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Submitted on 13 May 2016

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

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Received: 26 June 2015 – Published in Atmos. Chem. Phys. Discuss.: 7 September 2015
Revised: 22 January 2016 – Accepted: 14 February 2016 – Published: 3 March 2016

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 (NO + NO2 = NOx). The unique and distinctive 17O excess (\(\delta^{17}O - 0.52 \times \delta^{18}O\)) of ozone, which is transferred to NOx via oxidation, is a particularly useful isotopic fingerprint in studies of NOx transformations. Constraining the propagation of 17O excess within the NOx cycle is critical in polar areas, where there exists the possibility of extending atmospheric investigations to the glacial–interglacial timescale 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 2011/2012. Nitrate isotope analysis has been here combined for the first time with key precursors involved in nitrate production (NOx, O3, OH, HO2, RO2, etc.) and direct observations of the transferrable \(\Delta^{17}O\) 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 OH + NO2 pathway and using concurrent measurements of OH and NO2, we calculated a \(\Delta^{17}O\) signature for nitrate on the order of \((21–22 \pm 3)\%\). These values are lower than the measured values that ranged between 27 and 31\%. This discrepancy between expected and observed \(\Delta^{17}O(NO_3)\) values suggests the existence of an unknown process that contributes significantly to the atmospheric nitrate budget over this East Antarctic region. However, systematic errors or false isotopic balance transfer functions are not totally excluded.

1 Introduction

The search for ice core proxies to reconstruct past change of oxidative properties of the atmosphere is motivated by the need to simulate ozone and OH changes over preindustrial–industrial and glacial–interglacial timescales (Thompson, 1992; Wang and Jacob, 1998; Murray et al., 2014). Early ice core reconstructions of oxidants based on \(\mathrm{H_2O_2}\) (Sigg and Neftel, 1991) and HCHO (Staffelbach et al., 1991) measurements were hampered by the occurrence of post-depositional alteration of \(\mathrm{H_2O_2}\) and HCHO concentrations in the upper snowpack prior to preservation in the ice (Hutterli et
proximately 800 000 years (EPICA community members, Project for Ice Coring in Antarctica (EPICA) covering ap-
extracted at Dome C in the framework of the European
1100 km from the coastal research station Dumont d’Urville
East Antarctic Plateau (75°S).

2.1 Site description and scientific context

Dome C is situated 3233 m above sea level 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 years (EPICA community members,
2004) and Vostok covering the last 420 000 years (Petit et
al., 1999). In parallel, studies aiming to understand the mete-
orological, chemical, and physical factors governing the vari-
ability in trace constituents preserved in the ice were initiated
(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 Chem-
istry in the Antarctic Troposphere) field campaign revealed
a high level of photochemical activity. For example, the aver-
age summertime OH concentration (2 × 10⁶ cm⁻³) over the
South Pole was found to be similar to that of the tropical
marine boundary layer (MBL) (Mauldin et al., 2001). Unex-
pectedly high levels of nitric oxide (NO) were also detected,
with concentrations 1 to 2 orders of magnitude higher than
that typically observed in other remote regions (Davis et al., 2001). Model simulations revealed that the large OH concen-
trations observed at South Pole were a result of the ele-
vated NO level, which catalyzes a rapid cycling of HO₂ to
OH (Chen et al., 2004, 2001). The high concentrations of
NOx were also inferred to drive in situ photochemical pro-
duction of ozone during the ISCAT campaign (Crawford et
al., 2001). Surface ozone and NOx measurements at Dome C
suggest a similar level of enhanced oxidant production dur-
ing November–January (Frey et al., 2013, 2015; Legrand et
al., 2009).

Here we present measurements of δ¹⁵N and δ¹⁷O and
δ¹⁸O isotopic composition of atmospheric nitrate collected at
Dome C between November 2011 and January 2012. These
measurements were conducted within the framework of the
OPALE project (Oxidant Production over Antarctic Land and
its Export; Preunkert et al., 2012), which has provided an
opportunity to combine nitrate isotopic observations with a
wealth of meteorological and chemical observations, includ-
ing measurements of species involved in nitrate production
(NOx, O₃, OH, HO₂, RO₂, etc.). The primary objective of
this study was to reconcile observations of Δ¹⁷O for atmo-
spheric nitrate at Dome C with quantitative predictions
based on nitrate isozone mass balance and atmospheric chem-
istry parameters, a unique opportunity offered by the OPALE
campaign.

2 Methods

2.1 Site description and scientific context

Dome C is situated 3233 m above sea level 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 years (EPICA community members,
samples were obtained during the OPALE campaign (from November 2011 to January 2012). After each collection period, filters were removed from the HVAS and placed in clean 50 mL centrifuge tubes, which were sealed in plastic bags and stored at $-20^\circ$C. Upon arrival at our laboratory in Grenoble, atmospheric filter samples were extracted in 40 mL of ultra-pure water via centrifugation using Millipore Centricron® 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 isotopic analysis has been described in detail in Vicars et al. (2012) and 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):

$$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2. \quad \text{(R1)}$$

By coupling this routine ozone measurement technique with recent analytical developments in the $\Delta^{17}$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 $\Delta^{17}$O($\text{O}_3$)$_{\text{term}}$, as well as ozone’s bulk $\Delta^{17}$O value, denoted $\Delta^{17}$O($\text{O}_3$)$_{\text{bulk}}$ ($=2/3 \ \Delta^{17}$O($\text{O}_3$)$_{\text{term}}$) since all $^{17}$O excess is located at the two O$_3$ terminal atoms; Bhattacharyya 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 in. 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 (Savillex®) 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 coated prior to sample collection with 1 mL of a nitrite-based ozone sampling solution (0.1 M NaNO$_2$, 0.05 M K$_2$CO$_3$, 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 $\Delta^{17}$O($\text{O}_3$) 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 $-20^\circ$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 Centricron® 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 ($^{15}$N/$^{14}$N, $^{17}$O/$^{16}$O, $^{18}$O/$^{16}$O) was measured on a Finnigan™ MAT253 isotope ratio mass spectrometer (IRMS), equipped with a GasBench II 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$_2$O via the bacterial denitrification 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 briefly presented here.

Denitrifying bacteria (Pseudomonas aureofaciens) were cultured in nitrate-amended soy broth and incubated for 5 days in stopped glass bottles. Bacterial cultures, after concentration by centrifugation and resuspension, 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$_2$O) via bacterial denitrification was allowed to proceed overnight. The N$_2$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 O₂ and N₂. Following separation via gas chromatography, the O₂ and N₂ gas samples were directed into the ionization chamber of the IRMS. All analytical steps were identically 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 N₂ 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 their expected values. For the results reported here, the average uncertainties obtained for δ¹⁵O, Δ¹⁷O, and δ¹⁵N were 1.6, 0.5, and 1.0 ‰, respectively.

2.5 Complementary measurements

Concurrent chemical measurements were conducted at Dome C during the campaign include HONO (Legrand et al., 2014), HO₂ (= OH + HO₂ + RO₂) radicals (Kukui et al., 2014), O₃ (Legrand et al., 2016) and NO and NO₂ (Frey et al., 2015). Photolysis rate coefficients and meteorological parameters were also recorded.

3 Results and discussion

3.1 Isotope ratios of ozone and atmospheric nitrate

Atmospheric nitrate concentrations observed at Dome C during the campaign are presented in Fig. 1, and the corresponding nitrate Δ¹⁷O and δ¹⁵N values in Fig. 2. Atmospheric nitrate concentrations ranged between 20 and 90 ng m⁻³, with the maximum values occurring in mid-December 2011, concurrent with the period of intensive atmospheric sampling of the OPALE field campaign. These values are in good agreement with those observed during the 2007–2008 and 2009–2010 field studies conducted at Dome C by Frey et al. (2009) and Erbland et al. (2013), respectively.

Δ¹⁷O values for atmospheric nitrate ranged between 27.3 and 32.4 ‰, and those for δ¹⁵N between −42.8 and 1.7 ‰. The observed strongly depleted δ¹⁵N(NO₃⁻) values are in good agreement with those previously reported and having unambiguously attributed to the transformation of local snowpack NOₓ emissions via photochemistry in the boundary layer, which led to peaks in atmospheric nitrate concentration during the period from October to December (Erbland et al., 2013). As seen in Fig. 2, variations in Δ¹⁷O and δ¹⁵N were negatively correlated (r value of −0.86) and again show similar amplitude and phase to those reported in previous Erbland et al. (2013; Frey et al., 2009).

A time series showing the year-round record of Δ¹⁷O(O₃) bulk at Dome C in 2012 is presented in Fig. 3. Δ¹⁷O(O₃) bulk averaged 24.9 ± 1.9 ‰, derived from Δ¹⁷O(O₃)term values of 37.4 ± 1.9 ‰. As shown in Fig. 4, these Δ¹⁷O(O₃) bulk values are consistent with those observed in Grenoble (France), as well as with measurements conducted along a latitudinal transect from 50° S to 50° N in the Atlantic Ocean (Vicars and Savarino, 2014). Although the Δ¹⁷O(O₃)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 quite stable Δ¹⁷O(O₃)bulk value close to 26 ‰ that can be considered as representative of the OPALE campaign held 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 opportu-
nity to compare observed $\Delta^{17}$O(NO$_3$) values in the atmosphere to 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 $\Delta^{17}$O-excess transfer functions associated with the various nitrate production pathways (i.e., $\Delta^{17}$O(NO$_3$)$_i$ values) can be estimated as a function of the $\Delta^{17}$O of nitrate precursor gases (i.e., NO$_x$, O$_3$, OH, etc.) using mass balance calculations that trace the origin of oxygen atoms transferred during the chemical transformation of NO$_x$ in the atmosphere. All atmospheric nitrate production channels involve either NO$_2$ or a NO$_x$ reservoir species derived from NO$_2$ (e.g., N$_2$O$_5$). The first step in determining the $\Delta^{17}$O signature of each pathway is therefore a quantitative assessment of the steady-state $\Delta^{17}$O value of NO$_2$, which is typically calculated as a function of the $\Delta^{17}$O value of O$_3$ and the reaction dynamics involved in the conversion of NO to NO$_2$. As Dome C in summer is permanently under sunlight, photochemical inter-conversion of NO$_x$ continues:

\begin{align*}
\text{NO}_2 + h\nu &\rightarrow \text{NO} + \text{O}, \\
\text{NO} + \text{O}_3 &\rightarrow \text{NO}_2, \\
\text{NO} + \text{HO}_2/\text{RO}_2 &\rightarrow \text{NO}_2.
\end{align*}

At photochemical steady state (i.e., 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)

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

where the term in bracket represents the laboratory-deduced anomaly transfer function of the NO + O$_3$ reaction (Savarino et al., 2008). $\Delta^{17}\text{O(O}_3)_{\text{bulk}}$ the $\Delta^{17}$O excess of the bulk O$_3$ and $\alpha$ represents the fraction of the atmospheric NO$_2$ reservoir that has been produced through oxidation by O$_3$ rather than

Figure 3. $\Delta^{17}\text{O(O}_3)_{\text{bulk}}$ 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 (±1.7‰).

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

HO$_2$ / RO$_2$ at photochemical equilibrium (Alexander et al., 2009; Michalski et al., 2003; Morin et al., 2011; Röckmann et al., 2001):

$$
\alpha = \frac{k_{\text{NO} + \text{O}_3}[\text{NO}][\text{O}_3]}{k_{\text{NO} + \text{O}_3}[\text{NO}][\text{O}_3] + k_{\text{NO} + \text{HO}_2}[\text{NO}][\text{HO}_2]^*},
$$


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, 2015), 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 H + O$_2$ and R + O$_2$ during the OPALE campaign (Kukui et al., 2014), resulting in the formation of $[\text{HO}_2]^*$ devoid of any significant $^{17}$O excess (Morin et al., 2011). Using OPALE measurements of NO, O$_3$, OH and HO$_2$ / RO$_2$ (Frey et al., 2015; Kukui et al., 2014), along with temperature dependent reaction kinetics data obtained from Atkinson et al. (2004), we have calculated the diurnally mass-averaged trend in $\alpha$ for the month of December 2011 at Dome C. Measurements of $\Delta^{17}\text{O(O}_3)_{\text{bulk}}$ at Dome C during the OPALE campaign averaged $25 \pm 2\%e$, corresponding to $\Delta^{17}\text{O(O}_3)_{\text{term}}$ values of $37 \pm 2\%e$ (Fig. 4). Samples collected in December indicate $\Delta^{17}\text{O(O}_3)_{\text{bulk}}$ values close to $26\%e$ ($\Delta^{17}\text{O(O}_3)_{\text{term}} = 3/2\Delta^{17}\text{O(O}_3)_{\text{bulk}} = 39–40\%e$, Fig. 3), and we have therefore adopted a $\Delta^{17}\text{O(O}_3)_{\text{term}}$ value of $40\%e$ in the subsequent mass balance calculations, in good agreement with the predicted value from a 1-D at-
Table 1. Example of mass balance calculation of $\Delta^{17}$O for 19 December 2011 at 15:45 local time (UTC + 8 h).

<table>
<thead>
<tr>
<th>Conditions for 19 December 2011, 15:45</th>
<th>(10^5 \text{ molecules cm}^{-3} \text{s}^{-1})</th>
<th>(\Delta^{17} \text{O}_{\text{prod}}^c) in (%e)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Net sources of OH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1 HONO + (hv) (\rightarrow) OH + NO</td>
<td>5.1(^b)</td>
<td>32</td>
</tr>
<tr>
<td>P2 (\text{H}_2\text{O}_2 + hv \rightarrow 2 \text{OH})</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>P3 (\text{O}_3 + hv + \text{H}_2\text{O} \rightarrow 2 \text{OH})</td>
<td>0.6</td>
<td>20</td>
</tr>
<tr>
<td>P4 (\text{CH}_3\text{OOH} + hv \rightarrow \text{HO}_2 + \text{OH})</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td><strong>Recycling RO(_2) \rightarrow \text{OH}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P5 (\text{NO}_2 + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH})</td>
<td>7.7</td>
<td>0</td>
</tr>
<tr>
<td>P6 (\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2)</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td><strong>Net sink of OH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1 (\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2)</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>L2 (\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O})</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>L2 (\text{HCHO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO})</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>L4 (\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO}_3)</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>L5 (\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2)</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>L6 (\text{H}_2 + \text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O})</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>L7 (\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O})</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>L8 (\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O})</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td><strong>Net OH losses</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L9 (\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3)</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>L10 (\text{NO} + \text{OH} \rightarrow \text{HONO})</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>L11 (\text{OH} + \text{RO}_2 \rightarrow \text{products})</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>L12 (\text{OH} + \text{RO}_2\text{NO}_2 \rightarrow \text{products})</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>L13 (\text{OH} + \text{HONO} \rightarrow \text{NO}_2 + \text{H}_2\text{O})</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>L14 (\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3)</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td><strong>Isotope exchange</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_1) (\text{HQ} + \text{H}_2\text{O} \Leftrightarrow \text{HO} + \text{H}_2\text{Q})</td>
<td>24.3</td>
<td></td>
</tr>
<tr>
<td><strong>NO(_2) main source</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1 (\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2)</td>
<td>27.0</td>
<td>37</td>
</tr>
<tr>
<td><strong>(\alpha) = (N1/N1 + P5)</strong></td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>(\Delta^{17} \text{O} (\text{NO}_2))</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>**(\beta) = \sum L_i \left(\sum P_i \cdot \Delta^{17} \text{O}_i\right) / \sum L_i + E_1)</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>(\Delta^{17} \text{O} (\text{OH}))</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Production rates obtained from a 0-D box model (see Kukui et al., 2014, for details). \(^b\) HONO production rate divided by a factor of 4 to balance the HO\(_2\) radical budget (see Kukui et al., 2014, and Legrand et al., 2014, for justification). \(^c\) HONO is assumed to be formed by the photodissociation of nitrate in snow. \(\Delta^{17} \text{O} (\text{NO}_2)_{\text{snow}}\) is therefore assigned to HONO. The rest of the \(\Delta^{17} \text{O}\) excess transfer (i.e., P2 to P6 and N1) follows the rules established in Morin et al. (2011) and \(\Delta^{17} \text{O} (\text{O}_3)_{\text{bulk}} = 26\%e\).
spheric nitrate formation pathway is the gas-phase association mechanisms can be calculated. For summer conditions at NO\textsubscript{2} is essentially explained by the use of different temperatures and pressure (Michalski et al., 2014). This difference is essentially explained by the use of different \(\Delta^{17}\text{O}(\text{NO}_3)\) bulk (32\ ‰ in Michalski’s simulation, 26\ ‰ for our observations), which possibly corresponds to different conditions of the two studies.

By accounting for the origin of the oxygen atom transferred during the conversion of NO\textsubscript{2} to nitrate, the \(\Delta^{17}\text{O}\) signature of the nitrate produced through different reaction mechanisms can be calculated. For summer conditions at Dome C, it is reasonable to assume that the dominant atmospheric nitrate formation pathway is the gas-phase association of NO\textsubscript{2} and the OH radical (Alexander et al., 2009):

\[
\text{NO}_2 + \text{OH} + M \rightarrow \text{HNO}_3 + M, \tag{R5}
\]

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

\[
\Delta^{17}\text{O}(\text{NO}_3) = \frac{2}{3} \Delta^{17}\text{O}(\text{NO}_2) + \frac{1}{3} \Delta^{17}\text{O}(\text{OH}). \tag{3}
\]

In order to predict the \(\Delta^{17}\text{O}\) value of the nitrate produced through 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 erode the \(^{17}\text{O}\) excess of OH under humidity and temperature conditions typical of the midlatitudes (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 H\textsubscript{2}O can be determined as a function of the relative rates of the isotope exchange reaction and the main OH sink reactions:

\[
\beta = \frac{L}{L + k_{\text{H}_2\text{O}+\text{OH}[\text{H}_2\text{O}]}}
\]

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):

\[
\Delta^{17}\text{O}(\text{OH}) = \beta \times \Delta^{17}\text{O}(\text{OH})_{\text{prod}}. \tag{5}
\]

In plain words, Eqs. (4)–(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., \(\Delta^{17}\text{O} \approx 0\ ‰\)). Conversely, when water vapor concentrations are low and the rate of chemical loss is large relative to the rate of the isotopic exchange, \(\Delta^{17}\text{O}(\text{OH}) = \Delta^{17}\text{O}(\text{OH})_{\text{prod}}\). 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\textsubscript{2} as measured by Frey et al. (2015) represents at most only ca. 10\ ‰ (equivalent of ca. 1 \%/e) of the total sink of OH, which is predominantly dominated by reactions with CO, CH\textsubscript{4}, aldehydes and to a lesser extent by reactions with O\textsubscript{3}, H\textsubscript{2}, and NO. Thus, the possible overestimation of NO\textsubscript{2} concentration has only a minor effect on \(\beta\) 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 \(\beta\) 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 NO\textsubscript{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., \(P_{\text{water}} = 6.112 \times e^{(17.67 \times (T-273)) / 23.5}\), with \(P_{\text{water}}\) in hPa and \(T\) in K). The results of this calculation (Fig. 6) indicate that \(\beta\) varies between 0.70 ± 0.10 (1\ ‰) and 0.30 ± 0.10 from midnight to noon for conditions prevailing during the OPALE campaign, suggesting that, on a daily average basis, approximately 43\ ‰ of the \(\Delta^{17}\text{O}\) value originally present in OH is preserved from exchange with H\textsubscript{2}O, 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 between HO and HO\textsubscript{2}, and the different sources involved in OH formation. In the NO\textsubscript{3}-rich atmosphere at Dome C in summer, the O(\textsuperscript{1}D) + H\textsubscript{2}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 \(\Delta^{17}\text{O}(\text{OH})_{\text{prod}} = \sum P_i \times \Delta^{17}\text{O}_i\), 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
Table 2. Comparison of measured and calculated $\Delta^{17}$O(NO$_3^-$) values.

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>Measured</th>
<th>Calculated</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$ constrained by observations</td>
<td>$\alpha = 1$</td>
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<tr>
<td></td>
<td>$\Delta^{17}$O(OH)* based on HO$_x$ budget</td>
<td>$\Delta^{17}$O(OH)* based HO$_x$ budget</td>
</tr>
<tr>
<td>10–16 Dec</td>
<td>29.6</td>
<td>21.9</td>
</tr>
<tr>
<td>16–23 Dec</td>
<td>29.0</td>
<td>21.0</td>
</tr>
<tr>
<td>23–30 Dec</td>
<td>27.8</td>
<td>21.6</td>
</tr>
<tr>
<td>30 Dec–2 Jan</td>
<td>27.3</td>
<td>21.5</td>
</tr>
</tbody>
</table>

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

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

associated $^{17}$O excess (Morin et al., 2011). Observations at Dome C during the OPALe campaign indicate that the photolysis of HONO and the HO$_2$ + NO reaction may represent the most significant sources of OH at Dome C during the period of seasonal snowpack emissions (Kukui et al., 2014). However, the measurement of HONO (around few 10 pmol mol$^{-1}$) during OPALe, probably biased by HO$_2$NO$_2$ interference (Legrand et al., 2014), is incompatible with the HO$_x$ (= OH + HO$_2$ / HO$_x$) 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. (2015). Therefore, the production of OH by HONO photolysis is consequently adjusted and the 0-D box model (Kukui et al., 2014) is used to calculate all other production rates of OH. Note that, even when 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 OH$_{prod}$ isotope mass balance, $\Delta^{17}$O(OH)$_{prod}$ 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 $\Delta^{17}$O value of approximately 32%e, 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 $\Delta^{17}$O(NO$_3^-$)$_{lat} = \Delta^{17}$O(NO$_3^-$)$_{snow}$ 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 $\Delta^{17}$O(OH). $\Delta^{17}$O(OH) varies in a narrow range, between 1 and 3%e. An estimation of the $\Delta^{17}$O signature for the NO$_2$ + OH channel, $\Delta^{17}$O(NO$_3^-$)$_{R2}$, that accounts for the $^{17}$O excess carried by the OH radical results in values ranging between 20 and 23%e. Averaging over the same time period as the nitrate atmospheric sampling, diurnally integrated average $\Delta^{17}$O(NO$_3^-$) values of 21–22%e ± 3%e can be estimated for December (Table 2). These values are 6–8% lower than the observed atmospheric values for $\Delta^{17}$O(NO$_3^-$) (27–30%e during OPALe, Fig. 2 and Table 2). The source of discrepancy between observed and modeled $\Delta^{17}$O(NO$_3^-$) during OPALe is presently unknown, but we note that such underestimation of the modeled $\Delta^{17}$O(NO$_3^-$) versus the observed $\Delta^{17}$O(NO$_3^-$) was also pointed out in 3-D modeling of the nitrate $^{17}$O excess (Alexander et al., 2009). A critical evaluation may nevertheless offer some clues.

4 Discussion

4.1 Alternative sources of NO$_2$

A possible explanation for the underestimation of $\Delta^{17}$O(NO$_3^-$) involves halogen chemistry in the troposphere over the Antarctic Plateau (Bloss et al., 2010; Morin et al., 2008). Reactive halogen oxides (XO = BrO, ClO, IO, etc.) are produced through the reaction of halogen radicals (X) with ozone, a pathway that plays an important role in the catalytic process responsible for ozone depletion events (ODEs) observed in the Arctic boundary layer since the
The involvement of XO in the NOx cycle at Dome C would have important implications for the $\Delta^{17}O$ of atmospheric nitrate. The production of halogen oxide radicals proceeds through a direct transfer of a terminal oxygen atom from ozone to the NOx product (Zhang et al., 1997). Therefore, it is expected that the $\Delta^{17}O$ of XO is equal to $\Delta^{17}O(O_3)_{term}$, which means that the reaction of NO with XO is roughly equivalent to the NO + O3 reaction in terms of $\Delta^{17}O$ 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 $\Delta^{17}O$ transfer to NO2 by effectively increasing the value of $\alpha$. However, on the Antarctic Plateau, BrO did not exceed 2–3 pmol mol$^{-1}$ during the OPALE campaign (Frey et al., 2015). Including BrO chemistry would only increase $\alpha$ by 2% (due to the specific form of $\alpha \equiv 1/(1+x)$), which is too low to significantly influence $\Delta^{17}O(NO_2)$ and ultimately $\Delta^{17}O(NO_3^-)$. In the absence of measurements of other halogen we cannot completely rule out a role of the halogen chemistry there. However, even with $\alpha = 1$, its maximum but unrealistic value due to the high concentration of HO2, $\Delta^{17}O(NO_3^-)$ 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 $\Delta^{17}O(NO_3^-)$ could reach values greater than its primary snow nitrate source (i.e., $\Delta^{17}O(NO_2) > \Delta^{17}O(NO_3^-)_{snow} = 30–35%$ in summer at Dome C; Erbl and et al., 2013; Frey et al., 2009), still leaving the predicted $\Delta^{17}O(NO_3^-)$ underestimated with respect to atmospheric observations.

4.2 Alternative oxidation pathways of NO2

Considering R5 as the main source of HNO3, an alternative approach is to consider that OH bears a higher $\Delta^{17}O$ than the estimate calculated previously. Assuming a $\beta$ of 1, which seems again unrealistic, will increase $\Delta^{17}O(NO_3^-)$ by 1% at most (Table 2), still insufficient to explained atmospheric observations as NO + HO2 remain a major source of OH, independent of the assumed $\beta$.

Alternatively, if measured HONO concentrations are considered instead of those assumed to constrain by the NOx budget (i.e., 4 times lower than measured), average $\Delta^{17}O(NO_3^-)$ 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 $\Delta^{17}O(NO_3^-)$ 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. (2013, 2015) during two summer seasons at Dome C, clearly our current understanding of the NOx 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 NOx cycling through the R7 pathway, an increasing body of evidence points towards reactive halogen chemistry as a major NOx 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):
A critical analysis of the CHABLIS data led Bauguitte et al. (2012) to conclude that R8–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 XNO$_3$ uptake may also represent a significant source of nitrate at Dome C should halogen oxide radicals (XO) 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 XO combines with the N atom of NO$_2$ to form nitrate, thus transferring the isotopic signature of both XO and NO$_2$. The specific Δ$^{17}$O value induced by XNO$_3$ hydrolysis can thus be expressed as follows (Morin et al., 2007):

$$\Delta^{17}O(\text{NO}_3)_{R6} = \frac{2}{3} \Delta^{17}O(\text{NO}_2) + \frac{1}{3} \Delta^{17}O(O_3)_{\text{term}},$$

(7)

efficiently bypassing the OH $^{17}$O-excess budget. Through consideration of the increased Δ$^{17}$O transfer associated with R8, the observations of Δ$^{17}$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 XNO$_3$ hydrolysis. However, no sufficient halogen concentration has been observed on the Antarctic Plateau to sustain such a chemical pathway, but we note that chloride 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 Δ$^{17}$O(NO$_3^-$) values. This mechanism would represent a source of nitrate with a Δ$^{17}$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 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, it would act to increase the Δ$^{17}$O value of nitrate in the boundary layer relative to the local Δ$^{17}$O(NO$_3^-$)$_{R5}$ 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 Δ$^{17}$O(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).
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 $\delta^{15}$N and $\Delta^{17}$O values of atmospheric nitrate (see Sect. 3.1) provides at least one direct line of evidence that the high $\Delta^{17}$O(NO$_3^{-}$) values observed during spring and early summer could be associated with snowpack emissions of NO$_3^{-}$. 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 $\delta^{15}$N and $\Delta^{17}$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 NO$_3^{-}$ emissions arising from a winter-nitrified snowpack, possessed consistently higher $\Delta^{17}$O values than the nitrate sampled directly after this period. Conversely, in summer, atmospheric nitrate possesses a lower $\Delta^{17}$O and is $^{15}$N enriched with respect to early spring values as it is formed from a snowpack that has suffered several stages of denitrification, leading to $^{15}$N enrichment of the snowpack and the emitted NO$_3^{-}$. This finding suggests that the mechanism producing enhanced $\Delta^{17}$O(NO$_3^{-}$) values observed during early spring is tightly coupled in time and space with the intensity of NO$_3^{-}$ emissions from the snowpack, an observation very similar to that of Morin et al. (2012), who detected a similar relationship between $\delta^{15}$N and $\Delta^{17}$O for atmospheric nitrate in the springtime boundary layer over Barrow, Alaska ($71^\circ$N). The authors of that study attributed the observed correlation to the coupling of snowpack NO$_3^{-}$ 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 $\delta^{15}$N and $\Delta^{17}$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 during the period of polar sunrise. Alternatively, a correlation could result from an increased contribution to total OH production from the photolysis of HONO, which is co-emitted with NO$_3^{-}$ via nitrate photochemistry (Grannas et al., 2007) and may induce a larger $^{17}$O excess in OH as compared to the conventional O($^{17}$D) + H$_2$O pathway. Furthermore, the hydrolysis of NO$_3$ in snow, should it contribute significantly to nitrate production at Dome C, is likely amplified during periods when concentrations NO$_3$ 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 $\Delta^{17}$O transfer to nitrate. Our understanding of NO$_3^{-}$ chemistry above the snow surface at Dome C is therefore incomplete.

5 Conclusions

Constraining the propagation of ozone’s $^{17}$O-excess signature within the NO$_3$ cycle is critical in polar areas where the opportunity is offered to extend atmospheric investigations based on $\Delta^{17}$O measurements to the glacial–interglacial timescale 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$_3$ 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., NO$_2$ + OH) that contributes significantly to the atmospheric nitrate budget over Dome C. The strong negative correlation observed between the $\delta^{15}$N and $\Delta^{17}$O values of nitrate between October and December suggests that this unknown process scales with the intensity of the snowpack photochemistry. Potential explanations for this observation include (i) an increased $\Delta^{17}$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 $\Delta^{17}$O from ozone to nitrate. Systematic measurement error and/or false assumptions regarding $\Delta^{17}$O isotopic transfer functions cannot be completely excluded as potential causes for the observed discrepancy between the observed and modeled data. We encourage additional laboratory experiments to further reduce these uncertainties. However, given the other
lines of evidence presented here, we hypothesize that this discrepancy is due to an unknown or misunderstood component of the NO$_3$ photochemical cycle over the Antarctic Plateau. 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$_2$NO$_2$, isotope mass balance) observed during the OPALE experiments.

The Supplement related to this article is available online at doi:10.5194/acp-16-2659-2016-supplement.

Acknowledgements. The research leading to these results received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under the grant agreement number 237890. We would like to thank INSU for its financial support for lab experiments through its LEFE program. The Agence nationale de la recherche (ANR) is gratefully acknowledged for its financial support through the OPALE project (contract NT09-451281). The Institute Polaire Paul-Emile Victor (IPEV) supported the research and polar logistics through the program SUNITEDC No. 1011. This work has been partially supported by a grant from Labex OSUG@2020 (Investissements d’avenir – ANR10 LABX56). We would also like to thank all the field team members present during the OPALE campaign. Meteorological data were obtained from “IPEV/PNRA: Routine Meteorological Observation at Station Concordia”. B. Alexander and the anonymous reviewer are acknowledged for their critical comments and suggestions, which helped in improving the manuscript. Data are available in the Supplement.

Edited by: T. Röckmann

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