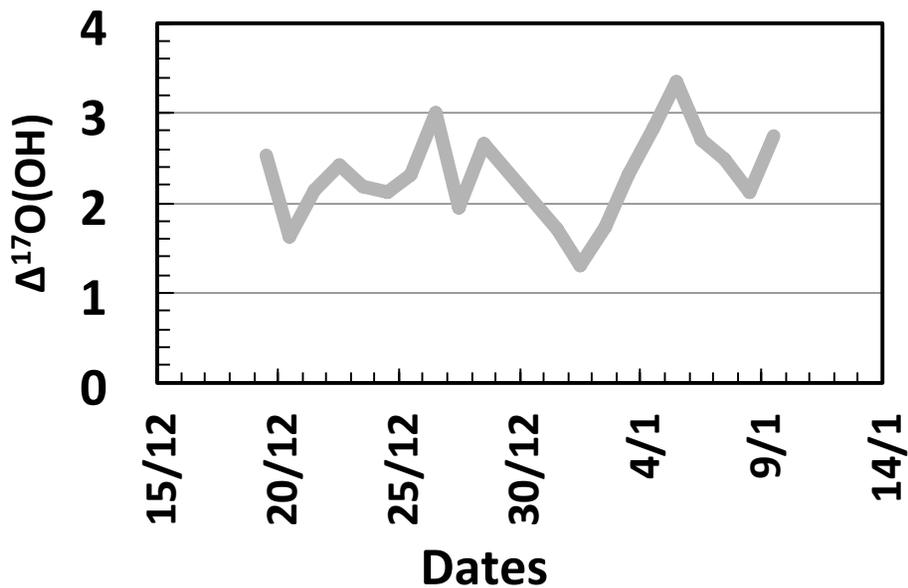


Figure 7. Same as Fig. 5 but for $\Delta^{17}\text{O}$ of OH.

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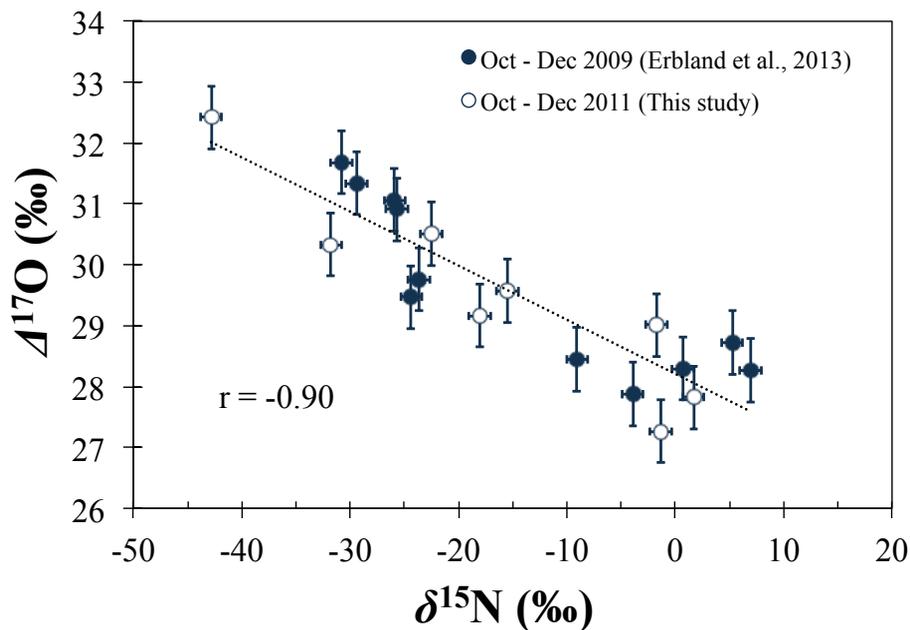


Figure 8. Relationship observed between the $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ values of atmospheric nitrate present at Dome C between October and December during both the 2009 and 2011 summer campaigns. Error bars indicate the typical analytical uncertainties associated with the measurements.

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