

Dear Editor,

Please find below:

- our point-by-point response to the review of Eric Wolff (Reviewer 1 had no comments)
- a marked-up manuscript version.

## Reply to the review of Eric Wolff

Once again, Prof. Eric Wolff is deeply thanked for his appreciation of this work as well as for his meticulous reading which helped us to improve this paper.

Replies to Prof. Wolff's remarks and suggestions are given below. For clarity, we keep the reviewer's comments in blue and italic while our response is in black font.

*The authors have really done a lot of work to the paper since the previous version, both as a result of the reviews and as a result of new ideas they have had themselves. This is good in the sense that they have very seriously addressed the comments of the reviewers, but of course hard for the reviewer because it is like reading a new paper. For this reason, there are still several comments on this version even though it is now good. In any case, the paper is now more logically organized; I am happy (with a small comment) with the way the number of recyclings is treated; and the discussion of how ice core data may be used is much more precise than I remember in the previous version. The paper is still a very difficult read in places but I don't think anything is incorrect, so readers can dip into the parts they need. It certainly provides a very nice basis for assessing and understanding the mass and isotopic measurements of nitrate in snow, and it should be published after minor corrections listed here.*

*Page 3, line 13. I think this is the first use of the abbreviation DC. If so, please give the definition first.*

The text has been updated accordingly.

*Page 7, line 9. I am not sure your description that your box has a large surface area "to neglect local lateral air movement" is really right, or perhaps not well expressed. You really do need lateral air movement because that is what takes FE out of the system. Wouldn't it be better to say that the box has an arbitrary surface area and shape such that conceptually there is a net lateral export (e.g. the box covers a part of the plateau with air being exported away from the plateau, not merely exchanged with similar neighboring boxes)? Perhaps I have this wrong but I don't see what you have in mind with the way you express it.*

It is indeed not clearly expressed how and why the size and shape of the modeled column are chosen. Following Pr. Wolff's suggestion, the text has been changed as follows: "with an arbitrary surface area and shape such that, conceptually, there is a net lateral export (e.g. the column covers a part of the East Antarctic plateau)".

*Page 8, line 15 "equations are written:"*

The text has been edited.

*Page 9, line 21. It's kind of odd to reference one of the authors in this way. It could be written "and unpublished data from the same experiments show that this observation can be extended..."*

The text has been updated accordingly.

*Page 9, line 29 "independent of"*

The text has been updated accordingly.

*Page 11, line 13. Surely you don't mean that HONO production has nil impact. Rather because the product contributes to the NO/NO<sub>2</sub> cycle just as NO<sub>2</sub> production does, it has the same impact and is folded into the photolysis described here as NO<sub>2</sub> production.*

We agree with Prof. Wolff. The end of the sentence has been changed as follows: "which would contribute to the NO/NO<sub>2</sub> cycle, similarly to the NO<sub>2</sub> production".

*Page 12, line 28 "translates into the following"*

The text has been updated accordingly.

*Page 15, line 20. I am confused here. I thought in these 45 snow pits you have only mass fraction, so I don't see how you calculate  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ?*

We agree that this sentence is confusing. It was written as follows: "From the fifty-one 50-cm snow pits [...], we also calculate  $m_{50\text{cm}}(\text{NO}_3^-)$  as well as  $\delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$  for the snow pits where  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  data are available."

*Page 17 line 18, should be  $1.0 \times 10^{-11}$  (the multiply sign is missing)*

The text has been updated accordingly.

*Page 20, line 23. I think the reader will think it quite strange that you don't even mention here what looks like a huge discrepancy between modelled and measured nitrate in 4g. I know you do discuss it later (page 29), so maybe at least refer to that here.*

In the "results" section (section 3.2), we only provide information about the simulated data (which are the new data brought by this study). The comparison of the observed and simulated data is only given in section 3.3. To recall this, we have added the following text: "We recall that only the simulated results are described in section 3.2. The reader may refer

to section 3.3 for a comparison of the simulated and observed data, in particular the discrepancy between simulated and observed nitrate mass fraction in the skin layer (Fig. 4g)".

*Page 24, line 10: "similar to"*

The text has been updated accordingly.

*Page 25, 3.3.2. I think I commented on this before and perhaps you answered somewhere (sorry if so). But to me it is not obvious at all in 6c that the data fit better if the cage effect is non-zero. The absolute values are better if it is zero. You suggest that the one with cage effect is better because the data show a similar decreasing trend, which may be true but is quite subtle. I think you may need to be clearer here.*

Thank you for pointing about that section 3.3.2 needs to be reformulated. We have rewritten it to clarify our points:

1. The way the cage effect is modeled allows to reproduce the observed positive  $^{17}E_{\text{app}}$  values
2. A non-zero  $f_{\text{cage}}$  value (cage effect is on) allows a qualitative reproduction of the  $\Delta^{17}\text{O}$  profiles in snow (decreasing trend and, thus, positive  $^{17}E_{\text{app}}$  values) but this choice is detrimental to the quantitative reproduction of the  $\Delta^{17}\text{O}$  values in snow.
3. Section 3.3.2 now ends with the following sentence: "We refer the reader to section 3.3.8 where the ability of the model to quantitatively reproduce the observed  $\Delta^{17}\text{O}$  values is discussed."

*Page 26, para 2. Do you mean that the flux measurements would not have registered NOx that was emitted from one layer but redeposited before it reached the lowest height of the measurements (I guess at 0.2 m or similar)?*

Yes, this is what we mean. However, the lowest height of the measurements is 0.01 m (Frey et al., 2013, 2015). We have added the following words to the text: "i.e. an upper limit when comparing to the observed NO<sub>2</sub> flux measured between 0.01 m and 1 m above the snowpack, Frey et al., 2013, 2015".

*Page 27, line 6: "net" not "next"*

The text has been updated accordingly.

*Page 28, this is fine but I think the use of the word "Yearly" in YANR is a bit confusing. You mean (I think) that you averaged the number of recyclings over each layer archived in a year. But you would have got the same result if you had averaged over 2 years or 10 years, so there is nothing special about the year. In my mind YANR sounds as if it is the number of*

*recyclings that occur in a year, which is not what you mean. It would be clearer to just call it ANR(FA) (average number of recyclings in archived layers), and simply make clear that you have averaged out any seasonal variability (which anyway is negligible by 0.5 m based on the figure you posted in your discussion comment).*

We acknowledge that the word “Yearly” is confusing and we follow Pr Wolff’s advice to change “YANR” into “ANR”. Also, we have added the following words: “ANR(FA) is calculated as [...], in order to average out any seasonal variability”.

*Page 41, section 4.1.6. You mentioned the role of Ca vs H+ for diffusion, but a greater potential issue is that if nitrate fixes to a dust particle that is embedded in a snow crystal (not at the surface) then escape of the products becomes unlikely (I guess that means the cage effect becomes greater). In that case an increase in FA/FPI would occur. I think you are saying that you would be able to assess this from 15N, which I accept may be the case, but I think you may want to spell out the circumstances in which it may occur (I think you have LGM data that address this).*

We have indeed LGM data to address this and we hope to submit them soon. In order to spell out the circumstances where nitrate photolysis could be weakened by enhanced cage recombination effects, we have added the following sentences to the end of the first paragraph of section 4.1.6: “In glacial conditions, nitrate archived in ice cores is mostly associated with calcium ions and it is known that dust inputs to Antarctica were high (Wolff et al., 2010). In such conditions, it is likely that atmospheric nitrate fixed to dust particles which could eventually be embedded in a snow crystal, thus increasing nitrate cage recombination effects and significantly hampering the release of nitrate photo-products to the atmosphere. The ice core interpretation method present here must therefore be followed in the case where elevated  $\delta^{15}\text{N}(\text{FA})$  values are measured, thus providing an evidence for the efficient photolytic nitrate removal from snow.”

*Table 2. In the excluded processes, shouldn’t you include change of actinic flux due to clouds and aerosol?*

We agree and the text “Change of actinic flux due to clouds and aerosol” was added to the excluded process of the atmospheric box.

*Fig 2, better in caption would be “Arrows entering from left and leaving to right represent inputs and outputs for each process” (if this is correct).*

This is correct. The caption has been changed accordingly.

*Fig 11. The orange box with all the 4 capdel170 values in is misleading. Anyone reading this casually would think you could derive these 4 quantities, but of course you can only derive one, making assumptions about the others. You need to redraw this so that it is obvious that*

*you cannot get 4 values from one. Perhaps just write “ $\Delta^{17}\text{O}$  from contributing processes” and let the reader learn in the text what combination is involved.*

We agreed that this orange box is misleading and appreciate Pr Wolff’s careful read of this schematic figure. We follow his advice and write “ $\Delta^{17}\text{O}$  from contributing processes” in the orange box at the bottom.

1 **Air-snow transfer of nitrate on the East Antarctic plateau –**  
2 **Part 2: An isotopic model for the interpretation of deep ice-**  
3 **core records**

4  
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15  
16 **Abstract**

17 Unraveling the modern budget of reactive nitrogen on the Antarctic plateau is critical for the  
18 interpretation of ice core records of nitrate. This requires accounting for nitrate recycling  
19 processes occurring in near surface snow and the overlying atmospheric boundary layer. Not  
20 only concentration measurements, but also isotopic ratios of nitrogen and oxygen in nitrate,  
21 provide constraints on the processes at play. However, due to the large number of intertwined  
22 chemical and physical phenomena involved, numerical modelling is required to test hypotheses  
23 in a quantitative manner. Here we introduce the model “TRansfer of Atmospheric Nitrate Stable  
24 Isotopes To the Snow” (TRANSITS), a novel conceptual, multi-layer and one-dimensional  
25 model representing the impact of processes operating on nitrate at the air-snow interface on the  
26 East Antarctic plateau, in terms of concentrations (mass fraction) and nitrogen ( $\delta^{15}\text{N}$ ) and  
27 oxygen isotopic composition ( $^{17}\text{O}$ -excess,  $\Delta^{17}\text{O}$ ) in nitrate. At the air-snow interface at Dome  
28 C (DC,  $75^{\circ}06'\text{S}$ ,  $123^{\circ}19'\text{E}$ ), the model reproduces well the values of  $\delta^{15}\text{N}$  in atmospheric and

1 surface snow (skin layer) nitrate as well as in the  $\delta^{15}\text{N}$  profile in DC snow including the  
2 observed extraordinary high positive values (around +300 ‰) below 20 cm. The model also  
3 captures the observed variability in nitrate mass fraction in the snow. While oxygen data are  
4 qualitatively reproduced at the air-snow interface at DC and in East Antarctica, the simulated  
5  $\Delta^{17}\text{O}$  values underestimate the observed  $\Delta^{17}\text{O}$  values by several ‰. This is explained by the  
6 simplifications made in the description of the atmospheric cycling and oxidation of  $\text{NO}_2$  as well  
7 as by our lack of understanding of the  $\text{NO}_x$  chemistry at Dome C. The model reproduces well  
8 the sensitivity of  $\delta^{15}\text{N}$ ,  $\Delta^{17}\text{O}$  and the apparent fractionation constants ( $^{15}\epsilon_{\text{app}}$ ,  $^{17}E_{\text{app}}$ ) to the snow  
9 accumulation rate. Building on this development, we propose a framework for the interpretation  
10 of nitrate records measured from ice cores. Measurement of nitrate mass fractions and  $\delta^{15}\text{N}$  in  
11 the nitrate archived in an ice core, may be used to derive information about past variations in  
12 the total ozone column and/or the primary inputs of nitrate above Antarctica as well as in nitrate  
13 trapping efficiency (defined as the ratio between the archived nitrate flux and the primary nitrate  
14 input flux). The  $\Delta^{17}\text{O}$  of nitrate could then be corrected from the impact of cage recombination  
15 effects associated with the photolysis of nitrate in snow. Past changes in the relative  
16 contributions of the  $\Delta^{17}\text{O}$  in the primary inputs of nitrate and the  $\Delta^{17}\text{O}$  in the locally cycled  $\text{NO}_2$   
17 and that inherited from the additional O atom in the oxidation of  $\text{NO}_2$  could then be determined.  
18 Therefore, information about the past variations in the local and long range processes operating  
19 on reactive nitrogen species could be obtained from ice cores collected in low accumulation  
20 regions such as the Antarctic plateau.

21

## 22 **1 Introduction**

23 Ice cores from the East Antarctic plateau provide long-term archives of Earth's climate and  
24 atmospheric composition such as past relative changes in local temperatures and global  
25 atmospheric  $\text{CO}_2$  levels (EPICA community members, 2004, for example). Soluble impurities  
26 have been used in such cores as tracers of biogeochemical processes. As the end product of the  
27 atmospheric oxidation of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), nitrate ( $\text{NO}_3^-$ ) is a major ion found in Antarctic  
28 snow (Wolff, 1995). Its primary origins are a combination of inputs from the stratosphere and  
29 from low latitude sources (Legrand and Delmas, 1986; Legrand and Kirchner, 1990).  
30 Stratospheric inputs of nitrate are believed to be mostly caused by the sedimentation of Polar  
31 Stratospheric Clouds (PSCs) in winter (Seinfeld and Pandis, 1998; Jacob, 1999). The  
32 interpretation of nitrate deep ice-core records remains elusive (e.g. Wolff et al., 2010) mainly



1 because its deposition to the snow is not irreversible (Traversi et al., 2014 and references  
2 therein) at low accumulation sites such as Dome C or Vostok (78°27'S, 106°50'E, elevation  
3 3488 m.a.s.l.).

4 Nitrate loss from snow can occur through the physical release of HNO<sub>3</sub> (via evaporation and/or  
5 desorption, also referred to as simply “evaporation”) or through the UV-photolysis of the NO<sub>3</sub><sup>-</sup>  
6 ion (Röthlisberger et al., 2000). At wavelengths ( $\lambda$ ) below 345 nm, NO<sub>3</sub><sup>-</sup> photolyses to form  
7 NO<sub>2</sub> (Chu and Anastasio, 2003) or NO<sub>2</sub><sup>-</sup> ion (Chu and Anastasio, 2007) which can form HONO  
8 at pH < 7. Nitrate photolysis is quantitatively represented by its rate constant ( $J$ ) expressed as  
9 follows:

$$10 \quad J = \int \Phi(\lambda, T) \sigma(\lambda, T) I(\lambda, \theta, z) d\lambda \quad (1)$$

11 with  $\Phi$  the quantum yield,  $\sigma$  the absorption cross section of NO<sub>3</sub><sup>-</sup>,  $I$  the actinic flux,  $\lambda$  the  
12 wavelength,  $T$  the temperature,  $\theta$  the solar zenith angle and  $z$  the depth. Two recent laboratory  
13 studies have investigated nitrate photolysis in ~~DC~~Dome C (DC, 75°06'S, 123°19'E) snow.  
14 Meusinger et al. (2014) have reported the quantum yields for the photolysis of either photolabile  
15 or buried nitrate. The terms “photolabile” and “buried” were introduced by Meusinger et al.  
16 (2014) as different “domains”, i.e. different physico-chemical properties of the region around  
17 the nitrate chromophore. Berhanu et al. (2014a) have reported the absorption cross-section of  
18 <sup>14</sup>NO<sub>3</sub><sup>-</sup> and <sup>15</sup>NO<sub>3</sub><sup>-</sup> in Antarctic snow at a given temperature, using a new semi-empirical zero  
19 point energy shift ( $\Delta ZPE$ ) model.

20 Nitrate deposition to the snow can occur through various mechanisms including co-  
21 condensation and dry deposition (Röthlisberger et al., 2000; Frey et al., 2009). Within the  
22 snowpack, nitrate can be contained as HNO<sub>3</sub> in the gas phase, adsorbed on the surface or  
23 dissolved in the snow ice matrix. It can be exchanged between these compartments by  
24 adsorption, desorption or diffusion processes (Dominé et al., 2007) which can lead to a  
25 redistribution of nitrate inside the snowpack, a process which tends to smooth the nitrate mass  
26 fraction profiles (Wagenbach et al., 1994). Phase change and recrystallization processes (snow  
27 metamorphism) can further promote the mobility of nitrate thus potentially modifying the  
28 location of nitrate (Dominé and Shepson, 2002; Kaempfer and Plapp, 2009), with implications  
29 for its availability for photolysis and desorption processes (Dominé and Shepson, 2002). For  
30 instance, it is more available for photolysis when adsorbed on the snow ice matrix surface where  
31 cage recombination effects are less likely to occur (Chu and Anastasio, 2003; Meusinger et al.,  
32 2014 and references therein).

1 The photolysis of nitrate has been identified to be an important mechanism for nitrate mass loss  
2 in the snow on the Antarctic plateau (Frey et al., 2009; France et al., 2011). One consequence  
3 of the release of nitrogen oxides through this process is the complex recycling of nitrate at the  
4 air-snow interface (Davis et al., 2008). Here we refer to “nitrate recycling” as the combination  
5 of NO<sub>x</sub> production from nitrate photolysis in snow, the subsequent atmospheric processing and  
6 oxidation of NO<sub>x</sub> to form atmospheric nitrate, the deposition (dry and/or wet) of a fraction of  
7 the product and the export of another fraction. Davis et al. (2008) and Frey et al. (2009)  
8 suggested the following conceptual model for nitrate recycling in the atmosphere-snow system  
9 for the Antarctic plateau where annual snow accumulation rates are low. The stratospheric  
10 component of nitrate is deposited to the surface in late winter, in a shallow surface snow layer  
11 of approximately uniform concentration (Savarino et al., 2007). The increase in surface UV  
12 radiation in spring initiates a photolysis-driven redistribution process of NO<sub>3</sub><sup>-</sup>, which continues  
13 throughout the sunlit season resulting in the almost complete depletion of the bulk snow nitrate  
14 reservoir. In summer, this results in a strongly asymmetric distribution of total NO<sub>3</sub><sup>-</sup> within the  
15 atmosphere-snow column as previously noted by Wolff et al. (2002), with the majority of the  
16 mass of nitrate residing in a “skin layer” (the top mm of snow, often under form of surface hoar)  
17 and only a small fraction in the atmospheric column above it or in the snow below.

18 The post-depositional processes as described above thus strongly imprint the stable isotopic  
19 composition of nitrate in snow at low accumulation sites (Blunier et al., 2005, Frey et al., 2009,  
20 Erbland et al., 2013). Nitrate is composed of N and O atoms and has the following stable isotope  
21 ratios: <sup>15</sup>N/<sup>14</sup>N, <sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O, from which isotopic enrichment values δ<sup>15</sup>N, δ<sup>17</sup>O, δ<sup>18</sup>O  
22 can be computed. The δ scale is defined as  $\delta = R_{\text{sp}}/R_{\text{ref}} - 1$  with  $R$  denoting the isotope ratios,  
23 the references being N<sub>2</sub>-AIR for N and VSMOW for O. The quantification of the integrated  
24 isotopic effects of post-depositional processes is achieved by calculating apparent fractionation  
25 constants (<sup>15</sup>ε<sub>app</sub>, <sup>17</sup>ε<sub>app</sub> and <sup>18</sup>ε<sub>app</sub>) from isotopic and mass fraction profiles of nitrate in the top  
26 decimeters of snow (Blunier et al., 2005, Frey et al., 2009, Erbland et al., 2013). For instance,  
27 <sup>15</sup>ε<sub>app</sub> is calculated from the following equation, which represents a Rayleigh model and assumes  
28 a single loss process and the immediate and definitive removal of the lost nitrate fraction:

$$29 \ln(\delta^{15}\text{N}_f + 1) = {}^{15}\epsilon_{\text{app}} \cdot \ln f + \ln(\delta^{15}\text{N}_0 + 1) \quad (2)$$

30 with δ<sup>15</sup>N<sub>f</sub> and δ<sup>15</sup>N<sub>0</sub> the δ-value in the remaining and initial snow nitrate,  $f$  is the remaining  
31 mass fraction. Comparing apparent fractionation constants obtained in the field to the  
32 fractionation constants associated with the physical and photochemical nitrate loss processes

1 has demonstrated that the UV-photolysis of nitrate is the dominant mass loss process on the  
 2 Antarctic plateau (Erbland et al., 2013). As a consequence,  $\delta^{15}\text{N}$  in nitrate archived beyond the  
 3 snow photic zone (the zone of active photochemistry) on plateau sites depends on  $^{15}\epsilon_{\text{pho}}$ , the  
 4  $^{15}\text{N}/^{14}\text{N}$  fractionation constant associated with nitrate photolysis (Frey et al., 2009; Erbland et  
 5 al., 2013) and the magnitude of the loss (1- $f$ ) (Eq. (2)). Because of its link with the residence  
 6 time of nitrate in the photic zone, a strong relationship has been found between the snow  
 7 accumulation rate ( $A$ ) and the degree of isotopic fractionation  $\delta^{15}\text{N}$  in the archived (asymptotic,  
 8 “as.”) nitrate (Freyer et al., 1996, Erbland et al., 2013). At a given actinic flux  $I$ , the  $^{15}\text{N}/^{14}\text{N}$   
 9 fractionation constant induced by nitrate photolysis is calculated as the ratio of the photolysis  
 10 rate constants:

$$11 \quad ^{15}\epsilon_{\text{pho}} = \frac{J'}{J} - 1 \quad (3)$$

12 with  $J$  and  $J'$  the photolytic rate constants of  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  respectively. The Rayleigh  
 13 distillation model applied to a single process in an open system gives the  $\delta^{15}\text{N}$  values in the  
 14 remaining fraction by applying Eq. (2) using  $^{15}\epsilon_{\text{pho}}$ .

15 The three stable isotopes of oxygen allow to define a unique tracer,  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$   
 16 which is referred to as “oxygen isotope anomaly” or also “ $^{17}\text{O}$ -excess”. An apparent  
 17 fractionation constant ( $^{17}E_{\text{app}}$ ) can be computed for  $\Delta^{17}\text{O}$  using Eq. (2), similarly to what can be  
 18 done for isotopic enrichment values ( $\delta$ ). Most oxygen-bearing species feature  $\Delta^{17}\text{O} = 0$  ‰ but  
 19 some species such as atmospheric nitrate can partially inherit the large positive oxygen isotope  
 20 anomaly transferred from ozone thus reflecting the relative contribution of various oxidants  
 21 involved in its formation (Michalski et al., 2003, Morin et al., 2007, 2008, 2009, 2011, Kunasek  
 22 et al., 2008, Alexander et al., 2009).

23 Erbland et al. (2013) documented year-round measurements of  $\Delta^{17}\text{O}$  in atmospheric and skin  
 24 layer nitrate at Dome C and on the Antarctic plateau, which revealed a photolytically driven  
 25 isotopic equilibrium between the two compartments, i.e. the  $\Delta^{17}\text{O}$  atmospheric signal is mostly  
 26 conserved in the skin layer. In contrast to  $\delta^{15}\text{N}$ , post-depositional processes have a small impact  
 27 on  $\Delta^{17}\text{O}$  in nitrate snow profiles (Frey et al., 2009) so that a large portion of the atmospheric  
 28 signature is transferred in snow nitrate at depth despite a small dampening effect (Erbland et  
 29 al., 2013). Indeed, laboratory studies have shown that although nitrate photolysis in snow has a  
 30 purely mass-dependent isotopic effect (i.e. in theory not impacting the  $\Delta^{17}\text{O}$ ), this process leads  
 31 to a lower  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in the remaining phase because of the cage recombination (hereafter

1 termed “cage effects”) of the primary photo-fragment of  $\text{NO}_3^-$  (McCabe et al., 2005).  
2 Immediately following nitrate photolysis, a fraction of the photo-fragment  $\text{NO}_2$  reacts back with  
3 OH radicals to form  $\text{HNO}_3$  but some of the OH radicals exchange O atoms with water molecules  
4 in the ice lattice, so that the recombined  $\text{HNO}_3$  contains an oxygen atom replaced by one  
5 originating from  $\text{H}_2\text{O}$  and featuring  $\Delta^{17}\text{O}(\text{H}_2\text{O}) = 0 \text{ ‰}$ .

6 This article is a companion paper of “Air-snow transfer of nitrate on the East Antarctic Plateau  
7 – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium in summer”,  
8 published in the same journal (Erland, et al., 2013). In this study, we test the nitrate recycling  
9 theory and evaluate it in light of the field isotopic measurements presented in Erland et al.  
10 (2013) and obtained at the air-snow interface at Dome C as well as in several shallow snow pits  
11 collected at this site and on a large portion of the East Antarctic plateau. Testing this theory  
12 requires the building of a numerical model which represents nitrate recycling at the air-snow  
13 interface and describes the evolution of the nitrogen and oxygen stable isotopic composition of  
14 nitrate with various constraints from key environmental variables such as the solar zenith angle  
15 and the available UV radiation. Various models have been developed to investigate the physical  
16 and chemical processes involving nitrate in snow and their impact on the atmospheric chemistry  
17 in Antarctica (Wang et al., 2007; Liao and Tan, 2008; Boxe and Saiz-Lopez, 2008) and in  
18 Greenland (Jarvis et al., 2008; 2009; Kunasek et al., 2008; Thomas et al., 2011; Zatko et al.,  
19 2013). Those models are adapted to short time periods (hours to days, typically) and focus on  
20 processes at play in the atmosphere and in the near-surface snowpack. In this article, we present  
21 a new model called TRANSITS (“TRansfer of Atmospheric Nitrate Stable Isotopes To the  
22 Snow”), which shares some hypotheses with the modeling effort of Wolff et al. (2002) and the  
23 conceptual model of Davis et al. (2008). Together with a more realistic representation of some  
24 processes, the main novelty brought by the TRANSITS model is the incorporation of the  
25 oxygen and nitrogen stable isotopic ratios in nitrate as a diagnostic and evaluation tool in the  
26 ideal case of the East Antarctic plateau where snow accumulation rates are low and where  
27 nitrate mass loss can be mostly attributed to UV-photolysis. The following key questions are  
28 addressed in this work:

- 29 1. Is the theory behind the TRANSITS model compatible with the available field  
30 measurements?
- 31 2. What controls the mass and isotopic composition ( $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ) of the archived  
32 nitrate?

1 The model is first described. Then it is evaluated by comparing its outputs to observations in  
2 the case of simulations at the air-snow interface at Dome C as well as in East Antarctic sites. A  
3 framework for the interpretation of the nitrate isotope record in deep ice cores is then given in  
4 light of sensitivity tests of the model.

5

## 6 **2 Description of the TRANSITS model**

### 7 **2.1 Overview**

8 TRANSITS is a multi-layer, 1-D isotopic model which represents a snow and atmosphere  
9 column with an arbitrary surface area ~~and shape such that, conceptually, there is a net lateral~~  
10 ~~export (e.g. the column covers a part of the taken sufficiently large to neglect local lateral air~~  
11 ~~mass movement (i.e. at the scale of the East Antarctic plateau)).~~ The snowpack is set to a  
12 constant height of one meter and a snow density ( $\rho$ ) is assumed to be constant. The one-meter  
13 snowpack is divided into 1000 layers of a 1-mm thickness, which means that the snow mass is  
14 the same in each layer. The atmospheric boundary layer (ABL) is represented by a single box  
15 of a constant height.

16 The aim of the model is to conceptually represent nitrate recycling at the air-snow interface  
17 (UV-photolysis of  $\text{NO}_3^-$ , emission of  $\text{NO}_x$ , local oxidation, deposition of  $\text{HNO}_3$ ) and to model  
18 the impact on nitrogen and oxygen stable isotopic ratios in nitrate in both reservoirs. For the  
19 sake of simplicity, we will focus on  $\delta^{17}\text{O}$  and  $\delta^{15}\text{N}$ ;  $\delta^{18}\text{O}$  is not included in the TRANSITS  
20 model. The TRANSITS model is neither a snowpack nor a gas-phase chemistry model and it  
21 does not aim at representing all the mechanisms responsible for nitrate mobility neither at the  
22 snowpack scale nor at the snow microstructure scale.

23 Figure1 provides an overview of the TRANSITS model. The loss of nitrate from snow is  
24 assumed to only occur through UV-photolysis, because the physical release of  $\text{HNO}_3$  is  
25 negligible (Erbland et al., 2013). TRANSITS does not treat different nitrate domains in snow  
26 and it is hypothesized that its photolysis only produces  $\text{NO}_2$ .  $\text{NO}_2$  undergoes local cycling with  
27  $\text{NO}$ , which modifies its oxygen isotope composition while the N atom is preserved. One  
28 computed year is divided into 52 time steps of approximately one week ( $\Delta t = 606\,877$  s), a time  
29 step sufficiently long to assume quantitative oxidation of  $\text{NO}_2$  into  $\text{HNO}_3$ . The chosen time step  
30 also allows to operate at the annual timescale, which is best suited to long simulation durations.  
31 For simplicity, we assume that  $\text{NO}_2$  oxidation occurs through reaction with OH radicals. The

1 deposition of atmospheric  $\text{HNO}_3$  is assumed to occur by the uptake at the surface of the  
 2 snowpack. Nitrate diffusion is assumed to occur in the snowpack at the macroscopic scale and  
 3 is solved at a time resolution 50 times shorter than the model main time resolution (i.e. approx.  
 4 3.4 hours).

5 The lower limit of the modeled snowpack is set at one meter depth, a depth below which the  
 6 actinic flux is always negligible. Below this depth, nitrate is considered to be archived. At every  
 7 time step, the new snow layer accumulated at the top pushes a layer of snow below one meter  
 8 depth. This snow layer is archived and its nitrate mass fraction is frozen (and denoted  $\omega(FA)$ ),  
 9 thus allowing the calculation of the archived nitrate mass flux ( $FA$ , the product of  $\omega(FA)$  and  
 10 the archived snow mass during one time step). Table 1 provides a glossary of the acronyms  
 11 used in this paper, as well as their definition.

## 12 2.2 Mass balance equations

13 In each box, the model solves the general “mass-balance” equation, which describes the  
 14 temporal evolution of the concentration of the species  $X$  (i.e. nitrate or  $\text{NO}_2$ ):

$$15 \frac{d}{dt} [X] = \sum_i P_i - \sum_j L_j \quad (4)$$

16 The isotopic mass-balance equations are written (Morin et al., 2011):

$$17 \frac{d}{dt} ([X] \times \delta^{15}\text{N}) = \sum_i (P_i \times \delta^{15}\text{N}_i(X)) - (\sum_j (L_j \times (\delta^{15}\text{N}(X) - {}^{15}\epsilon_j))) \quad (5)$$

$$18 \frac{d}{dt} ([X] \times \Delta^{17}\text{O}) = \sum_i (P_i \times \Delta^{17}\text{O}_i(X)) - (\sum_j L_j) \times \Delta^{17}\text{O}(X) \quad (6)$$

19 where  $P_i$  and  $L_j$  respectively represent sources and sinks rates and  $\delta^{15}\text{N}_i(X)$  and  $\Delta^{17}\text{O}_i(X)$  the  
 20 isotopic compositions of the  $i$  sources. A  ${}^{15}\text{N}/{}^{14}\text{N}$  fractionation constant ( ${}^{15}\epsilon_j$ ) can be associated  
 21 with loss process  $j$ . Within each box, incoming fluxes are positive and outgoing fluxes are  
 22 negative. The concentration of nitrate in a snow layer is handled as “nitrate mass fraction”  
 23 which is denoted  $\omega(\text{NO}_3^-)$ .

24 For simplicity, fluxes will be hereafter denoted “ $FY$ ”, with “ $Y$ ” a chain of capital letters. The  
 25 primary input of nitrate to the modeled atmosphere is denoted  $FPI$  and is the combination of a  
 26 stratospheric flux ( $FS$ ) and the horizontal long distance transport ( $FT$ ) of nitrate. Therefore,  $FPI$   
 27 =  $FS + FT$ . The two primary origins of nitrate are defined by constant  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  signatures  
 28 denoted  $\Delta^{17}\text{O}(FS)$ ,  $\Delta^{17}\text{O}(FT)$ ,  $\delta^{15}\text{N}(FS)$  and  $\delta^{15}\text{N}(FT)$ . The secondary source of nitrate to the  
 29 atmosphere is the local oxidation of  $\text{NO}_2$  occurring after nitrate photolysis in the snow ( $FP$ ).

1 Nitrate is removed from the atmospheric box via two processes. Large scale horizontal air  
2 masses movement can lead to a loss of nitrate, hereafter named “horizontal export flux” ( $FE$ ).  
3 The export of nitrate is assumed to preserve the  $\Delta^{17}O$  and  $\delta^{15}N$  values. Nitrate can also be lost  
4 via deposition ( $FD$ ) to the snow, which is the sole nitrate source to the snowpack. This flux is  
5 obtained by solving the mass balance in the atmospheric box and is added to the topmost layer  
6 of the snowpack at each model time step.

7 The loss of nitrate from the snowpack is assumed to occur through nitrate UV-photolysis only.  
8 Within the snowpack, nitrate is redistributed by macroscopic diffusion, which is assumed to  
9 preserve  $\Delta^{17}O$  and  $\delta^{15}N$ .

### 10 2.3 Physical properties of the atmosphere and the snowpack

11 The height of the ABL is denoted  $h_{AT}$ . This single atmospheric box is assumed to be well mixed  
12 at all times which is justified at the time resolution of the model (ca. one week). Hereafter we  
13 denote  $\gamma(NO_3^-)$  the nitrate concentration in the atmospheric box. In TRANSITS, the time  
14 evolution of this variable is prescribed by observations.

15 Physical properties of the snowpack influencing radiative transfer in snow are fixed, according  
16 to a typical Dome C snowpack with a constant layering throughout the year as defined in France  
17 et al. (2011): it is made of 11 and 21 cm of soft and hard windpack snow at the top and hoar-  
18 like snow below with their respective snow densities, scattering and absorption coefficients at  
19 350 nm. At Dome C, the e-folding attenuation depths (denoted  $\eta$ ) for the three snow layers are  
20 fairly constant in the range 350–400 nm (France et al., 2011) and unpublished data from the  
21 same experiments show that this observation can be extended to the 320–350 nm ~~range (James~~  
22 ~~France, unpublished)~~. The snow optical properties taken at 350 nm are therefore assumed to be  
23 valid for the whole 280–350 nm range of interest for nitrate photolysis. This hypothesis is  
24 supported twofold. First, e-folding attenuation depths measured at Alert, Nunavut show no  
25 significant sensitivity to wavelengths in the 310–350 nm range (King and Simpson, 2001).  
26 Secondly,  $\eta$  values measured in a recent laboratory study only show a weak (10 %) decrease  
27 from 350 nm to 280 nm (Meusinger et al., 2014). Under Dome C conditions, the absorption of  
28 UV by impurities is small and the depth attenuation of UV light is mostly driven by light  
29 scattering (France et al., 2011). As a consequence,  $\eta$  is assumed to be independent ~~of~~ the  
30 impurities content in the snow, in this case, nitrate itself.

1 While optical calculations are based on a realistic snowpack, nitrate mass and isotopic  
2 computations are performed assuming a constant snow density, which simplifies the  
3 computation. One consequence of this simplification is that our modeled e-folding depths are  
4 independent of snow density, which we acknowledge is not realistic (Chan et al., 2015).

5 Assuming that the snow density is constant means that the snowpack does not undergo  
6 densification. For simplicity, we also hypothesize that no sublimation, wind redistribution, melt  
7 nor flow occur and that the surface of the snowpack is assumed to be flat and insensitive to  
8 erosion.

## 9 **2.4 Parameterization of chemical processes**

10 Figure2 provides an overview of the physical and chemical processes included in TRANSITS  
11 as well as the parameters and input variables of interest for each process. Table 22 lists the  
12 chemical and physical processes included or not in the model. A description of the  
13 parameterization of each process is given below.

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### 14 **2.4.1 Nitrate UV-photolysis**

15 Nitrate photolysis is at the core of the model. At each time step, the photolyzed nitrate mass in  
16 a layer equals  $e^{-J\Delta t} \times m$ , where  $m$  is the initial nitrate mass in the layer and  $J$ , the photolysis  
17 rate constant of  $\text{NO}_3^-$  (Eq. (1)). The UV actinic fluxes ( $I$ ) required for the calculation of  $J$  have  
18 been computed in the 280–350 nm range using offline runs of the TUV-snow radiative-transfer  
19 model (Lee-Taylor and Madronich, 2002). TUV-snow has been run for the DC location and  
20 snowpack for various dates (i.e. solar zenith angle,  $\theta$ ), assuming a clear aerosols-free sky and  
21 using the extraterrestrial irradiance from Chance and Kurucz (2010) and a constant Earth-Sun  
22 distance as that of 27 December 2010. Ozone profiles from 25 to 500 DU with a resolution of  
23 25 DU have been used to run the radiative transfer model. Next, we denote  $k$  the “photic zone  
24 compression factor”, which represents variations of depth of the photic zone under the effect of  
25 changes in physical properties of the snowpack due to snow metamorphism or in chemical  
26 properties. In Eq. (1), the term “ $z$ ” is therefore replaced by “ $z / k$ ”. A typical Dome C snowpack  
27 is represented by  $k$  value of 1. Lower  $k$  values mean that the UV radiation is extinguished more  
28 rapidly with depth. Last, we denote  $q$  the “actinic flux enhancement factor”, which accounts  
29 for variations in the actinic flux received at the snow surface and hence at depth. This parameter  
30 represents changes in the actinic flux emitted from the Sun or changes in the Earth-Sun distance



1 due to variations in the Earth's orbit. In Eq. (1), the term " $I$ " is therefore replaced by " $q \times I$ ". In  
2 the modern DC case,  $q$  is set to 1.

3 Another key control on  $J$  is the quantum yield ( $\Phi$ ), a parameter which is strongly governed by  
4 nitrate location in the snow ice matrix and which corresponds to nitrate availability to  
5 photolysis. Nitrate is assumed to deposit to the snow under the form of  $\text{HNO}_3$  but its adsorption  
6 and/or dissociation to  $\text{NO}_3^- + \text{H}^+$  are not explicitly represented. Indeed, modeling nitrate  
7 location in the snow is well beyond the scope of the present study and a recent molecular  
8 dynamic study demonstrated the fast ionization of  $\text{HNO}_3$  (picosecond time scale) at the ice  
9 interface (Riikonen, Parkkinen, Halonen, & Gerber, 2014). For the sake of simplicity, we  
10 assume that nitrate location in the snow ice matrix is constant. Therefore,  $\Phi$  is set to a constant  
11 value.

12 Nitrate photolysis is assumed to only produce  $\text{NO}_2$ . We acknowledge that other volatile nitrogen  
13 species such as  $\text{NO}$  or  $\text{HONO}$  may be produced. However, the photolysis of  $\text{HONO}$  in the  
14 atmosphere would rapidly produce  $\text{NO}$ , which would contribute to the  $\text{NO}/\text{NO}_2$  cycle, similarly  
15 to the  $\text{NO}_2$  production cycle and hence have a nil impact in terms of N mass balance.

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16 In the model,  $^{15}\epsilon_{\text{pho}}$  is explicitly calculated at each time step and in each snow layer using Eq.  
17 (3). Because the layering of the physical properties of snow is fixed,  $^{15}\epsilon_{\text{pho}}$  is constant with time.  
18 In the UV-spectral range (280-350 nm), we have earlier assumed that e-folding depth is constant  
19 with wavelength; therefore, even though  $\rho$  modulates the e-folding depth,  $^{15}\epsilon_{\text{pho}}$  is independent  
20 of  $\rho$  as well as of depth, in agreement with the laboratory study of Berhanu et al. (2014a) and  
21 the field study of Berhanu et al. (2014b). As a consequence, the modeled  $^{15}\epsilon_{\text{pho}}$  is entirely  
22 determined by the spectral distribution of the UV radiation received at the surface of the  
23 snowpack. The Rayleigh fractionation model applied to nitrate photolysis allows calculating  
24 the  $\delta^{15}\text{N}$  in the photolyzed nitrate applying Eq. (2) with the use of  $^{15}\epsilon_{\text{pho}}$ , and  $\delta^{15}\text{N}$  in the  
25 remaining nitrate by simple mass balance. Nitrate photolysis is assumed to be a mass dependent  
26 process so that the  $\Delta^{17}\text{O}$  in the initial, photolyzed and remaining nitrate is kept the same.

#### 27 **2.4.2 Cage effect**

28 A constant fraction of the photolyzed nitrate (denoted  $f_{\text{cage}}$ ) is assumed to undergo cage  
29 recombination so that the photo-fragment  $\text{NO}_2$  reacts back with  $\text{OH}$  to re-form  $\text{HNO}_3$ . In the  
30 cage effect process,  $\text{OH}$  is assumed to undergo an isotopic exchange with the water molecules

1 of the ice lattice, so that the recombined HNO<sub>3</sub> contains an oxygen atom originating from H<sub>2</sub>O  
2 and featuring  $\Delta^{17}\text{O}(\text{H}_2\text{O}) = 0 \text{ ‰}$  (McCabe et al., 2005).

3

#### 4 **2.4.3 Emission of NO<sub>2</sub> and photochemical steady-state**

5 The total photolytic flux (*FP*) represents the potential emission of NO<sub>2</sub> from the snow to the  
6 atmosphere in accordance with the terminology used in France et al. (2011) and is the sum of  
7 the photolytic fluxes originating from each snow layer. A simple isotopic mass balance is  
8 applied to calculate the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  of the photolytic loss flux *FP*. The extraction of NO<sub>2</sub>  
9 from the snowpack is assumed to preserve its chemical and isotopic integrity, i.e. it does not  
10 undergo any chemical reaction or any isotopic fractionation in the snowpack.

11 Atmospheric chemistry is not explicitly modeled but only conceptually represented.  $\Delta^{17}\text{O}(\text{NO}_2)$   
12 is calculated following the approach of Morin et al. (2011), i.e. assuming Photochemical  
13 Steady-State (PSS) of NO<sub>x</sub> (when the photolytic lifetime of NO<sub>x</sub> is shorter than 10 minutes), an  
14 assumption which is valid for most of the sunlit season ( $\tau(\text{NO}_2) < 10$  minutes from September  
15 27 to March 7, Frey et al. (2013, [2014](#)[2015](#))). We therefore denote  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ , the  $\Delta^{17}\text{O}$   
16 value harbored by NO<sub>2</sub> after its local cycling, which is represented by (Morin et al., 2008, 2011):

$$17 \Delta^{17}\text{O}(\text{NO}_2, \text{PSS}) = \alpha \times \Delta^{17}\text{O}_{\text{O}_3+\text{NO}}(\text{NO}_2) \quad (7)$$

18 with  $\alpha$ , a variable which accounts for the perturbation of the Leighton cycle by various radicals  
19 such as peroxy radicals (RO<sub>2</sub>) and halogen oxides. For simplicity, we only consider BrO, HO<sub>2</sub>  
20 and CH<sub>3</sub>O<sub>2</sub> as the species perturbing the Leighton cycle. The  $\alpha$  variable is calculated at each  
21 time step as in Eq. (8) assuming  $\Delta^{17}\text{O}(\text{HO}_2) = \Delta^{17}\text{O}(\text{CH}_3\text{O}_2) = 0 \text{ ‰}$  (Morin et al., 2011). Recent  
22 observations at DC seem to support the assumption  $\Delta^{17}\text{O}(\text{CH}_3\text{O}_2) = 0 \text{ ‰}$  because CH<sub>3</sub>O<sub>2</sub> may  
23 entirely originate from the reaction R + O<sub>2</sub> or photolysis of species (CH<sub>3</sub>CHO) featuring  $\Delta^{17}\text{O}$   
24 = 0 ‰ (Kukui et al., 2014). The assumption  $\Delta^{17}\text{O}(\text{HO}_2) = 0 \text{ ‰}$  is also supported by the same  
25 observations although 5 % of HO<sub>2</sub> originate from the reaction O<sub>3</sub> + OH which leads to  
26  $\Delta^{17}\text{O}(\text{HO}_2) > 0 \text{ ‰}$ . For simplicity, we stick to the assumption  $\Delta^{17}\text{O}(\text{HO}_2) = 0 \text{ ‰}$ .

$$27 \alpha = \frac{k_{\text{O}_3+\text{NO}}[\text{O}_3] + k_{\text{BrO}+\text{NO}}[\text{BrO}]}{k_{\text{O}_3+\text{NO}}[\text{O}_3] + k_{\text{HO}_2+\text{NO}}[\text{HO}_2] + k_{\text{CH}_3\text{O}_2+\text{NO}}[\text{CH}_3\text{O}_2] + k_{\text{BrO}+\text{NO}}[\text{BrO}]} \quad (8)$$

28 with temperature- and pressure-dependent kinetic rate constants from Atkinson et al. (2004,  
29 2006, 2007) and the mixing ratios of O<sub>3</sub>, BrO, HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> at the surface. Savarino et al.

1 (2008) have measured that O<sub>3</sub> preferentially transfers one of its terminal O atom when oxidizing  
2 NO with a probability of 92 % which translates into the following equation:

$$3 \Delta^{17}\text{O}_{\text{O}_3+\text{NO}}(\text{NO}_2) \times 10^3 = 1.18 \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} \times 10^3 + 6.6 \quad (9)$$

4 with  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ , the isotopic anomaly of local bulk ozone. The O atom in BrO originates from  
5 the terminal oxygen atom of ozone through its reaction with bromine (Morin et al., 2007 and  
6 references therein). For simplicity, we assume that the O atom transferred during the NO  
7 oxidation by O<sub>3</sub> and BrO is identical.

8

#### 9 **2.4.4 Local oxidation of NO<sub>2</sub>**

10 NO<sub>2</sub> is directly converted to HNO<sub>3</sub> with the preservation of the N atom. However, a local  
11 additional oxygen atom is incorporated. This is a reasonable assumption given the short  
12 chemical lifetime of NO<sub>x</sub> with respect to NO<sub>2</sub> + OH (in the order of hours) in comparison with  
13 the approximately one-week time step used in the model. The  $\Delta^{17}\text{O}$  of HNO<sub>3</sub> is given by Eq.  
14 (10).

$$15 \Delta^{17}\text{O}(\text{HNO}_3) = \frac{2}{3}\Delta^{17}\text{O}(\text{NO}_2) + \frac{1}{3}\Delta^{17}\text{O}(\text{add O}) \quad (10)$$

16 Similarly to the local cycling of NO<sub>2</sub>, the local oxidation of this species is only conceptually  
17 represented. For simplicity, we assume that the formation of HNO<sub>3</sub> only occurs through the  
18 pure daytime channel, i.e. the reaction of NO<sub>2</sub> and OH:  $\Delta^{17}\text{O}(\text{add. O}) = \Delta^{17}\text{O}(\text{OH})$ .

19 In the framework of the OPAL campaign,  $\Delta^{17}\text{O}(\text{OH})$  has been discussed in a submitted paper  
20 (Savarino et al., submitted). The results of this study show that  $\Delta^{17}\text{O}(\text{OH})$  varies in a narrow  
21 range, between 1 and 3 ‰, around summer solstice 2011-2012. As a result, we set  $\Delta^{17}\text{O}(\text{OH}) =$   
22 3‰ throughout the entire sunlit season.

## 23 **2.5 Parameterization of physical processes**

### 24 **2.5.1 Snow accumulation**

25 The snow accumulation thickness depends on the snow accumulation rate ( $A$ ) as well as on  
26 snow density ( $\rho$ ). Older layers are buried, preserving their nitrate mass and isotopic  
27 composition. Immediately after snow accumulation, the modeled snowpack is resampled at a  
28 1-mm resolution ( $\Delta z = 1$  mm).

1

## 2 2.5.2 Nitrate horizontal export

3 The export flux ( $FE$ ) is modeled as a constant fraction of all incoming nitrate fluxes to the  
4 atmosphere  $FE = f_{\text{exp}} \times (FP + FS + FT)$ , assuming that  $\text{NO}_x$  conversion to  $\text{HNO}_3$  is instantaneous  
5 and that nitrate is homogeneous in the atmospheric box, at the chosen time step.

## 6 2.5.3 Nitrate deposition to the snow

7 The deposited flux ( $FD$ ) and its isotopic composition ( $\Delta^{17}\text{O}(FD)$  and  $\delta^{15}\text{N}(FD)$ ) are obtained  
8 by solving Eqs. (4) to (6) (Fig.2). For the sake of simplicity, the downward deposition flux is  
9 modeled assuming a pure physical deposition of  $\text{HNO}_3$  on the top layer of the snowpack. The  
10 deposition process is assumed to preserve  $\Delta^{17}\text{O}$ . This process is associated with a  $^{15}\text{N}/^{14}\text{N}$   
11 fractionation constant ( $^{15}\epsilon_{\text{dep}}$ ).

## 12 2.5.4 Nitrate diffusion in the snowpack

13 Nitrate diffusion in the snowpack leads to changes in nitrate mass fraction and isotope profiles  
14 in the snowpack, and it is represented by the use of a diffusivity coefficient denoted  $D$  and by  
15 a zero-flux boundary condition at the top and at the bottom of the snowpack ( $z = 1 \text{ m}$ ) :

$$16 \begin{cases} \frac{\partial \omega(z,t)}{\partial t} = D \frac{\partial^2 \omega(z,t)}{\partial z^2} \\ \frac{\partial \omega(\text{top},t)}{\partial z} = 0 \\ \frac{\partial \omega(\text{bot},t)}{\partial z} = 0 \end{cases} \quad (11)$$

17 with  $\omega(z, t)$ , the nitrate mass fraction in each layer and  $z$  and  $t$  the space and time, respectively.  
18 Given the assumption of a constant snow density and a uniform mesh grid, Eq. (11) also applies  
19 to the snow mass in the layer ( $m$ ). Equation (11) is solved at a time step of 3.4 hours (i.e. 50  
20 times shorter than the main time step of the model), which must respect the following:  $\frac{(\Delta z)^2}{3.4 \text{ h}} \ll$   
21  $D$ . Space and time derivatives are approximated by the finite difference method.

22

## 1 3 Model evaluation

### 2 3.1 Method: observational constraints, model setup and runs

3 To evaluate the model, we study its ability to reproduce the present-day observations at Dome  
4 C and across East Antarctica. To this end, a realistic simulation of TRANSITS is compared to  
5 the data observed at the air-snow interface at Dome C and in the top 50 cm of snow in East  
6 Antarctica.

#### 7 3.1.1 Observational constraints

8 Most of the observed data originate from Erbland et al. (2013). Atmospheric nitrate  
9 concentration and isotopic measurements were measured 2-m above ground at Dome C during  
10 the years 2007-2008 (Frey et al., 2009) and 2009-2010 (Erbland et al., 2013). In this second  
11 study, nitrate mass fraction and isotopic composition have also been measured in the skin layer  
12 (the  $(4 \pm 2)$  mm of top snow) and for the 2009-2010 period. Nitrate mass fractions and isotopic  
13 profiles are available from three 50-cm snow pits sampled at Dome C during the austral  
14 summers 2007-2008 and 2009-2010 (Frey et al., 2009, Erbland et al., 2013). From these snow  
15 pits data and from the DC mean snow density profile given by Libois et al. (2014), we calculate  
16  $m_{50\text{cm}}(\text{NO}_3^-)$ ,  $\delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$ , the integrated nitrate mass and isotopic  
17 composition per unit horizontal surface area in the top 50 cm of the snowpack.  $\text{NO}_x$  emission  
18 fluxes were measured at Dome C from 22 December 2009 to 28 January 2010 (Frey et al.,  
19 2013).

20 Forty-five 50-cm deep snow profiles were collected at DC from February 2010 to February  
21 2014 and nitrate mass fractions were measured as in Erbland et al. (2013). These previously  
22 unpublished profiles have been collected approximately every month by the DC overwintering  
23 team. From the fifty-one 50-cm snow pits collected at DC (45 unpublished and 6 published in  
24 Röthlisberger et al., 2000, Frey et al., 2009, France et al., 2011 and Erbland et al., 2013), we  
25 also calculate  $m_{50\text{cm}}(\text{NO}_3^-)$  as well as  $\delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$  for the snow pits  
26 where  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  data are available.

27 In East Antarctica, nitrate isotopic and mass fraction measurements are available from twenty-  
28 one 50-cm depth snow pits including the 3 DC snow pits presented above (Erbland et al., 2013).  
29 They were sampled along two transects which link D10 (a location in the immediate vicinity of  
30 the French Dumont d'Urville station) to DC and DC to Vostok. The samples collection and

1 analysis as well as the data reduction are described in Erbland et al. (2013). Reduced data  
2 include the asymptotic mass fraction ( $\omega(\text{as.})$ ) and isotopic composition ( $\delta^{15}\text{N}(\text{as.})$  and  
3  $\Delta^{17}\text{O}(\text{as.})$ ) which represent nitrate below the zone of active nitrate mass loss in the top  
4 decimeters of snow, and  $^{15}\epsilon_{\text{app}}$  and  $^{17}E_{\text{app}}$  apparent fractionation constants.

### 5 **3.1.2 TRANSITS simulations**

#### 6 **Simulation at the air-snow interface at Dome C**

7 Table 3 gives a summary of the parameters and variables used for the TRANSITS DC realistic  
8 simulation. Below, we discuss their choice. Note that the adjustment parameters ( $\Phi$ ,  $f_{\text{exp}}$ ,  $f_{\text{cage}}$ ,  
9  $D$  and  $^{15}\epsilon_{\text{dep}}$ ) were adjusted manually and not set by an error minimizing procedure.

10 The thickness of the atmospheric boundary layer is set to a constant value of 50 meters, a value  
11 which sits between the median wintertime value (ca. 30 m) simulated by Swain and Gallée  
12 (2006) and the mean value simulated around 27 December 2012 (Gallée et al., 2014). The time  
13 series of the nitrate concentration in the atmospheric box was obtained by smoothing the  
14 atmospheric measurements performed at Dome C in 2009-2010 (Erbland et al., 2013).

15 Stratospheric denitrification is responsible for the input of an estimated nitrogen mass of  $(6.3 \pm$   
16  $2.6) \times 10^7$  kgN per year (Muscari and de Zafra, 2003), a value three times higher than the  
17 estimate of Wolff et al. (2008). Taking into account the area inside the Antarctic vortex where  
18 intense denitrification occurs ( $(15.4 \pm 3.0) \times 10^6$  km<sup>2</sup>, Muscari and de Zafra, 2003), this gives  
19 a flux of  $FS = (4.1 \pm 2.5) \times 10^{-6}$  kgN m<sup>-2</sup> a<sup>-1</sup>. The modeled stratospheric flux is set to occur  
20 constantly for a duration of 12 weeks (approx. 3 months) from June 21 to September 13, the  
21 period when the mean air temperature at 50 mb allows the formation of PSCs of type I ( $T <$   
22  $78$  °C) (NOAA observations in 2008, available at  
23 <http://www.cpc.ncep.noaa.gov/products/stratosphere/polar/polar.shtml>). Transitions before  
24 and after the twelve-week  $FS(t)$  plateau are assumed to be linear and last 4 weeks (Fig. 4a). The  
25  $\delta^{15}\text{N}(FS)$  value is set to 19 ‰ as estimated by Savarino et al. (2007) based on computations  
26 from chemical mechanisms, fractionation factors, and isotopic measurements. No direct  
27 measurement of  $\Delta^{17}\text{O}$  in stratospheric nitrate exists. Savarino et al. (2007) estimated that  $\Delta^{17}\text{O}$   
28 is higher than 40 ‰ and we set  $\Delta^{17}\text{O}(FS)$  to 42 ‰.

29 There is no estimate of the nitrogen mass flux received on the Antarctic continent by long range  
30 transport ( $FT$ ). In the absence of such information and for simplicity, we assume that, annually,  
31  $FS/FPI = 50$  %. This means that the annual fluxes  $FT$  and  $FS$  are equal. We also assume a

1 uniform distribution of  $FT$  throughout the year. We agree that this hypothesis is debatable given  
2 that air mass movement into the Antarctic plateau may be hampered at times when the polar  
3 vortex is strongest. As for the flux, the  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  of this nitrate source are not known.  
4 However, we assume that it features  $\delta^{15}\text{N}(FT) = 0 \text{ ‰}$  and  $\Delta^{17}\text{O}(FT) = 30 \text{ ‰}$ , which represent  
5 averaged values for tropospheric nitrate in pristine areas in low/middle latitudes (Morin et al.,  
6 2009). Annual snow accumulation rates measured at Dome C vary considerably at the inter-  
7 annual timescale as a result of snow redistribution by the wind (Libois et al., 2014). For  
8 example, years with net ablation are as frequent as 15 %. The same process also affects the  
9 distribution of snow accumulation rates at a sub-annual timescale. For the sake of simplicity,  
10 the annual snow accumulation rate is set to a constant value of  $28 \text{ kg m}^{-2} \text{ a}^{-1}$  (93 mm of snow  
11 per year for  $\rho = 300 \text{ kg m}^{-3}$ ) which is representative of the Dome C site (Frezzotti et al., 2004,  
12 Libois et al., 2014). We also assumed a uniform distribution of snow accumulation within the  
13 computed year. Snow densities also vary considerably at the decimeter-scale both horizontally  
14 and vertically (Libois et al., 2014). To simplify, the snow density has been set to  $300 \text{ kg m}^{-3}$ ,  
15 the average value found for the snow top layers at Dome C (France et al., 2011). This value is  
16 close to the average value ( $316 \text{ kg m}^{-3}$ ) observed in a mean 25-cm depth DC profile (Libois et  
17 al., 2014). We note that our choice of snow density for the nitrate mass and isotopic calculations  
18 is consistent with that used for the optical calculations in the soft windpack layer at the surface,  
19 where most of the action occurs.

20 The adjustment parameter  $^{15}\epsilon_{\text{dep}}$  (representing the  $^{15}\text{N}/^{14}\text{N}$  fractionation associated with  $\text{HNO}_3$   
21 deposition) is set to a value of  $+10 \text{ ‰}$  in order to match the shift in  $\delta^{15}\text{N}$  between observed  
22 atmospheric and skin layer nitrate (Erbland et al., 2013). The diffusivity coefficient is set to  $1.0$   
23  $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The fraction of nitrate fluxes which is horizontally exported from the atmospheric  
24 box is adjusted to a constant value of  $f_{\text{exp}} = 20 \text{ ‰}$ . The parameter  $\Phi$  is adjusted to a constant  
25 value of  $0.026$  and the magnitude of the cage effect is adjusted using a constant parameter of  
26  $f_{\text{cage}} = 0.15$ , which means that 15 % of the photolyzed nitrate undergoes cage recombination and  
27 isotopic exchange with water.

28 We used absorption cross sections of  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  in snow recommended by Berhanu et  
29 al. (2014a). The TUV-snow model used to model the actinic flux in the DC snowpack was run  
30 using constant  $k$  and  $q$  parameters set to 1. An additional input is the ozone column and we used  
31 the measurements at Dome C over the 2000-2009 period. The 2000-2005 data were derived  
32 from the measurements made by the Earth Probe Total Ozone Mapping Spectrometer

1 (EP/TOMS) and processed by the NASA (data obtained at <http://ozoneaq.gsfc.nasa.gov/>). The  
2 2007-2009 data were obtained from the “Système d’Analyse par Observation Zénithale”  
3 (SAOZ) observation network at ground (data obtained at <http://saoz.obs.uvsq.fr/index.html>).  
4 Weekly averages have been calculated over the 2000-2009 period and converted to obtain the  
5 same resolution (25 DU) than that used for the offline runs of the TUV-snow model (Fig.3).

6 The variable  $\alpha$  has been calculated from Eq. (8) using weekly average mixing ratios of  $O_3$   
7 measured at Dome C in 2007-2008 (Legrand et al., 2009). During the OPALÉ campaign, Frey  
8 et al. (2014,2015) have measured BrO mixing ratios of 2–3 pptv. We assume that [BrO] is  
9 constant throughout the year and equal to 2.5 pptv. Air temperatures and pressures at each time  
10 step were calculated from the 3-hour observations from the Concordia Automatic Weather  
11 Station (AWS 8989) in 2009-2010 (University of Wisconsin-Madison, data available at  
12 <ftp://amrc.ssec.wisc.edu/pub/aws/q3h/>, accessed July 4 2013). Mixing ratios of  $HO_2$  and  $CH_3O_2$   
13 were deduced from those of  $RO_2$  assuming  $RO_2 = HO_2 + CH_3O_2$  and  $[HO_2] / [RO_2] = 0.7$  (Kukui  
14 et al., 2014). Mixing ratios of  $RO_2$  were estimated from their linear relationship with  $J(NO_2)$ :  
15  $[RO_2] / (\text{molecule m}^{-3}) = 7.25 \times 10^{15} \times (J(NO_2) / \text{s}^{-1})$  (Figure 3b in Kukui et al., 2014). The time  
16 series of  $J(NO_2)$  was calculated with the TUV model for the appropriate solar zenith angle.

17 We note that Frey et al. (2014,2015) have measured high  $[NO_2]/[NO]$  ratios which are not  
18 consistent with other measurements available at Dome C. The authors suggest that an unknown  
19 mechanism which converts NO into  $NO_2$  or interferences in the  $NO_x$  measurements are  
20 responsible for the discrepancy observed. Given that the oxidant budget is not yet fully resolved  
21 at DC, we stick to our simple parameterization of the local resetting of the oxygen isotopic  
22 composition of  $NO_2$  (Eq (7)). We recall that we have made various simplifications in the  
23 description of the local cycling and oxidation of  $NO_2$ . These assumptions include:  $\Delta^{17}O(HO_2)$   
24 = 0 ‰, the simplified description of  $\Delta^{17}O(OH)$ , the simplified NO to  $NO_2$  conversion reaction  
25 scheme (and the potential greater influence of  $O_3$ ) and, eventually, the neglected nighttime  $NO_2$   
26 oxidation pathway at the beginning and end of the sunlit season (which, again, involves  $O_3$ ).  
27 For these reasons, we anticipate that the  $\Delta^{17}O$  values simulated by TRANSITS at DC will  
28 represent the lower bound of the observations, because  $O_3$ -dominated oxidation will imply  
29 larger  $\Delta^{17}O$  values.

### 30 **Simulations across East Antarctica**

31 Sampled sites on the D10-DC-Vostok route are characterized by a wide range of annual snow  
32 accumulation rates which gradually drop from 558  $\text{kg m}^{-2} \text{a}^{-1}$  close to the coast (D10) to 20  $\text{kg}$



1  $\text{m}^{-2} \text{a}^{-1}$  high on the plateau (around Vostok) (Erbland et al., 2013). The simulation of nitrate in  
2 East Antarctic snowpacks and the investigation of TRANSITS's ability to reproduce such wide  
3 snow accumulation conditions, we consider 10 test sites whose snow accumulation rates are  
4 [20, 25, 30, 40, 50, 75, 100, 200, 300, 600]  $\text{kg m}^{-2} \text{a}^{-1}$ , respectively. For simplicity, we consider  
5 that  $A$  is the sole variable used to characterize different sites from the coast to the plateau in  
6 East Antarctica. All the other parameters and variables are kept the same of those for DC.  
7 TRANSITS is therefore run in the DC realistic configuration described above. This means that  
8 we do not consider changes in latitude, elevation or ozone column conditions which would  
9 impact the TUV-modeled actinic fluxes. Also, the physical, optical and chemical properties of  
10 the snowpacks are considered constant. No changes in atmospheric temperature (which would  
11 affect  $D$ ) and local atmospheric chemistry are taken into account and the horizontal export of  
12 nitrogen from locations on the plateau to those close to the coast is not modeled. Last, we  
13 hypothesize that the time series of atmospheric nitrate concentrations are the same than that  
14 measured at DC. This assumption is supported by the observation of Savarino et al. (2007) who  
15 show comparable atmospheric nitrate concentration time series at the coastal Dumont d'Urville  
16 station and at DC.

17 The parameters and variables used for the DC realistic simulation as well as those used for the  
18 simulations across East Antarctica are given in Table 3.

### 19 **3.1.3 Model initialization and output data**

20 The 1-m snowpack is initialized with a constant nitrate profile of  $\omega(\text{NO}_3^-) = 50 \text{ ngNO}_3^- \text{ g}^{-1}$ ,  
21  $\Delta^{17}\text{O}(\text{NO}_3^-) = 30 \text{ ‰}$  and  $\delta^{15}\text{N}(\text{NO}_3^-) = 50 \text{ ‰}$ . The atmosphere box is initialized with  $\gamma(\text{NO}_3^-) =$   
22  $5 \text{ ngNO}_3^- \text{ m}^{-3}$  and  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  values of 30 ‰ and 5 ‰, respectively.

23 The model is run for a time sufficiently long to allow it to converge (e.g. 25 years for DC  
24 conditions). Raw data generated by the model are processed to obtain the time series of  
25 concentration and isotopic composition of atmospheric nitrate and in a top skin layer of 4 mm,  
26 the depth profiles of mass fraction,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  in snow nitrate and the time series of the  $\text{NO}_2$   
27 flux from the snow to the atmosphere.

28 From the simulated profiles of nitrate mass and isotopic composition in snow, we calculate the  
29 apparent fraction constants ( $^{15}\epsilon_{\text{app}}$  and  $^{17}E_{\text{app}}$ ) as in Erbland et al. (2013). Also, the nitrate mass  
30 and isotopic composition in the top 50 cm are calculated. We recall that the model also

1 computes the simulated mass fraction and isotopic composition in the archived nitrate, which  
2 can be compared to the observed asymptotic values.

### 3 3.2 Results

4 In this section, we briefly describe the simulated results. A comparison between the model  
5 results and the observations data will be given in the “evaluation and discussion” section. We  
6 note that the model results are insensitive to the values used for the model’s initialization.

#### 7 3.2.1 Simulation results at the DC air-snow interface

8 Figure 44 gives the results at the air-snow interface for the DC-like realistic simulation:  
9 simulated nitrate concentrations,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  in both the atmospheric and skin layer  
10 compartments as well as the simulated fluxes ( $FD$ ,  $FE$ ,  $FP$ ) together with the observations at  
11 Dome C in 2007-2008 and 2009-2010. Table 44 gives a summary of averages and  
12 minimum/maximum of the simulated values in the atmosphere and skin layer.

13 In the atmospheric compartment, the average nitrate concentration is  $32 \text{ ng m}^{-3}$  which represents  
14 an average mass of  $3.6 \times 10^{-4} \text{ mgN m}^{-2}$ . Atmospheric concentrations start to rise by the  
15 beginning of August and peak at  $110 \text{ ng m}^{-3}$  at the end of November to get back to winter  
16 background values ( $5 \text{ ng m}^{-3}$ ) in March. The simulated annual weighted  $\delta^{15}\text{N}$  value is  $+0.2 \text{ ‰}$ .  
17 Simulated atmospheric  $\delta^{15}\text{N}$  values first show a 20 ‰ decrease in spring from the winter mean  
18 value of approx.  $+10 \text{ ‰}$ , which concurs with the beginning of the increase in atmospheric  
19 concentrations (mid-Aug. to mid-Oct.) and then an increase at a rate of approx.  $10 \text{ ‰ per month}$ .  
20 The highest atmospheric  $\delta^{15}\text{N}$  value is approx.  $+20 \text{ ‰}$  and is simulated in early February. The  
21 simulated annual weighted  $\Delta^{17}\text{O}$  value is  $23.7 \text{ ‰}$ . The highest atmospheric  $\Delta^{17}\text{O}$  values are  
22 simulated in winter ( $39.3 \text{ ‰}$  in Jul.-Aug.). They rapidly decrease by  $18 \text{ ‰}$  from mid-Aug. to  
23 October, remain stable around  $22 \text{ ‰}$  throughout the summer and slowly start to rise in February  
24 to reach winter values in July.

25 In the skin layer compartment, the average simulated nitrate mass fraction is  $3074 \text{ ng g}^{-1}$ , which  
26 represents an average mass of  $0.8 \text{ mgN m}^{-2}$ . Skin layer mass fractions start to rise in June when  
27 the stratospheric nitrate input occurs and peak at  $5706 \text{ ng g}^{-1}$  at the end of December to gradually  
28 get back to winter background values ( $700 \text{ ng g}^{-1}$ ) in June. We recall that only the simulated  
29 results are described in section 3.2. The reader may refer to section 3.3 for a comparison of the  
30 simulated and observed data, in particular the discrepancy between simulated and observed

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1 nitrate mass fraction in the skin layer (Fig. 4g). The simulated annual weighted  $\delta^{15}\text{N}$  value is  
2 +34.9 ‰. Simulated ~~atmospheric~~  $\delta^{15}\text{N}$  values in the skin layer and atmosphere show similar  
3 variations:  $\delta^{15}\text{N}$  values in the skin layer are stable in winter (+20 ‰), decrease by 5 ‰ in spring,  
4 increase at a rate of approx. 20 ‰ per month in summer, reach a maximum value of +60 ‰ in  
5 early February before decreasing at a rate of ca. 10 ‰ per month in winter. The simulated  
6 annual weighted  $\Delta^{17}\text{O}$  value is 25.5 ‰. Here, simulated atmospheric  $\Delta^{17}\text{O}$  values in the skin  
7 layer and atmosphere show similar variations: maximum  $\Delta^{17}\text{O}$  values in skin layer are simulated  
8 in winter (38.9 ‰ in Jul.-Aug.), rapidly decrease by 18 ‰ from mid-Sep. to October and remain  
9 stable around 21 ‰ throughout the summer and slowly start to rise in February to reach winter  
10 values in July.

11 The comparison of those two compartments shows that the average nitrate mass in the skin  
12 layer compartment is 2300 times higher than that in the atmospheric compartment. Also, we  
13 observe that nitrate mass fractions in the skin layer start to rise two months earlier than  
14 atmospheric concentrations do and that the summer maxima is simulated one month later.  
15 Annual weighted  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values in the skin layer are shifted by +34.7 ‰ and +1.7 ‰,  
16 respectively, compared to the atmospheric value. Variations in  $\delta^{15}\text{N}$  in both compartments are  
17 in phase, however, the spring decrease in  $\delta^{15}\text{N}$  values is smaller in the skin layer than in the  
18 atmosphere and the increasing rate in summer is two times higher. Consequently, the difference  
19 between  $\delta^{15}\text{N}$  values in skin layer and atmospheric nitrate varies from +10 ‰ in winter to 38  
20 ‰ in summer. Variations in  $\Delta^{17}\text{O}$  values in both compartments are almost in phase. The  
21 difference between  $\Delta^{17}\text{O}$  in skin layer and atmospheric nitrate is variable and negative in winter,  
22 increases in spring to reach +8 ‰ and is stable and slightly negative (-1 ‰) in summer.

23 Figure [55](#) and Table 5 give the snowpack results for the DC-like realistic simulation: simulated  
24 nitrate mass fraction and isotopic composition in the top 50 cm of snow and in the archived flux  
25 as well as the simulated apparent fractionation constants. The simulated nitrate mass in the top  
26 50 cm (Fig. [55a](#)) shows an average value of  $(8.1 \pm 1.6) \text{ mgN m}^{-2}$  (mean  $\pm 1 \sigma$ ). The simulated  
27  $m_{50\text{cm}}(\text{NO}_3^-)$  varies in the range 6.2–11.0  $\text{mgN m}^{-2}$  with its maximum reached by the end of  
28 September and its minimum reached by the end of January. The simulated isotopic composition  
29 of nitrate in the top 50 cm shows weighted averages of +100.5 ‰ and 23.3 ‰ for  $\delta^{15}\text{N}$  and  
30  $\Delta^{17}\text{O}$ , respectively (Figs. [55c](#) and [55f](#)). The two time series also show cycles with variations  
31 respectively in anti-phase and in phase with variations of  $m_{50\text{cm}}(\text{NO}_3^-)$ .  $\delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$  and  
32  $\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$  respectively vary in the 77.4–127 ‰ and 20.0–27.4 ‰ ranges.

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1 The simulated  $^{15}\text{N}/^{14}\text{N}$  apparent fractionation constant shows an annual average of  $(-49.5 \pm 3.7)$   
2 ‰ with weak annual variations (from -43.0 to -53.6 ‰) (Fig. 55d). The annually averaged  $^{15}\epsilon_{\text{app}}$   
3 value is slightly higher than the annual weighted mean  $^{15}\epsilon_{\text{pho}}$  value (-55.1 ‰). Compared to  
4  $^{15}\epsilon_{\text{app}}$ ,  $^{17}E_{\text{app}}$  shows variations of greater relative amplitude (from 0.7 to 2.4 ‰) with an annual  
5 average of  $(1.4 \pm 0.6)$  ‰.

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6 Figure 66 shows the specific case of the simulated snow nitrate for the week of December 24  
7 in the case of the DC realistic simulation. Simulated nitrate mass fractions decrease by more  
8 than two orders of magnitude in the top 15 cm and  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values increase and decrease  
9 with depth from 40 ‰ to a mean background value above 290 ‰ and from 21 ‰ to a mean  
10 background value below 18 ‰ at around 20-30 cm depth, respectively. The simulated profiles  
11 are smooth and a small secondary peak can be observed in the mass fraction profile at around  
12 9 cm depth, a depth which corresponds to one year of snow accumulation.

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13 Table 6 gives the simulated nitrate mass fluxes and their isotopic composition in the case of the  
14 DC realistic simulation. The  $FA/FPI$  ratio for the DC-like simulation is 1.8 ‰, which means  
15 that a small fraction of the primary input flux of nitrate is archived below one meter. The  
16 remaining fraction ( $FE/FPI = 1 - FA/FPI = 98.2$  ‰) is exported outside the atmospheric box.  
17 The photolytic, deposition and export fluxes show a peak whose timing follows the sunlit  
18 season (Fig. 4a). The annual photolytic flux is  $32.1 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  and is compensated by  
19 an annual deposition flux of  $32.2 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$ . Annually, the simulated  $FD$  and  $FP$  fluxes  
20 represent four times the primary input flux of nitrate ( $FD \approx FP \approx 4 \times FPI$ ). In the archived  
21 nitrate, the simulated mass fraction,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values are constant throughout the season:  
22  $23.0 \text{ ng g}^{-1}$ , 318 ‰ and 17.8 ‰, respectively (Fig. 5, Tab. 6).

23

### 24 3.2.2 Simulation results across East Antarctica

25 Figure 77 shows the results for the TRANSITS simulations across East Antarctica in which  
26 only the snow accumulation rate is varied. The simulated  $^{15}\text{N}/^{14}\text{N}$  apparent fractionation  
27 constants are low ( $(-46.1 \pm 2.2)$  ‰,  $n = 4$ ) for East Antarctic plateau sites ( $A \leq 50 \text{ kg m}^{-2} \text{ a}^{-1}$ ,  
28 Erbland et al., 2013) and close to zero ( $(-10.3 \pm 9.0)$  ‰,  $n = 3$ ) for coastal sites ( $A \geq 200 \text{ kg m}^{-2}$   
29  $\text{a}^{-1}$ ). Also, simulated plateau sites feature an average  $^{17}E_{\text{app}}$  value, which is significantly positive  
30 ( $(+1.0 \pm 0.3)$  ‰, Fig. 77b). The simulated archived flux ( $FA$ ) and  $\Delta^{17}\text{O}(FA)$  both decrease with

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1 increasing  $1/A$  (Figs. 77e and 7d). Simulated  $\delta^{15}\text{N}(FA)$  values monotonically increase with  
2 increasing  $1/A$ .

3 Figure 88 presents the same results in a different way. Panel a is a “modified Rayleigh plot”  
4 where  $\ln(\delta^{15}\text{N}(FA) + 1)$  is represented as a function of  $\ln(FA)$  (which equals  $\ln(\omega(FA) \times A)$ )  
5 instead of  $\ln(\omega(FA))$ . In this representation, we observe that the simulated data fall on a line  
6 whose slope is -0.064. Fig. 88b shows that  $\Delta^{17}\text{O}(FA)$  and  $\delta^{15}\text{N}(FA)$  (Fig. 88b) are negatively  
7 correlated.

### 9 3.3 Evaluation and discussion

10 In this section, we evaluate the model results in light of the observational constraints described  
11 above. In particular, we attempt to state clearly the observations, which are well reproduced by  
12 the model and those which are not. In the sections below, we also discuss the choice of the  
13 adjustment parameters which were made to run TRANSITS.

#### 15 3.3.1 Validation of the mass loss, diffusion and $^{15}\text{N}/^{14}\text{N}$ fractionation 16 process

17 The nitrate mass loss is quantitatively represented in the TRANSITS model. Indeed, Fig. 66a  
18 shows that nitrate mass fractions decrease by a factor 10 in the top 10 cm of the snowpack in  
19 agreement with observations. Also, the simulated archived nitrate mass fractions values are  
20 consistent with the observations (Fig. 55). This means that the nitrate mass fraction lost by  
21 photolysis ( $1-f$ ) and calculated from the photolytic rate constant ( $J$ , Eq. (1)) is quantitatively  
22 simulated by TRANSITS model runs.

23 Nitrate- $\delta^{15}\text{N}$  isotopic profiles in snow also show that the  $^{15}\text{N}/^{14}\text{N}$  fractionation associated with  
24 nitrate photolysis is quantitatively represented within the uncertainties. Indeed, the DC realistic  
25 simulation reproduces well the depth profile of  $\delta^{15}\text{N}$  in snow nitrate as observed on Fig. 6b with  
26 simulated  $\delta^{15}\text{N}$  values as high as 150 ‰ at 10 cm depth. First, the simulated  $^{15}\text{N}/^{14}\text{N}$  apparent  
27 fractionation constants are consistent with the observations at Dome C (Fig. 55d) and for  
28 plateau sites ( $A \leq 50 \text{ kg m}^{-2} \text{ a}^{-1}$ , Fig. 77a). This means that the absorption cross sections used  
29 for  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  (Berhanu et al., 2014a) and the variables used in the TUV-snow model  
30 ( $\text{O}_3$  column) allow a quantitative description of the  $^{15}\text{N}/^{14}\text{N}$  fractionation constant associated

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1 with nitrate photolysis ( $^{15}\epsilon_{\text{pho}}$ , Eq. (3)). Secondly, the  $\delta^{15}\text{N}$  values in the archived nitrate is well  
2 reproduced by the model: the simulated  $\delta^{15}\text{N}(\text{FA})$  value (318 ‰) compares well with the  
3 observations (from 275 to 300 ‰, Fig. 55f). This is a further evidence that the nitrate mass  
4 fraction lost by photolysis ( $1-f$ ) are quantitatively simulated by TRANSITS model runs. Indeed,  
5 using a quantum yield of  $2.1 \times 10^{-3}$  at 246 K as in France et al. (2011) not only leads to  
6 unrealistic  $\text{FA}/\text{FPI}$  ratio (71 %) and  $\omega(\text{FA})$  value (917 ng g<sup>-1</sup>) but also to a very small  $\delta^{15}\text{N}(\text{FA})$   
7 value (+20.3 ‰), which clearly reflects a weak recycling and an overestimate of primary nitrate  
8 trapped in snow. The adjusted photolytic quantum yield of  $\Phi = 0.026$  allows computing a  
9 consistent variation range of  $\delta^{15}\text{N}$  in nitrate archived at depth. Given the choice of a modeled  
10 cage effect of  $f_{\text{cage}} = 0.15$ , we obtain an apparent modeled quantum yield of  $0.85 \times 0.026 \approx$   
11 0.022, a value smaller than the mean value for buried nitrate (0.05) but higher than the smallest  
12 value observed for this domain (0.003) (Meusinger et al., 2014).

13 Additionally, we observe from Fig. 6a that the simulated profiles are smooth and that a small  
14 secondary peak can be observed in the simulated mass fraction profile at around 9 cm depth,  
15 consistent with some. Such smooth profiles can only be simulated because nitrate diffusion was  
16 taken into account and turning this process off leads to simulated mass fraction and isotope  
17 profiles in the snow showing unrealistic spiky seasonal variations similar ~~toas~~ those simulated  
18 by Wolff et al. (2002) and France et al. (2011). The secondary peak observed in simulated  
19 nitrate mass fraction profiles (at 9 cm depth, which corresponds to one year of snow  
20 accumulation) represents nitrate residual from the previous year's skin layer. This is consistent  
21 with secondary peaks observed in some snow pits on the Antarctic plateau, e.g. snow pits S1  
22 (at 10 cm depth), S2 (at 7 and 17 cm depth) and S3 (around 10 cm depth) in Supplementary  
23 Information, Erbland et al. (2013). Since TRANSITS is able to reproduce such a feature, we  
24 conclude that a simplified description of nitrate diffusion (i.e. constant diffusion coefficient) is  
25 not detrimental.

26 The adjusted value used for  $D$  can be compared to the effective diffusivity of nitric acid in snow  
27 (denoted  $D_{\text{eff}}$ ) as calculated in Herbert et al. (2006) and by assuming that the snow layers are  
28 always under-saturated in nitrate. Such approach is followed because  $\text{HNO}_3$  is a sticky gas.  
29 According to Herbert et al. (2006), the  $D_{\text{eff}}$  is a function of the diffusivity of  $\text{HNO}_3$  in the  
30 interstitial air which depends on temperature and pressure (Massmann, 1998). Using a Specific  
31 Surface Area of snow of 38 m<sup>2</sup> kg<sup>-1</sup> (Gallet et al., 2011), a snow density of 300 kg m<sup>-3</sup>, the  
32 median temperature and pressure for DC summer 2012 (Kukui et al., 2014) and a partition

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1 coefficient in the uptake of  $\text{HNO}_3$  on ice (Crowley et al., 2010), we find  $D_{\text{eff}} = 7.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$   
2 <sup>1</sup>. Our adjusted value for  $D$  ( $1.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ) is close to the effective diffusivity of nitric acid  
3 in snow (denoted  $D_{\text{eff}}$ ) and more than three orders of magnitude higher than the diffusion  
4 coefficient of nitrate ion in a single monocrystal of ice calculated at the same temperature ( $2.6$   
5  $\times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ , Thibert and Dominé, 1998), which means that the macroscopic mobility of nitrate  
6 in the snowpack is mostly the consequence of  $\text{HNO}_3$  mobility in the interstitial air. We recall  
7 that our description of nitrate diffusion in the snowpack is basic and that the picture may well  
8 be more complicated with, e.g. wind pumping effects and temperature gradients in snow.

9

### 10 3.3.2 Validation of the cage effects

11 ~~The choice of a non-zero value for  $f_{\text{cage}}$  allows generating decreasing  $\Delta^{17}\text{O}$  profiles in snow in~~  
12 ~~accordance with the observations in three snow pits from DC (Fig.6c). The choice of a non-~~  
13 ~~zero value for  $f_{\text{cage}}$  allows to reproduce the positive apparent  $^{17}\text{O}$ -excess fractionation constant~~  
14 ~~( $^{17}E_{\text{app}}$ ) which are observed at DC (from  $(+1.2 \pm 0.3) \text{ ‰}$  to  $(+2.3 \pm 0.7) \text{ ‰}$  in summer, Fig.5g)~~  
15 ~~and on the Antarctic plateau (Frey et al., 2009, Erbland et al., 2013). Indeed, Fig.5g shows that~~  
16 ~~the simulated  $^{17}E_{\text{app}}$  values at DC are positive while a TRANSITS model run with the cage~~  
17 ~~effects switched off (i.e.  $f_{\text{cage}} = 0$ ) leads to a simulated mean December/January  $^{17}E_{\text{app}}$  value~~  
18 ~~almost nil:  $(+0.3 \pm 0.2) \text{ ‰}$  (date not shown). The simulation across East Antarctica confirms~~  
19 ~~the ability of the model to reproduce the sensitivity of  $\Delta^{17}\text{O}$  to the nitrate mass loss (Fig.7b).~~  
20 ~~(Fig.7). Indeed, for sites with  $A \leq 50 \text{ kg m}^{-2} \text{ a}^{-1}$ , the model calculates a mean  $^{17}E_{\text{app}}$  value of~~  
21  ~~$(+1.0 \pm 0.3) \text{ ‰}$  for the December/January period while the observed average value is  $(+2.0 \pm$   
22  ~~$1.2) \text{ ‰}$  (mean  $\pm 1 \sigma$ ,  $n = 10$ ). The model therefore confirms On this figure, the decreasing trend~~  
23 ~~in the data overlaps with additional variability in  $\Delta^{17}\text{O}$ . A better metric to evaluate the changes~~  
24 ~~in  $\Delta^{17}\text{O}$  associated with depth, i.e. with the loss of nitrate, is the apparent  $^{17}\text{O}$ -excess~~  
25 ~~fractionation constant,  $^{17}E_{\text{app}}$ . Fig.5g shows that the simulated  $^{17}E_{\text{app}}$  values at DC are positive,~~  
26 ~~consistently with the observations, confirming the decreasing contribution of cage~~  
27 ~~recombination effects to  $\Delta^{17}\text{O}(\text{NO}_3)$  (McCabe et al., 2005, Frey et al., 2009). We observe that~~  
28 ~~an  $f_{\text{cage}}$  parameter set to 0 would have led to a mean December/January  $^{17}E_{\text{app}}$  value almost nil:~~  
29  ~~$(+0.3 \pm 0.2) \text{ ‰}$ , as originally observed in the lab by McCabe et al. (2005).~~~~

30 Fig.6c shows that a non-zero value for  $f_{\text{cage}}$  allows to generate decreasing  $\Delta^{17}\text{O}$  profiles in snow  
31 in accordance with the observations in three snow pits from DC and with the simulated and  
32 observed positive  $^{17}E_{\text{app}}$  values. While this subtle depth trend is reproduced by the model, we

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1 observe from the same figure that, quantitatively, the choice of a non-zero value for  $f_{\text{cage}}$  is  
2 detrimental to the reproduction of the  $\Delta^{17}\text{O}$  values of nitrate in the top 50 cm of snow. Indeed,  
3 modeled  $\Delta^{17}\text{O}$  values in the 40–50 cm depth range are approx. 18 ‰ and 23.5 ‰ in the cases  
4 where the cage effects are switched on and off, respectively, in comparison with observed  $\Delta^{17}\text{O}$   
5 values in the 27–30 ‰ range. We refer the reader to section 3.3.8 where the ability of the model  
6 to quantitatively reproduce the observed  $\Delta^{17}\text{O}$  values is discussed.~~The simulation across East~~  
7 ~~Antarctica confirms the ability of the model to reproduce the sensitivity of  $\Delta^{17}\text{O}$  to the nitrate~~  
8 ~~mass loss (Fig. 7). Indeed, for sites with  $A \leq 50 \text{ kg m}^{-2} \text{ a}^{-1}$ , the model calculates a mean  $^{17}\text{E}_{\text{app}}$~~   
9 ~~value of  $(+1.0 \pm 0.3) \text{ ‰}$  for the December/January period while the observed average value is~~  
10  ~~$(+2.0 \pm 1.2) \text{ ‰}$  (mean  $\pm 1 \sigma$ ,  $n = 10$ ). We observe that an  $f_{\text{cage}}$  parameter set to 0 would have~~  
11 ~~led to a mean December/January  $^{17}\text{E}_{\text{app}}$  value almost nil:  $(+0.3 \pm 0.2) \text{ ‰}$ .~~

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### 13 3.3.3 Validation of the macroscopic fluxes

14 The primary input flux of nitrate to the air-snow system ( $FPI$ ) derived from Muscari and de  
15 Zafra (2003) (and from our assumption  $FT = FS$ ) is realistic. Indeed, simulated and observed  
16 East Antarctica data almost fall on the same line of slope -0.065 in the modified Rayleigh plot  
17 (Fig. 88a). In this representation, changing  $FPI$  leads to the horizontal shift of the simulated data  
18 thus confirming the realistic value of  $FPI = 8.2 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$ . We note that our simulation  
19 in East Antarctica is very simple because it only takes into account changes in snow  
20 accumulation rates, which are large on the D10–DC–Vostok route. A more sophisticated  
21 simulation along this line is beyond the scope of the present study because it would require  
22 including a radiative transfer model such as TUV-snow (or such as TARTES, Libois et al.,  
23 2014) in TRANSITS in order to deal with latitudinal and elevation changes. Also, the  
24 simulation should take into account boxes from Vostok to D10 with the exchange of nitrate  
25 horizontally exported from the center of the continent towards the coast, basically changing our  
26 1-D model into a 2-D model.

27 The maximum value of the photolytic flux ( $FP$ ) simulated for DC is  $3.27 \times 10^{-12} \text{ kgN m}^{-2} \text{ s}^{-1}$   
28 (Fig. 4a, Tab. 6), a value around 40 times higher than that obtained by France et al. (2011). This  
29 difference is not surprising since we are using a quantum yield 12 times higher than France et  
30 al. (2011). The different scaling may be explained by the differences in the complexities of the  
31 two models (TRANSITS includes recycling and a net export). The observed median  $\text{NO}_x$   
32 emission fluxes are  $1.6 \times 10^{-13} \text{ kgN m}^{-2} \text{ s}^{-1}$  and  $3.7 \times 10^{-13} \text{ kgN m}^{-2} \text{ s}^{-1}$  over the 22 December

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1 2009 to 28 January 2010 period (Frey et al., 2013) and the 1 December 2011 to 12 January 2012  
2 period (Frey et al., ~~2014~~2015), respectively. Our computed median NO<sub>2</sub> fluxes over the same  
3 periods are  $2.8 \times 10^{-12}$  kgN m<sup>-2</sup> s<sup>-1</sup> and  $3.3 \times 10^{-12}$  kgN m<sup>-2</sup> s<sup>-1</sup>, i.e. values respectively 18 and 9  
4 times higher than in the observations by Frey et al. (2013, ~~2014~~2015).

5 The discrepancy between simulated and observed *FP* values may be explained by the fact that  
6 *FP* represents the potential flux of NO<sub>2</sub> emitted from the snow to the atmosphere, i.e. an upper  
7 limit when comparing to the observed NO<sub>2</sub> flux (measured between 0.01 m and 1 m above the  
8 snowpack, Frey et al., 2013, 2015). TRANSITS does not take into account various potential  
9 processes affecting NO<sub>x</sub> emission from snow, such as gas-phase diffusion or chemical  
10 conversion prior to emission and forced ventilation from the snowpack (France et al., 2011;  
11 Frey et al., 2013; Meusinger et al., 2014). Future improvements of the model could include an  
12 explicit representation of the vertical transport of NO<sub>2</sub> within and outside the snowpack with  
13 the following processes: NO<sub>x</sub> diffusion, wind pumping, chemical conversion and deposition  
14 prior to the net emission from the snow, the latter depending on oxidant levels in firn air (HO<sub>x</sub>,  
15 O<sub>3</sub>, and maybe halogens, Zatko et al., 2013). Another improvement could be the modeling of  
16 two nitrate domains (photolabile and buried nitrate, Meusinger et al., 2014).

17 We note that if HONO production is greater than assumed at Dome C, following the recent  
18 laboratory study of Scharko et al. (2014), this will not change the main conclusions of this  
19 study. Indeed, the photolytically produced HONO will be photolyzed to form NO in the  
20 atmosphere and this NO would simply enter the NO/NO<sub>2</sub> cycles where oxygen isotopes are  
21 reset.

22 The parameterization of HNO<sub>3</sub> deposition is simplistic since it solves the mass balance equation  
23 (Eq. (4)) in order to reproduce the nitrate concentration in the atmosphere. A sensitivity test of  
24 TRANSITS has been run using nitrate atmospheric concentrations 10 times higher than the  
25 ideal DC time series used for the DC realistic simulation. The higher nitrate concentration in  
26 the atmosphere had no significant impact on any of the nitrate reservoirs both in terms of mass  
27 and isotopic composition. Indeed, in the case of the DC realistic simulation, the atmospheric  
28 nitrate mass represent a 1/2300<sup>th</sup> and a 1/22500<sup>th</sup> of nitrate mass in the skin layer and in the top  
29 50 cm, respectively. Future improvements of the model could use a physical description of the  
30 deposition of HNO<sub>3</sub> using for example a vertical deposition velocity.

31 Hereafter, the ratio *FA/FPI* is termed the “nitrate trapping efficiency” because it reflects the  
32 fraction of nitrate that is trapped below the photic zone. In the DC realistic simulation, the

1 nitrate trapping efficiency is 1.8 % (Tab. 6), which means that only a small fraction of the  
2 primary nitrate is archived. Consequently, the next export of nitrate is significant ( $FE = 98.2$  %  
3 of the nitrate of primary origin =  $8.05 \times 10^{-6}$  kgN m<sup>-2</sup> a<sup>-1</sup>, Tab. 6) and reflects the chosen adjusted  
4 value of  $f_{exp}$  (0.2). To the best of our knowledge, there is no observation that could  
5 independently corroborate this  $FE$  value because it would require the direct measurement of  
6 this flux. We however point out that a non-zero  $f_{exp}$  parameter is necessary to reproduce realistic  
7  $\delta^{15}N$  values both in the atmosphere and skin layer. Indeed, when running the model with  $f_{exp} =$   
8 0,  $\delta^{15}N$  values in those compartments become highly negative ( $\leq -120$  ‰) which is clearly not  
9 realistic when compared to the observations (Figs. 44e and 44h) and seen in Frey et al. (2009).  
10 Also, in such conditions, the model does not converge within a reasonable time and simulated  
11 nitrate endlessly builds up in the photic zone.

12 The parameter  $f_{exp}$  can however be related to physical variables. Indeed, it represents the  
13 competition between the export of NO<sub>y</sub> (NO<sub>2</sub> or HNO<sub>3</sub>) and the deposition of (to make it  
14 simple) HNO<sub>3</sub>. Let us consider atmospheric NO<sub>2</sub> and HNO<sub>3</sub> at steady-state. The deposition of  
15 NO<sub>2</sub> is neglected because it is a factor  $8.0 \pm 3.2$  slower than that of HNO<sub>3</sub> (Zhang, et al., 2009).  
16 Also, oxidation by OH is considered to be the only channel of NO<sub>2</sub> oxidation (an assumption  
17 valid in summer). Following the approach of Jacob (1999), a summertime value for  $f_{exp}$  can be  
18 approached by considering the chemical lifetime of NO<sub>2</sub> with respect to its oxidation by OH,  
19 the residence time of atmospheric NO<sub>2</sub> against horizontal export and that of atmospheric HNO<sub>3</sub>  
20 against deposition and horizontal export processes. Using kinetic rate constants from Atkinson  
21 et al. (2004),  $T$ ,  $P$ , wind speeds and OH mixing ratios for mean summertime conditions at DC  
22 (Kukui, et al., 2014), HNO<sub>3</sub> dry deposition velocity from Huey et al. (2004), and vertical and  
23 horizontal characteristic dimensions of 100 m (average summertime boundary layer height,  
24 Gallée et al., 2014) and 400 km (Antarctic plateau width), respectively, we obtain  $f_{exp} = 0.20$ , a  
25 value which equals the value used to adjust the model but which is rather fortuitous. Indeed, we  
26 acknowledge that this calculation suffers from a number of uncertainties, e.g. using kinetic rate  
27 constants of NO<sub>2</sub> + OH from Sander et al. (2006), we obtain  $f_{exp} = 0.36$ . Future improvements  
28 of the model could aim at a physical parameterization of the nitrate export.

29

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### 3.3.4 Validation of the residence time in the photic zone and calculation of the average number of recyclings

Results from the East Antarctica simulations show that the observed linear  $\delta^{15}\text{N}(FA)$  versus  $1/A$  relationship (Freyer et al., 1996, Erbland et al., 2013) is very well reproduced (Fig. 77c). This demonstrates that the residence time of nitrate in the snowpack zone of active photochemistry is treated in a realistic manner in the model. When snow accumulation rates get very low ( $A < 20 \text{ kg m}^{-2} \text{ a}^{-1}$ ), simulated  $\delta^{15}\text{N}(FA)$  values do not seem to reach an asymptotic value as observed in the field where  $\delta^{15}\text{N}(as.)$  seems to reach a plateau not exceeding 360 ‰ (Fig. 77c). This observed feature could be the result of the different nitrate locations on snow grains, with buried nitrate (Meusinger et al., 2014) whose photolysis is, constituting a lower limit in the photolysis loss process.

Nitrate recycling at the air-snow interface at DC is illustrated by the simulated macroscopic photolytic and deposition fluxes at the snowpack surface. Indeed,  $FP$  and  $FD$  almost equilibrate and these annual fluxes are 4 times higher than the annual primary input of nitrate ( $FPI$ , Tab. 6).

Here, our main focus is on nitrate which is archived below the zone of active photochemistry because only that is ultimately archived in ice cores. One key question is to determine the “~~Yearly~~ Average Number of Recyclings” which was undergone by the archived nitrate (hereafter denoted  $\overline{YANR}(FA)$ ). To this end, a new tracer, denoted  $CYCL$ , has been introduced in the TRANSITS model. In a given box (snow layer or atmosphere),  $CYCL$  represents the average number of recyclings undergone by nitrate in the considered box. The  $CYCL$  variable follows a numerical treatment comparable to that of  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ , i.e. a “recycling” (instead of an isotopic) mass balances, diffusion and the calculation of  $CYCL$  values in the macroscopic fluxes ( $FP$ ,  $FD$ ,  $FE$ ,  $FA$ ). The  $CYCL$  value for primary nitrate is set to 0 and  $CYCL$  variables in the boxes are incremented by 1 each time  $\text{NO}_2$  molecules cross the air-snow interface.  $\overline{YANR}(FA)$  is calculated as a mass-weighted average of the  $CYCL$  values of the 52 snow layers which are archived below 1 m over the course of one year, in order to average out any seasonal variability.

Following the above approach for the Dome C simulation, we obtain  $\overline{YANR}(FA) = 4.0$  for the last layer before leaving the photic zone which means that, on average, the archived nitrate at Dome C has undergone 4.0 recyclings (i.e. loss, local oxidation, deposition). We recall that this number of recyclings represents an average value for the archive nitrate. Considering individual

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1 ions in the archived nitrate, the range of number of recyclings must be wide since some ions  
2 may well have travelled through the entire snowpack zone of active photochemistry without  
3 been recycled while some did undergo many recyclings.

4 Figure 77g shows the  $\overline{Y}_{ANR}(FA)$  values calculated for the 10 simulated sites in East Antarctica.  
5 We observe that  $\overline{Y}_{ANR}(FA)$  is proportional to  $1/A$  for  $A \geq 50 \text{ kg m}^{-2} \text{ a}^{-1}$  which means that the  
6 burial of nitrate (i.e. the residence time of nitrate in the photic zone) determines the  $\overline{Y}_{ANR}(FA)$   
7 value. On the Antarctic plateau, where snow accumulations rates are below this threshold value,  
8  $\overline{Y}_{ANR}(FA)$  reaches a plateau on the order of 4 recyclings. Concurrently, we observe that  $FP$   
9 remains constant at  $32.8 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  (data not shown) because increasing residence time  
10 of nitrate in the photic zone with decreasing snow accumulation rates lead to a nitrate mass  
11 fraction profile in snow which becomes more asymmetric with most of nitrate getting confined  
12 in a thinner layer at the top. As a result,  $FP$  levels off due to the negative feedback of the  
13 decreasing nitrate mass fractions at depth. Figure 77g clearly shows the following relationship  
14 between  $\overline{Y}_{ANR}(FA)$  and  $FP$ :  $\overline{Y}_{ANR}(FA) = \frac{FP}{FPI}$ . This finding represents an independent  
15 confirmation of the definition given by Davis et al. (2008) on the basis of the macroscopic  
16 yearly primary and photolytic fluxes: the “Nitrogen Recycling Factor”, NRF = ratio of nitrogen  
17 emission and nitrogen deposition. While we are satisfied to end up with the Davis et al. (2008)  
18 expression for  $\overline{Y}_{ANR}(FA)$  using our independent model-based tracer experiment, it must be  
19 noted that we define  $\overline{Y}_{ANR}$  as the average number of recyclings undergone by the archived  
20 nitrate while Davis et al (2008) define it as the “nitrogen recycling factor within a  
21 photochemical season”.

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### 23 3.3.5 Validation of the nitrate mass in each compartment

24 Nitrate mass in the different compartments is reasonably well reproduced by the model. Indeed,  
25 the simulated average nitrate mass in the atmospheric compartment represents a  $1/22500^{\text{th}}$  of  
26 that in the top 50 cm of snow and this is consistent with observations in 2009-2010 where this  
27 ratio is  $1/8300$  (Tables 4 and 5, considering a constant boundary layer height of 50 m). Also,  
28 the annual variations in nitrate mass fractions in the skin layer are well reproduced by the model:  
29 deviations from the winter background values occur during the sunlit season to reach a  
30 maximum in December (Fig. 4g). We however note that the period of high values above  
31 background is longer (September to April) for the simulation than in the observations

1 (October/February). Lastly, simulated nitrate mass in the top 50 cm of snow has been shown to  
2 increase in winter and to decrease during the sunlit season (Fig. 5a), similarly to the observed  
3 data: the average winter  $m_{50\text{cm}}(\text{NO}_3^-)$  value ( $(3.6 \pm 0.5) \text{ mgN m}^{-2}$ , May to Nov.) is higher than  
4 the average summer value ( $(3.2 \pm 1.2) \text{ mgN m}^{-2}$ , Dec. to Apr.). In winter, the input and output  
5 to the nitrate reservoir in the top 50 cm of snow are the deposition and archiving fluxes,  
6 respectively. During this season, the deposition flux is greater than the archiving flux which  
7 leads to an increase in  $m_{50\text{cm}}(\text{NO}_3^-)$ . When the sunlit season starts, the additional photolysis  
8 output flux starts, leading the sum  $FA + FP$  to exceed  $FD$  and thus decreasing  $m_{50\text{cm}}(\text{NO}_3^-)$ .

9 Additionally, the simulated average mass ratio between the skin layer and the top 50 cm of  
10 snow is 10 % (Tables 4 and 5), a value approx. 3 times higher than the 2009-2010 observed  
11 value (3 %, considering a snow density of  $300 \text{ kg m}^{-3}$  for the skin layer snow). This discrepancy  
12 is accompanied by a factor 2.4 between simulated and observed annual average  $m_{50\text{cm}}(\text{NO}_3^-)$   
13 values ( $(8.1 \pm 1.6) \text{ mgN m}^{-2}$  versus  $(3.4 \pm 1.0) \text{ mgN m}^{-2}$ , Fig. 5a) and by a factor 7.9 between  
14 simulated and observed annual average mass fractions in the skin layer ( $3074 \text{ ng g}^{-1}$  versus  $390$   
15  $\text{ng g}^{-1}$ , Fig. 4g). Nitrate mass in the top 50 cm and in the skin layer are therefore higher in the  
16 DC simulation than in the observations and nitrate in the skin layer is more concentrated in the  
17 simulation.

18 Fully resolving these discrepancies is beyond the scope of this paper. However, we first note  
19 that lower observed skin layer mass fractions could be linked to heterogeneities in sampling the  
20 skin layer (whose thickness is  $(4 \pm 2) \text{ mm}$ , Erbland et al., 2013), especially when considering  
21 that different overwintering people were involved in this task. For instance, sampling 6 mm  
22 instead of 4 mm could lead to the sampling of a more diluted skin layer. However, we  
23 acknowledge that this sampling issue would have a limited impact on the observed skin layer  
24 mass fractions. Secondly, higher simulated annual  $m_{50\text{cm}}(\text{NO}_3^-)$  values could be the result of the  
25 time-response of the modeled snowpack to past changes in primary input fluxes. Indeed, when  
26 run in the DC realistic simulation with a multiplication of  $FPI$  by a factor 10 after 25 years of  
27 simulation, TRANSITS shows a time-response of approximately 21 years. This means that the  
28 snowpack requires 21 years to reach stable  $m_{50\text{cm}}(\text{NO}_3^-)$  values again. As a consequence, the  
29 different  $m_{50\text{cm}}(\text{NO}_3^-)$  value observed today at Dome C could reflect changes in primary input  
30 flux conditions as far back as one or two decades in the past. A third explanation involves the  
31 absence of a snow erosion process during which wind blows away a significant fraction of the  
32 non-cohesive skin layer. This process would decrease nitrate mass fractions in the skin layer as

1 observed in the field around 10 January 2010 (Erbland et al., 2013) and, in turn, decrease nitrate  
2 mass fractions in the snow layers below.

3

### 4 **3.3.6 Validation of the $\delta^{15}\text{N}$ values in each compartment**

5 In section 3.2.1, we have seen that the simulated  $\delta^{15}\text{N}$  profiles in snow are consistent with the  
6 observations. In particular, apparent  $^{15}\text{N}/^{14}\text{N}$  fractionation constants are well reproduced  
7 leading the simulation of realistic  $\delta^{15}\text{N}(\text{FA})$  values. In this section, we compare the simulated  
8 and observed time series of  $\delta^{15}\text{N}$  in the atmospheric and skin layer nitrate.

9 Overall, the annual variations of  $\delta^{15}\text{N}$  values in skin layer and atmospheric nitrate are generally  
10 well reproduced by the model although some discrepancies can be noted (Figs. 4e and 4h). For  
11 example, the winter observed  $\delta^{15}\text{N}$  values and 10 ‰ shift between atmosphere and snow are  
12 well simulated supporting the choice of the  $^{15}\text{N}/^{14}\text{N}$  fractionation constant associated with the  
13 deposition of nitric acid (+10 ‰), the positive sign of  $^{15}\epsilon_{\text{dep}}$  being consistent with a dry  
14 deposition of  $\text{HNO}_3$ . Also, the spring variations and timing of atmospheric  $\delta^{15}\text{N}$  are well  
15 reproduced. Indeed, the lowest  $\delta^{15}\text{N}$  values in the atmospheric nitrate occur in October  
16 (simulated: -25.3 ‰, observed: -17.0 ‰, Fig. 44e) when the stratospheric input has stopped and  
17 when the UV radiation becomes significant to encourage the production of isotopically depleted  
18  $\text{NO}_x$  from the snowpack. The return to positive atmospheric  $\delta^{15}\text{N}(\text{NO}_3^-)$  values in summer is  
19 faster at Dome C than it has been observed at DDU and this feature has been attributed to the  
20 longer exposure time of nitrate at the snow surface at Dome C (Savarino et al., 2007; Frey et  
21 al., 2009). TRANSITS confirms this suggestion when run with the higher snow accumulation  
22 rate which characterizes DDU (data not shown). At Dome C, shortly after the decrease,  $\delta^{15}\text{N}$   
23 values rapidly start to rise again because the nitrate in snow becomes more enriched in  $^{15}\text{N}$  and  
24 the extracted  $\text{NO}_2$  has rising  $\delta^{15}\text{N}$  values as well. With large  $\theta$  values at the end of the summer,  
25 the apparent ozone column crossed by the UV rays is more important and the photolytic  
26 fractionation constant ( $^{15}\epsilon_{\text{pho}}$ ) becomes more negative (Fig. 55d). This leads to decreasing  $\delta^{15}\text{N}$   
27 values extracted from the snowpack even if the enrichment does not stop there. Finally,  
28 wintertime values of  $\delta^{15}\text{N}$  are reached back by the end of April/beginning of May when the  
29 nitrate photolysis stops.

30 The simulated annual variation of skin layer  $\delta^{15}\text{N}$  is also consistent with the observations.  
31 However, the spring decrease observed in 2009-2010 is more marked than the simulation one

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1 (25 ‰ and 5 ‰, respectively, Fig. 4h). One reason is that the simulated  $\delta^{15}\text{N}$  values in skin  
2 layer start to rise 1.5 months earlier than in the observations (Fig. 4h). Although simulated  $\delta^{15}\text{N}$   
3 values start to rise earlier, we note that the summer increasing rate in skin layer  $\delta^{15}\text{N}$  values is  
4 similar in the simulations and in the observations (approx. +20 ‰ per month). One consequence  
5 of the 1.5 month delay between simulated and observed skin layer  $\delta^{15}\text{N}$  values is that the  $\delta^{15}\text{N}$   
6 difference between skin layer and atmospheric nitrate at the end of the summer is greater in the  
7 simulation than it is for the observation (approx. +40 ‰ versus +20 ‰). Focusing on the  
8 beginning of the skin layer,  $\delta^{15}\text{N}$  records (Fig. 44h) shows that the end of summer 2008-09 was  
9 different than the next year, with differences up to 40 ‰ between the simulation and  
10 observation. In particular, the large observed variations which lead to skin layer  $\delta^{15}\text{N}$  values as  
11 high as +60 ‰ (Erbland et al., 2013) are not reproduced by the model. This could be the result  
12 of snow sampling effects (i.e. local spatial heterogeneity or different sampling of the operator  
13 in the field).

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14

### 15 **3.3.7 Photolytically-driven dynamic equilibrium at the air-snow interface**

16 The simulated variations of  $\Delta^{17}\text{O}$  in the atmospheric and skin layer compartments are consistent  
17 with the observations, i.e.  $\Delta^{17}\text{O}$  decreases from high winter values to the lowest values in the  
18 middle of summer (Figs. 4f and 4i). The model also reproduces well the small negative  
19 difference between the atmospheric and skin layer annual weighted  $\Delta^{17}\text{O}$  values (simulated: -  
20 1.2 ‰, observed: -2.3 ‰). When considering the annual variability of the difference in  $\Delta^{17}\text{O}$  in  
21 the atmosphere and skin layer, the model reproduces well the important shift in early October  
22 (simulated: -8 ‰, observed: -7 ‰) as well as the small negative shift by the end of the summer  
23 (simulated: approx. -2 ‰, observed: approx. -2 ‰).

24 The above observations show that TRANSITS is able to qualitatively reproduce the  $\Delta^{17}\text{O}$   
25 variations in nitrate for each compartment. Concurrent variability in  $\Delta^{17}\text{O}$  in atmospheric and  
26 skin layer nitrate indicate equilibrium at the air-snow interface. The simulated and observed  
27 differences between  $\Delta^{17}\text{O}$  in the atmosphere and skin layer are the result of their respective  
28 nitrate reservoirs and indicate that the isotopic equilibrium is dynamic. Further evidence for the  
29 different size reservoir is that the (oxygen and nitrogen) isotope time series in the skin layer are  
30 smoother than in the atmosphere (Fig. 44).

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1 The photolytic and deposition fluxes in summer show that there is an intense nitrate recycling  
2 at the air-snow interface at this season (Fig. 44a), a feature which is confirmed by our calculation  
3 of the average number of recyclings undergone by the archived nitrate ( $\overline{ANR}(FA) = 4.0$ ). The  
4 local signature of  $\text{NO}_2$  cycling and oxidation harbored by  $\Delta^{17}\text{O}$  is therefore incorporated in skin  
5 layer nitrate. Given the good qualitative agreement between the simulated and observed  $\Delta^{17}\text{O}$   
6 in skin layer nitrate throughout the year, we conclude that TRANSITS has a realistic  
7 representation of the local cycling and oxidation of  $\text{NO}_2$  in the atmosphere.

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8 We also observe that TRANSITS reproduces well the  $\Delta^{17}\text{O}(FA)/\delta^{15}\text{N}(FA)$  anti-correlation and  
9 general trend in the case of the simulation across East Antarctica (Fig. 88c). This anti-correlation  
10 is partly the result of the cage recombination effects but some of it is also due to the greater  
11 incorporation of the summertime isotopic signature of the local cycling and oxidation of the  
12 photolytically produced  $\text{NO}_2$ . On the same figure, the observations show a large scattering of  
13 approx. 5 ‰ when compared to data simulated by TRANSITS. One reason for that is the  
14 inability of the model to reproduce variations of  $\Delta^{17}\text{O}$  in nitrate below 20 cm which can be as  
15 high as 5 ‰ (Fig. 66c). Such variations may be linked to variability in ozone column, snow  
16 accumulation, local atmospheric chemistry, primary inputs of nitrate from one year to another  
17 which are not accounted for by TRANSITS. McCabe et al. (2007) first observed such 2–3 years  
18 period cycles in a 6-m snow pit from South Pole and attributed these cycles to variability in the  
19 stratospheric ozone column or to stratospheric nitrate import; the same periodicity in  $\Delta^{17}\text{O}$  is  
20 found in DC surface snow (Frey et al., 2009, Erbland et al., 2013). Future work should  
21 investigate the impact of the variations in the ozone column on the  $\Delta^{17}\text{O}$  in the archived nitrate.

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22 Quantitatively speaking,  $\Delta^{17}\text{O}$  values in the atmosphere, skin layer, in the top 50 cm of snow  
23 and in the archived nitrate are not well reproduced. Indeed, the simulated annual weighted  $\Delta^{17}\text{O}$   
24 values in the atmosphere and skin layer are approx. 6 ‰ lower than in the observations (23.7  
25 ‰ versus 29.4 ‰ and 25.5 ‰ versus 31.7 ‰, respectively). The same is observed for simulated  
26  $\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}(FA)$  values (Figs. 5f and 5h). From Figs. 44f and 44I, we observe that  
27 wintertime  $\Delta^{17}\text{O}$  values in atmospheric and skin layer nitrate are reasonably well reproduced  
28 while most of the discrepancies are observed in summer.

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29



### 3.3.8 On the discrepancies between simulated and observed $\Delta^{17}\text{O}$ values

In the previous section, we have shown that the model reproduces well the winter  $\Delta^{17}\text{O}$  values as well as the variations in  $\Delta^{17}\text{O}$  values in the different compartments. However, a quantitative transcription of the information harbored by the oxygen isotopes is not achieved yet by TRANSITS. In particular, the summer  $\Delta^{17}\text{O}$  values are 8 to 10 % lower in the simulations than in the observations (Fig. 44). We recall that a number of simplifications have been made in the description of the local cycling and oxidation of  $\text{NO}_2$ , thus leading to the simulation of  $\Delta^{17}\text{O}$  values which must be considered as lower bounds.

First, the local oxidation of  $\text{NO}_2$  has been assumed to only occur through the daytime channel, i.e. through the oxidation by OH. In order to verify this hypothesis, we calculate  $r(\text{OH vs O}_3) = v(\text{OH}) / (v(\text{OH}) + v(\text{O}_3))$ , the relative apportioning of the daytime and nighttime  $\text{NO}_2$  oxidation channel, with the assumption that the latter occurs through  $\text{NO}_2 + \text{O}_3$ . For the calculation of  $r(\text{OH vs O}_3)$ , we use kinetic rate constants from Atkinson et al. (2004), ozone mixing ratios from Legrand et al. (2009) and OH mixing ratios are extrapolated from  $J(\text{NO}_2)$  calculated by TRANSITS and using the relationship  $[\text{OH}]/(\text{molecule m}^{-3}) = 2.5 \times 10^{14} \times J(\text{NO}_2)/\text{s}^{-1}$  (Kukui et al., 2014). For the realistic DC simulation,  $r(\text{OH vs O}_3)$  is higher than 0.95 from the fourth week after sunrise to the second week before sunset, i.e. for more than 90 % of the sunlit season. We also note that for the periods when  $r(\text{OH vs O}_3) < 0.95$ , the actinic flux is at maximum 6 % of the maximum actinic flux calculated for summer solstice. The calculation of a *FP*-weighted average of  $r(\text{OH vs O}_3)$  gives 99 % which means that over the sunlit season, the daytime oxidation channel of  $\text{NO}_2$  is almost 100 times faster than the nighttime oxidation channel. This result supports our choice of the simple representation of  $\text{NO}_2$  oxidation (by OH only) in TRANSITS and cannot explain the discrepancy in the  $\Delta^{17}\text{O}$  values simulated in summer. However, we acknowledge that species such as halogen oxides (denoted XO) could compete with OH in the oxidation of  $\text{NO}_2$ , thus importing high  $\Delta^{17}\text{O}$  values (Savarino et al., submitted).

Secondly, the calculation of  $\Delta^{17}\text{O}(\text{OH})$  has been simplified by assuming a constant value throughout the entire sunlit season. Given the low temperatures at the beginning and end of the sunlit season, we acknowledge that  $\Delta^{17}\text{O}(\text{OH})$  values may be higher at these periods because of the less efficient isotopic exchange in the removal of the  $\Delta^{17}\text{O}$  by OH inherited during its formation and because of the potential higher contribution of ozone photolysis in its production (Morin et al., 2011).

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1 Thirdly, the cycling of  $\text{NO}_2$  is assumed to be in photochemical-steady state and therefore  
2  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$  can be calculated following Eq. (7). For the DC realistic simulation, the  
3 computed  $\alpha$  variable varies in the range 0.80–1 with the minimum value calculated a few weeks  
4 after summer solstice when  $\text{O}_3$  mixing ratio reach its minimum (Legrand et al., 2009), and the  
5 maximum value calculated at the beginning and at the end of the sunlit season. The *FP*-  
6 weighted annual average value of  $\alpha$  is 0.86, which shows that the Leighton cycle is significantly  
7 perturbed by  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  and the transfer of the  $^{17}\text{O}$ -excess harbored by ozone to  $\text{NO}_2$  is  
8 not 100 % efficient. The hypothesis of an annually constant BrO mixing ratio of 2.5 pptv is  
9 crude because it must be lower at the beginning and end of the sunlit season. However, we  
10 observe that BrO marginally contributes to  $\alpha$  at these periods. Also, while a TRANSITS  
11 simulation with  $\alpha$  set to 1 allows a better agreement with the observations, the simulated  $\Delta^{17}\text{O}$   
12 values are still too low (e.g. in this case, the minimum summertime  $\Delta^{17}\text{O}$  values in skin layer,  
13 atmospheric and archived nitrate are 24.3 ‰, 25.4 ‰ and 20.0 ‰, respectively). This small  
14 experiment indicates that our current knowledge of the  $\text{NO}_x$  processing at Dome C is not  
15 complete and that some of our hypothesis should not be valid. In particular, the hypothesis of  
16 the photochemical steady-state of  $\text{NO}_x$  could be questioned. Indeed, we recall that the  $\text{NO}_x/\text{HO}_x$   
17 chemistry at Dome C is not yet completely understood (Kukui et al., 2014 and OPALE special  
18 issue) and a nitrogen species ( $\text{HNO}_4$  or unknown species) is expected to disturb the  $\text{NO}_x$   
19 photochemical cycle leading to the high  $\text{NO}_2/\text{NO}$  ratio observed by Frey et al., [2014–2015](#)  
20 and/or to participate in the oxidation of  $\text{NO}_2$  (via e.g. XO, Savarino et al., submitted).

21 Fourthly, the  $\Delta^{17}\text{O}$  value associated with the stratospheric flux of nitrate could be higher than  
22 the 42 ‰ value used in our simulations and initially suggested by Savarino et al. (2007). In  
23 particular, it could explain the 2–3 years period observed in  $\Delta^{17}\text{O}(\text{NO}_3^-)$  from snow pits at South  
24 Pole (McCabe et al., 2007) and at Dome C (Frey et al., 2009; Erbland et al., 2013). Also, the  
25 model would benefit from a better description of the timing of the long-distance transport flux  
26 of nitrate and the time series of the  $\Delta^{17}\text{O}$  value associated with it both of which were set constant  
27 throughout the season in our simulations.

28 While a number of isotopic information are still required to produce more realistic simulations  
29 at Dome C, we acknowledge that the most critical requirement is a better understanding of the  
30  $\text{NO}_x$  chemistry on the Antarctic plateau. Integrating a more realistic chemistry in TRANSITS  
31 will probably amplify the intense  $\text{NO}/\text{NO}_2$  cycling in the atmosphere and not fundamentally  
32 change the nature of the processes at play at the air-snow interface of DC. However, we

1 anticipate that the type of archived information below the photic zone will not change, mostly  
2 because the seasonal  $\Delta^{17}\text{O}$  variations in atmospheric and skin layer nitrate are well reproduced.

3

#### 4 **4 A framework for the interpretation of nitrate isotope records in ice cores**

5 In section 3, we have run a DC realistic simulation as well as simulations representing various  
6 sites in East Antarctica. We have shown that the model reproduced reasonably well the  
7 available mass and isotopic observations. While a quantitative reproduction of  $\Delta^{17}\text{O}$  values in  
8 atmospheric and skin layer nitrate could not be achieved (mostly because of a lack of  
9 understanding of the  $\text{NO}_x$  chemistry at Dome C), we have shown that variations in  $\Delta^{17}\text{O}$  values  
10 in these compartments were well reproduced.

11 In this section, we develop a framework for the interpretation of nitrate records in ice cores in  
12 the case where Dome C conditions apply. To this end, a large number of sensitivity tests of the  
13 TRANSITS model were run. Potentially measurable quantities in ice cores are  $\omega(\text{FA})$ ,  $\delta^{15}\text{N}(\text{FA})$   
14 and  $\Delta^{17}\text{O}(\text{FA})$  (e.g. Hastings et al., 2005, Frey et al., 2009). Given snow accumulation rates  
15 derived independently, one can also obtain  $\text{FA} = \omega(\text{FA}) \times A$ .

#### 16 **4.1 Parameters and variables controlling FA and $\delta^{15}\text{N}(\text{FA})$**

##### 17 **4.1.1 Sensitivity tests: description and results**

18 The sensitivity of the model is tested in simple cases where single variables and parameters are  
19 changed. For each simulation, the model was run for 25 years (i.e. until convergence). The  
20 realistic simulation for DC is used as the reference simulation. Tab.5 provides an overview of  
21 the variations imposed on the tested variables and parameters. The five following variables and  
22 parameters have been set to 0 (Tab.5):  $^{15}\epsilon_{\text{dep}}$ ,  $\Delta^{17}\text{O}(\text{FS})$ ,  $\Delta^{17}\text{O}(\text{FT})$ ,  $\Delta^{17}\text{O}(\text{OH})$  and  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ .  
23 The  $\delta^{15}\text{N}(\text{FS})$  and  $\delta^{15}\text{N}(\text{FT})$  parameters have been changed to 119 ‰ and 100 ‰, respectively.  
24 The parameters  $FPI$  and  $h_{\text{AT}}$  were multiplied by a factor 10. The mixing ratios of  $[\text{BrO}]$ ,  $[\text{O}_3]$ ,  
25  $[\text{HO}_2]$  and  $[\text{CH}_3\text{O}_2]$  were multiplied by a factor 2. The nine following variables and parameters  
26 have been changed by +20 %:  $FS/FPI$ ,  $f_{\text{cage}}$ ,  $f_{\text{exp}}$ ,  $A$ ,  $\rho$ ,  $k$ ,  $q$ ,  $\Phi$  and  $D$ . The sensitivity to the snow  
27 accumulation distribution in the year has been tested by running the model with summer snow  
28 accumulation rates two times higher than the winter rates and vice versa. The sensitivity to  $T$   
29 has been tested by shifting the observed atmospheric temperature time series by -10 K. The  
30 model sensitivity to the ozone column has been run for four simulations: with constant ozone

1 columns of 100 DU, 300 DU and 500 DU as well as with an ozone hole of 100 DU from Aug.  
2 to Nov. and an ozone column of 300 DU the rest of the time. Last, the sensitivity of the model  
3 to the atmospheric nitrate concentrations has been tested by running it with concentrations ten  
4 times higher than in the realistic DC simulation. The total number of simulations is then 31,  
5 which includes the reference simulation.

6 For each test, the following outputs ( $FA$ ,  $FA/FPI$ ,  $\delta^{15}N(FA)$  and  $\Delta^{17}O(FA)$ ) were calculated.  
7 The description and results of the tests scenarios are given in Tab.5. As an example and a  
8 guideline to read Tab.5, we describe the result for the test where the snow accumulation rate  
9 was changed. The value used in the reference simulation is  $28 \text{ kg m}^{-2} \text{ a}^{-1}$  and that of the tested  
10 scenario is 20 % greater (i.e.  $33.6 \text{ kg m}^{-2} \text{ a}^{-1}$ ). Tab.5 indicates that such an increase in  $A$  leads  
11 to an increase of the archived nitrate mass flux from 1.77 % to 3.90 % of the primary nitrate  
12 mass flux.  $\Delta^{17}O$  in the archived nitrate is increased by 0.8 ‰. Conversely,  $\delta^{15}N$  in the archived  
13 nitrate is decreased by 53.8 ‰ from 317.7 ‰ to 263.9 ‰.

14 Table 5 shows that two parameters and variables have no impact at all on the archived nitrate:  
15  $h_{AT}$  and  $\gamma(\text{NO}_3)$ . The reason is that the nitrate mass in the atmospheric box is negligible when  
16 compared to the nitrate reservoir in snow as discussed previously (section 3.3.5). The parameter  
17  $FPI$  is the only one affecting  $FA$ , while  $FA$  and  $FPI$  are linearly linked (i.e.  $FA/FPI$  remains  
18 constant), but this does not modify  $\delta^{15}N(FA)$ . The  $\delta^{15}N$  signatures in the primary nitrate sources  
19 ( $\delta^{15}N(FS)$  and  $\delta^{15}N(FT)$  and the  $^{15}\text{N}/^{14}\text{N}$  fractionation constant associated with deposition  
20 ( $^{15}\epsilon_{\text{dep}}$ ) have an impact on  $\delta^{15}N(FA)$ . Likewise, some parameters only impact  $\Delta^{17}O(FA)$  such as  
21 the  $\Delta^{17}O$  signature in the primary nitrate sources ( $\Delta^{17}O(FS)$  and  $\Delta^{17}O(FT)$ ),  $\Delta^{17}O$  of bulk ozone,  
22  $\Delta^{17}O$  of OH and parameters and variables driving the local cycling and oxidation of  $\text{NO}_2$ :  $[\text{O}_3]$ ,  
23  $[\text{BrO}]$ ,  $[\text{HO}_2]$ ,  $[\text{CH}_3\text{O}_2]$  and  $T$ .

24 The other parameters and variables impact at the same time  $FA$ ,  $FA/FPI$ ,  $\delta^{15}N(FA)$  and  
25  $\Delta^{17}O(FA)$ . These are:  $f_{\text{cage}}$ ,  $f_{\text{exp}}$ ,  $A$ ,  $\rho$ ,  $k$ ,  $q$ ,  $\Phi$ ,  $D$ ,  $FS/FPI$ , the snow accumulation distribution and  
26 the  $\text{O}_3$  column.

#### 27 **4.1.2 Modified Rayleigh plots**

28 From ice cores, one can measure  $\delta^{15}N(FA)$ ,  $\Delta^{17}O(FA)$ ,  $\omega(FA)$  and the annual snow  
29 accumulation rates ( $A$ ) thus allowing the calculation of  $FA = \omega(FA) \times A$ . In this section and the  
30 following, we attempt to provide an interpretation for  $\delta^{15}N(FA)$  values measured from ice cores.  
31 To this end, we use a data representation which we term “modified Rayleigh plot” where

1  $\ln(\delta^{15}\text{N}(FA) + 1)$  is plotted against  $\ln(FA)$  rather than  $\ln(\omega(FA))$ , since it includes the variability  
2 in  $A$  in contrast to  $\omega(FA)$ . Fig. 9 summarizes the results obtained for most of the sensitivity tests  
3 which impact  $FA/FPI$ ,  $FA$  and  $\delta^{15}\text{N}(FA)$ , i.e. tests where the following variables are changed :  
4  $\Phi$ ,  $A$ ,  $\rho$ ,  $k$ ,  $q$ ,  $f_{\text{cage}}$ ,  $f_{\text{exp}}$ ,  $D$ ,  $FS/FPI$ ,  $FPI$ ,  $\text{O}_3$  column and the snow accumulation distribution in  
5 the year. The thick black dashed curve in Fig. 9 represents the DC realistic simulation in which  
6  $\Phi$  is varied to obtain changes in  $FA$  and  $\delta^{15}\text{N}(FA)$ . The curve is almost linear with a slope of -  
7 0.064 passing through the “starting point” whose coordinates are  $(\ln(FPI), \ln(\delta^{15}\text{N}(FPI) + 1))$ .  
8 For instance, this means that a decrease in the archived flux ( $FA$ , i.e. changes in  $FA/FPI$ )  
9 corresponds to an increase in  $\delta^{15}\text{N}(FA)$ .

10 Most of the sensitivity simulation outputs fall on the thick black dashed curve, which represents  
11 the DC realistic simulation. We also observe from Fig. 9 that some simulations fall on curves  
12 which have different slopes or which have the same slope but different starting points. The  
13 parameters and variables are therefore sorted in 3 groups: those which control the “starting  
14 point”, those which control the slope in the modified Rayleigh plot and those which control the  
15 horizontal and vertical distances from the starting point, i.e. the final position on the curve.

#### 16 **4.1.3 Controls on the “starting point”**

17 Fig. 9 shows that the starting point is determined by  $FPI$  and  $\delta^{15}\text{N}(FT)$  and  $\delta^{15}\text{N}(FS)$ . On one  
18 hand, changes in  $FPI$  lead to a horizontal shift of the starting point (green star in Fig. 9) and, all  
19 other things being equal, to a horizontal shift of the entire line in this plot. On the other hand,  
20 changes in the  $\delta^{15}\text{N}$  value in the primary input ( $\delta^{15}\text{N}(FT)$  and  $\delta^{15}\text{N}(FS)$ ) lead to a vertical shift  
21 of the starting point and the entire curve. Changes in the  $f_{\text{exp}}$  also result in a slight horizontal  
22 shift of the simulated “archived point”. Indeed,  $f_{\text{exp}}$  sets the net horizontal export of nitrate from  
23 the atmospheric box, which results in more or less of the primary input flux lost through this  
24 process. In the case of an increasing  $f_{\text{exp}}$  parameter, the “apparent”  $FPI$  is therefore shifted to  
25 lower  $FPI$  values.

26 Sensitivity tests where  $\delta^{15}\text{N}(FT)$  and  $\delta^{15}\text{N}(FS)$  were shifted by +100 ‰ show that significant  
27 amounts of the nitrogen signatures of the primary nitrate inputs are preserved (71 % and 58 %,   
28 respectively, Tab.5), even if the recycling of nitrate has led to a 300 ‰ increase in  $\delta^{15}\text{N}(FA)$ .  
29 Therefore,  $\delta^{15}\text{N}(FA)$  harbors a fraction of the nitrogen isotopic signature of the primary inputs  
30 of nitrate but we note that it remains almost insignificant given the observed low variability of  
31  $\delta^{15}\text{N}(FT)$  ([-10, +10] ‰, Morin et al., 2009).

#### 4.1.4 Controls on the slope

Figure 9 shows that only the ozone column controls the slope of the curve. The spectral distribution of the actinic flux determines the  $^{15}\text{N}/^{14}\text{N}$  fractionation constant associated with nitrate photolysis ( $^{15}\epsilon_{\text{pho}}$ ) (Frey et al., 2009) and hence the slope of the curve. In the case of the DC reference simulation, a yearly mean apparent fractionation constant ( $^{15}\epsilon_{\text{app}}$ ) of -55.1 ‰ was calculated for  $^{15}\epsilon_{\text{pho}}$  ranging from -52.9 to -78.8 ‰ (Tab.5). The variability of the curvature of the thick back curve representing the DC reference simulation in Fig. 9 is linked to the greater incorporation of the summertime value of  $^{15}\epsilon_{\text{pho}}$  (Fig. 5d): when  $FA/FPI$  increases,  $^{15}\epsilon_{\text{pho}}$  gets less negative and the curvature decreases. Therefore, the slope of the thick dashed lines in the modified Rayleigh plots is slightly more negative (-0.064 = -64 ‰) than  $^{15}\epsilon_{\text{app}}$ .

Lower ozone columns have a strong impact on  $FA$  and  $\delta^{15}\text{N}(FA)$ :  $FA$  is lower while  $\delta^{15}\text{N}(FA)$  is higher (Fig. 9). The first effect is explained by higher amounts of UV radiation which reach the ground and so increase the photolysis rates. The second effect is linked to the fact that a lower ozone column leads to less negative  $^{15}\epsilon_{\text{pho}}$  values, as observed in spring during the ozone hole period (Figs. 3 and 5d). Indeed, a lower ozone column allows UV radiations of shorter wavelengths in the 280–350 nm range to reach the ground, i.e. a shift to the blue of the UV spectra, therefore resulting in less negative  $^{15}\epsilon_{\text{pho}}$  values (Frey et al., 2009). Referring to Eq. (2), our sensitivity tests reveals that changes in the ozone column result in changes in UV flux (i.e. in  $f$ ) which overweight the effect due to the UV spectra shift (i.e. in  $^{15}\epsilon_{\text{pho}}$ ). From our sensitivity tests, we also observe that an ozone hole in late winter/spring (Aug. to Nov.) significantly imprints  $\delta^{15}\text{N}(FA)$  (Fig. 9). Therefore, we suggest that  $\delta^{15}\text{N}(FA)$  archived over the last decades at Dome C and other East Antarctic plateau sites could potentially be imprinted by changes in the ozone column, especially in Spring when stratospheric ozone destruction processes occur.

#### 4.1.5 Controls on the distance from the starting point and along the slope

In the modified Rayleigh plot, the horizontal distance from the starting point is  $\ln(FA) - \ln(FPI) = \ln(FA/FPI)$ , i.e. the horizontal distance from the starting point is directly linked to the trapping efficiency. This quantity is therefore equivalent to the  $f$  term used in Eq. (2) because it reflects the nitrate fraction remaining in snow below the photic zone. The trapping efficiency and the intensity of the photolysis are linked because a more intense photolysis is necessary to lead to a lower nitrate trapping efficiency.

1 In the modified Rayleigh plot, the vertical distance from the starting point is  $\ln(\delta^{15}\text{N}(FA) + 1)$   
2  $-\ln(\delta^{15}\text{N}(FPI) + 1)$ . Fig. 9 shows that, at first order, the vertical and horizontal distance from  
3 the starting point are linked by the slope. This means that at a given slope in the modified  
4 Rayleigh plot, i.e. at a given spectral distribution of the actinic flux,  $\ln(\delta^{15}\text{N}(FA) + 1)$  is linearly  
5 linked with  $\ln(FA/FPI)$ , i.e.  $\delta^{15}\text{N}(FA)$  is linked with the trapping efficiency.

6 Our sensitivity tests have shown that the nitrate trapping efficiency is controlled by  $\Phi, A, \rho, k,$   
7  $q, f_{\text{cage}}, f_{\text{exp}}, D, FS/FPI, \text{O}_3$  column and the snow accumulation distribution in the year. Indeed,  
8  $\Phi, f_{\text{cage}}, q$  and  $\text{O}_3$  column are key parameters and variables in controlling the photolytic mass  
9 loss while  $A, \rho, k, D$  and the seasonality in snow accumulation determine nitrate exposure time  
10 to the actinic flux. Considering the seasonality of snow accumulation, we observe that it plays  
11 a minor role in setting  $FA/FPI$  and hence  $\delta^{15}\text{N}(FA)$ . The reason is that, in DC conditions, nitrate  
12 residence time in the photic zone is very long and set by the other parameters and variables at  
13 play in the photolytic process. The same applies to the  $FS/FPI$  ratio: the impact on nitrate  
14 trapping efficiency is small.

15 The case of the export flux parameter,  $f_{\text{exp}}$ , is different. Indeed, it does not impact the residence  
16 time of nitrate in the photic zone, nor does it impact its photolytic loss. However, an increase  
17 in  $f_{\text{exp}}$  results in a greater export of atmospheric nitrate, which is depleted in  $^{15}\text{N}$  with respect to  
18 nitrate in snow (data not shown in Tab.5). In fact, the increase in  $f_{\text{exp}}$  also leads to higher  
19  $\delta^{15}\text{N}(FA)$  and  $\delta^{15}\text{N}(FE)$  values. In the two simulations tested,  $\delta^{15}\text{N}(FE)$  is always smaller than  
20  $\delta^{15}\text{N}(FPI)$ , which means that the “removal” of nitrate featuring  $\delta^{15}\text{N}(FE) \leq \delta^{15}\text{N}(FPI)$  is  
21 compensated by the increase of  $\delta^{15}\text{N}$  in the archived nitrate. This increase in  $\delta^{15}\text{N}(FA)$  is  
22 therefore not due to an increased photolysis intensity but to the isotopic mass balance.

23 The parameters and variables  $\Phi, k, A, \rho$  and  $q$  have the largest impact on the nitrate trapping  
24 efficiency ( $FA/FPI$ ), which mostly impacts  $\delta^{15}\text{N}(FA)$ . The fact that they control  $FA/FPI$  and  
25  $\delta^{15}\text{N}(FA)$  to a similar extent is not surprising since  $k, A, \rho$  and  $q$  are intimately linked together  
26 in determining the residence time in the photic layer and so the exposure time of nitrate to near-  
27 surface conditions.

28 In this paper, the model does not aim at representing the counter ion of nitrate. However, we  
29 acknowledge that the diffusion of nitrate may be different depending on the nature of its counter  
30 ion ( $\text{H}^+$  or, e.g.  $\text{Ca}^{2+}$ ), especially when glacial conditions are considered (Röthlisberger et al.,  
31 2000).

#### 4.1.6 Method to interpret $FA$ and $\delta^{15}N(FA)$ measured in ice cores

In this section we summarize our recommended approach to interpret nitrate isotope records in ice cores. The approach [presented here](#) is valid provided that pieces of evidence show that the nitrate recycling (i.e. loss, local oxidation and deposition) observed today has also occurred in the past. In glacial conditions, nitrate archived in ice cores is mostly associated with calcium ions and it is known that dust inputs to Antarctica were high (Wolff et al., 2010). In such conditions, it is likely that atmospheric nitrate fixed to dust particles which could eventually be embedded in a snow crystal, thus increasing nitrate cage recombination effects and significantly hampering the release of nitrate photo-products to the atmosphere. The ice core interpretation method present here must therefore be followed in the case where ~~The measurement of~~ elevated  $\delta^{15}N(FA)$  values are measured, thus providing an ~~could be an~~ evidence for the efficient photolytic nitrate removal from snow.

Information potentially accessible from ice cores are  $\omega(FA)$  and  $\delta^{15}N(FA)$ . Knowledge on the past snow accumulation rates (deduced from other proxies) allow the calculation of  $FA = \omega(FA) \times A$ . If  $FA$  and  $\delta^{15}N(FA)$  data align in the modified Rayleigh plot, one can deduce that the ozone column is likely to have remained constant through time and its value can be inferred from the slope of the curve (e.g. lower right panel in Fig. 9). In this case as well,  $FPI$  is likely to have remained constant through time and its value can be retrieved, provided that  $\delta^{15}N(FPI)$  have remained constant as well and that one can assume its value. If the data do not align in the modified Rayleigh plot, it is likely that either or both the ozone column and  $FPI$  have varied over time. If an assumption on the ozone column can be made or if this information can be obtained from other considerations, one can determine past changes in  $FPI$  provided that an assumption on  $\delta^{15}N(FPI)$  can be made. Fig. 11 gives a schematic of the method to determine  $FPI$  from the measurement of  $\omega(FA)$  and  $\delta^{15}N(FA)$  in ice cores. As discussed above, a portion of  $\delta^{15}N(FT)$  and  $\delta^{15}N(FS)$  is left in  $\delta^{15}N(FA)$ . However,  $\delta^{15}N(FT)$  and  $\delta^{15}N(FS)$  are small when compared to the ca. 250 ‰ added under the effect of nitrate recycling at the air-snow interface, thereby erasing information on  $\delta^{15}N(FT)$  and  $\delta^{15}N(FS)$ . In other words,  $\delta^{15}N(FA)$  is almost insensitive to change of  $\delta^{15}N(FT)$  and  $\delta^{15}N(FS)$ .

#### 4.2 Parameters and variables controlling $\Delta^{17}O(FA)$

The parameters and variables controlling  $\Delta^{17}O(FA)$  can be sorted in four groups:



- 1 -  $f_{\text{cage}}$ , which controls the cage effects,
- 2 - those which impact  $FA/FPI$ , which sets the magnitude of loss and hence the
- 3 magnitude of the cage effects,
- 4 -  $\Delta^{17}\text{O}(FT)$  and  $\Delta^{17}\text{O}(FS)$ , which set  $\Delta^{17}\text{O}$  in the primary source of nitrate
- 5 -  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$ ,  $\Delta^{17}\text{O}(\text{OH})$ ,  $[\text{BrO}]$ ,  $[\text{HO}_2]$ ,  $[\text{CH}_3\text{O}_2]$ ,  $[\text{O}_3]$  and  $T$  which set  $\Delta^{17}\text{O}$  in the
- 6 secondary source of nitrate in the atmosphere.

#### 7 **4.2.1 Correction of the reduction in $\Delta^{17}\text{O}(FA)$ imposed by cage effects**

8 We have shown that cage recombination effects following nitrate photolysis in snow lead to  
 9 positive simulated  $^{17}E_{\text{app}}$  values in snow. For instance, for DC realistic conditions (i.e. for  $f_{\text{cage}}$   
 10  $= 0.15$  and  $FA/FPI = 1.8\%$ ),  $\Delta^{17}\text{O}(FA)$  is reduced by  $\approx 6\%$  because of cage effects (Fig. 6c).  
 11 To calculate the reduction in  $\Delta^{17}\text{O}(FA)$  as a result of cage recombination effects, we have run  
 12 TRANSITS in the DC realistic simulation by varying  $\Phi$  from 0 to 0.036 and with an  $f_{\text{cage}}$   
 13 parameter set to 0 and 0.15 in order to switch the cage effects on and off, respectively.

14 We denote  $\Delta^{17}\text{O}(FA, \text{corr.})$ , the  $\Delta^{17}\text{O}(FA)$  value corrected from cage effects, which was  
 15 estimated here by setting  $f_{\text{cage}} = 0$ . Figure 10c shows that for  $\ln(FA/FPI) < -2$  (i.e.,  $FA/FPI < 14$   
 16 %), the  $\Delta^{17}\text{O}(FA, \text{corr.})/\Delta^{17}\text{O}(FA)$  ratio is linear with  $\ln(FA/FPI)$ :  $\Delta^{17}\text{O}(FA, \text{corr.})/\Delta^{17}\text{O}(FA) =$   
 17  $-0.063 \times \ln(FA/FPI) + 1.052$ . In section 4.1.6, we have shown that the  $FA/FPI$  ratio can be  
 18 retrieved from the measurement of  $\delta^{15}\text{N}(FA)$  given an hypothesis on the  $\text{O}_3$  column and  
 19  $\delta^{15}\text{N}(FPI)$ . Using this approach,  $\Delta^{17}\text{O}(FA)$  is corrected from the cage effect.

20 From Figure 10b, we observe that  $\Delta^{17}\text{O}(FA, \text{corr.})$  reaches a plateau at around 23.5‰ for low  
 21 nitrate trapping efficiencies ( $\ln(FA/FPI) < -3$ , i.e.  $FA/FPI < 5\%$ ). Although we anticipate that  
 22  $\Delta^{17}\text{O}(FA, \text{corr.})$  is mostly controlled by the local cycling and oxidation of  $\text{NO}_2$  (as previously  
 23 observed from sensitivity tests), there is still the need to separate the  $\Delta^{17}\text{O}$  impact of local  
 24 cycling and oxidation of  $\text{NO}_2$  from those of  $\Delta^{17}\text{O}(FT)$  and  $\Delta^{17}\text{O}(FS)$ .

#### 25 **4.2.2 Contributors to $\Delta^{17}\text{O}(FA, \text{corr.})$**

26 In this section, we consider  $\Delta^{17}\text{O}(FT)$ ,  $\Delta^{17}\text{O}(FS)$ ,  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$  and  $\Delta^{17}\text{O}(\text{add. O})$  which  
 27 impact  $\Delta^{17}\text{O}(FA, \text{corr.})$ . To determine the scaled contributions of the variable  $\Delta^{17}\text{O}(X)$ , we have  
 28 run the TRANSITS model with this variable set to 0. We denote  $\overline{\Delta^{17}\text{O}(FA)}$  the  $\Delta^{17}\text{O}(FA)$  value  
 29 obtained when  $\Delta^{17}\text{O}(X)$  has been set to 0. From the previous section, we can calculate

1  $\overline{\Delta^{17}\text{O}(\text{FA, corr.})}$  based on the computed  $\text{FA}/\text{FPI}$  value. For  $\Delta^{17}\text{O}(\text{X})$ , we calculate the scaled  
2 contribution to  $\Delta^{17}\text{O}(\text{FA, corr.})$  as  $(\Delta^{17}\text{O}(\text{FA, corr.}) - \overline{\Delta^{17}\text{O}(\text{FA, corr.})}) / \Delta^{17}\text{O}(\text{X})$ .

3 Figure 10d shows the obtained scaled contributions to  $\Delta^{17}\text{O}(\text{FA, corr.})$ . For example, for  
4  $\ln(\text{FA}/\text{FPI}) < -3$ , we observe that the statistical contribution of the variable  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$  to  
5 the budget of  $\Delta^{17}\text{O}(\text{FA, corr.})$  is 55 %, which means that if  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS}) = 20$  ‰, then this  
6 variable will contribute to  $\Delta^{17}\text{O}(\text{FA, corr.})$  by as much as  $0.55 \times 20 = 11$  ‰. For the same nitrate  
7 trapping efficiency,  $\Delta^{17}\text{O}(\text{FT})$  contributes much less, i.e. by 13 % of  $\Delta^{17}\text{O}(\text{FT})$ , which is to say  
8 by 3.9 ‰ for  $\Delta^{17}\text{O}(\text{FT}) = 30$  ‰.

9 From the same panel, we observe that for  $\ln(\text{FA}/\text{FPI}) < -2$ , the scaled contributions of  
10  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$  and  $\Delta^{17}\text{O}(\text{add. O})$  to  $\Delta^{17}\text{O}(\text{FA, corr.})$  is greater than 50 % and 25 % of their  
11 respective values, i.e. a sum which is three times the scaled contributions of  $\Delta^{17}\text{O}(\text{FT})$  and  
12  $\Delta^{17}\text{O}(\text{FS})$ , which contribute to less than 14 % and 11 % of their respective values. This means  
13 that, in the conditions tested (i.e. low trapping efficiencies which characterize the Antarctic  
14 plateau),  $\Delta^{17}\text{O}(\text{FA, corr.})$  is poorly controlled by  $\Delta^{17}\text{O}(\text{FS})$  and  $\Delta^{17}\text{O}(\text{FT})$  and dominated by  
15 local cycling and oxidation of  $\text{NO}_2$ . We note that, for very low nitrate trapping efficiencies  
16 ( $\ln(\text{FA}/\text{FPI}) < -3$ ), the sum of the scaled contributions of  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS}) + \Delta^{17}\text{O}(\text{add. O})$  and  
17 of  $\Delta^{17}\text{O}(\text{FS}) + \Delta^{17}\text{O}(\text{FT})$  reach a plateau at 82 % and 18 %, respectively. From Fig. 10a, we  
18 observe that these plateaus are consistent with  $\overline{\text{ANR}(\text{FA})}$  values ( $\approx \text{FD}/\text{FPI}$ ) around 4, i.e. the  
19 archived nitrate has been recycled 4 times on average and is therefore mostly secondary nitrate  
20 which has been locally reformed

21 For low nitrate trapping efficiencies, we also observe that the scaled contribution of  $\Delta^{17}\text{O}(\text{FT})$   
22 increases while that of  $\Delta^{17}\text{O}(\text{FS})$  decreases. This is linked to the preferential incorporation, yet  
23 small, of the local  $\Delta^{17}\text{O}$  signature on the summertime primary source of nitrate.

24 Figure 10e represents an application of what precedes in the case of Dome C, i.e. using  
25  $\Delta^{17}\text{O}(\text{FT}) = 30$  ‰,  $\Delta^{17}\text{O}(\text{FS}) = 42$  ‰,  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS}) = 31.3$  ‰ and  $\Delta^{17}\text{O}(\text{add. O}) = 3$  ‰.  
26 Figure 10f reproduces the relationship between  $\delta^{15}\text{N}(\text{FA})$  and  $\text{FA}/\text{FPI}$  as a function of ozone  
27 column. In the case of the present-day DC conditions (realistic DC  $\text{O}_3$  column and  $\delta^{15}\text{N}(\text{FA})$  in  
28 range [151, 334] ‰, Fig. 7c), we find that the relative contribution of  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  
29  $\Delta^{17}\text{O}(\text{add. O})$ ,  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$  to  $\Delta^{17}\text{O}(\text{FA, corr.})$  are in the following ranges: [52, 55]  
30 %, [26, 28] %, [11, 13] % and [5, 9] %, respectively. In DC conditions,  $\Delta^{17}\text{O}(\text{FA, corr.})$  therefore  
31 harbors almost two third of the oxygen isotope signature of the local cycling and oxidation of  
32  $\text{NO}_2$  and the remaining signature of primary inputs of nitrate is small. This is such because the

1 archived nitrate has undergone 4.0 cycles before being ultimately trapped in snow below the  
2 photic zone (Fig. 10a).

3

#### 4 **4.2.3 Method to interpret $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$ derived from ice cores** 5 **measurements**

6 In this section, we suggest a method to interpret  $\Delta^{17}\text{O}(\text{FA})$  values measured from ice cores. In  
7 section 4.2.1, we have provided a method to correct  $\Delta^{17}\text{O}(\text{FA})$  from cage effects from the  
8 knowledge of the variations in nitrate trapping efficiency ( $\text{FA}/\text{FPI}$ ) which, we recall, can be  
9 determined from  $\delta^{15}\text{N}(\text{FA})$  values and hypothesis on past variations in  $\delta^{15}\text{N}(\text{FPI})$  and in the  
10 ozone column (see also Fig. 11). In this way, we obtain a time series of  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  in the  
11 past, a variable which is only influenced by past changes in  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  $\Delta^{17}\text{O}(\text{add. O})$ ,  
12  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$  and that of their scaled contributions, as shown in the previous section.

13 To determine the variations in the scaled contributions of  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  $\Delta^{17}\text{O}(\text{add. O})$ ,  
14  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$ , we use the nitrate trapping efficiency determined in section 4.1.6.  
15 Assumptions or evidence on past changes in one or several of the four variables controlling  
16  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  (i.e.  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  $\Delta^{17}\text{O}(\text{add. O})$ ,  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$ ) allow to  
17 determine past changes in the other ones. For instance, assuming that  $\Delta^{17}\text{O}(\text{add. O})$ ,  $\Delta^{17}\text{O}(\text{FT})$   
18 and  $\Delta^{17}\text{O}(\text{FS})$  have remained constant over time allows to determine past changes in the local  
19 cycling of  $\text{NO}_2$  above the East Antarctic plateau.

20 Fig. 11 gives a schematic of the method to determine  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  as well as in the scaled  
21 contributions of  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  $\Delta^{17}\text{O}(\text{add. O})$ ,  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$  from the measurement  
22 of  $\omega(\text{FA})$ ,  $A$ ,  $\delta^{15}\text{N}(\text{FA})$  and  $\Delta^{17}\text{O}(\text{FA})$  in ice cores.

23 If we assume that modern conditions in East Antarctica have prevailed in the past, we anticipate  
24 from Fig. 10 that almost two third of the variations  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  are the result of variations  
25 in  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$  and  $\Delta^{17}\text{O}(\text{add. O})$ . In this case, the potential for  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  to trace past  
26 changes in atmospheric oxidation at the global scale is weak. However, in such conditions,  
27  $\Delta^{17}\text{O}(\text{FA}, \text{corr.})$  would rather hold information about the local and summertime atmospheric  
28 oxidation above the East Antarctic plateau.

29

## 1 5 Summary and conclusions

2 The TRANSITS model is a conceptual, multi-layer, 1-D isotopic model which represents the  
3 air-snow transfer of nitrate and its isotopic composition on the Antarctic plateau at around a  
4 one-week time resolution. It rests on the conceptual model initially proposed by Davis et al.  
5 (2008) and on the fact that nitrate photolysis is the process dominating nitrate mass loss at the  
6 low accumulation sites which characterize the Antarctic plateau (Frey et al., 2013; Erbland et  
7 al., 2013). The particularity of TRANSITS is its representation of the isotopic composition of  
8 nitrate ( $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ).

9 When using a realistic scenario representing the Dome C conditions, the model reproduces well  
10 the variations in concentrations and isotopic time series observed in the atmospheric and skin  
11 layer compartments, thus supporting the theory of Davis et al. (2008). While the nitrogen  
12 isotope ratio is well reproduced by the model, the simulated  $\Delta^{17}\text{O}$  data in the air-snow interface  
13 are lower than the observations. This has been attributed to simplifications in the description of  
14 the local cycling and oxidation of  $\text{NO}_2$ . One consequence is that simulated  $\Delta^{17}\text{O}$  values in the  
15 snowpack and in the archived nitrate are lower than the observations. Nevertheless, cage  
16 recombination effects occurring in snow are well reproduced by the model as shown by the  
17 agreement between the simulated and observed values of the apparent fractionation constant  
18 ( $^{17}E_{\text{app}}$ ). The representation of nitrate diffusion within the snowpack allows simulating nitrate  
19 mass fraction and isotope depth profiles, which are consistent with observations. Under the DC  
20 realistic simulation conditions, the quantum yield imposed to reproduce the observations  
21 (0.026) is compatible with the idea that nitrate lies in two different domains (Meusinger et al.,  
22 2014). The comparison of the simulated and observed  $\text{NO}_2$  fluxes shows that the simulation is  
23 9 to 18 times higher than the observed flux at Dome C in 2009-2010 and 2011-2012. This  
24 discrepancy could result from the simplifications made in the model regarding the fates of the  
25 nitrate photolysis products.

26 TRANSITS has been used to investigate the spatial variability in the mass and isotopic  
27 composition of the nitrate archived from the Antarctic coast to the plateau (Dome C to Vostok)  
28 obtained from 21 snow pits collected from 2007 to 2010 (Erbland et al., 2013). Using the  
29 realistic simulation and the snow accumulation range observed on the zone of interest (from 20  
30 to  $600 \text{ kg m}^{-2} \text{ a}^{-1}$ ), we have shown that, in present-day conditions, changes in snow accumulation  
31 rates are sufficient to explain the first order variations of  $\delta^{15}\text{N}$  in the archived nitrate. This  
32 suggests that the principles at the heart of the model (i.e. photolytic mass loss, isotopic

1 fractionation and exposure time of nitrate) are adequate. Moreover, the use of a nitrate primary  
2 input flux of  $8.2 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  is consistent with the observations.

3 We proposed some improvements and guidelines for future work on the TRANSITS model.  
4 First, the model requires that NO<sub>x</sub> chemistry at Dome C should be fully understood, in  
5 particular the high NO<sub>2</sub>/NO ratio observed (Frey et al., [2014](#)[2015](#)). Then, the model will benefit  
6 from the measurements of  $\Delta^{17}\text{O}(\text{NO})$ ,  $\Delta^{17}\text{O}(\text{NO}_2)$  or  $\Delta^{17}\text{O}$  in other key species participating in  
7 the oxidation scheme (HO<sub>2</sub>, RO<sub>2</sub>, BrO). Additional processes or mechanisms could be  
8 implemented, such as nitrate pools featuring different photolytic capacities, modeled by  
9 different quantum yield that would vary in space and time. Some additional parameters could  
10 also be taken into account such as the latitude of the simulated site to better represent plateau  
11 sites other than Dome C. The radiative transfer model TARTES (Libois et al., 2013) could be  
12 explicitly incorporated into TRANSITS. This would allow the modeling of the e-folding  
13 attenuation depth dependence with respect to the physical and chemical properties of the  
14 snowpack. The explicit representation of the export and depositions fluxes (using horizontal  
15 and vertical air mass velocities, respectively) could also be explored as well as the explicit  
16 description of the erosion of the snow surface by the wind.

17 A framework for the interpretation of nitrate isotope records in ice cores is proposed. From ice  
18 cores, the following data are accessible:  $\omega(\text{FA})$ ,  $\delta^{15}\text{N}(\text{FA})$ ,  $\Delta^{17}\text{O}(\text{FA})$  and the annual snow  
19 accumulation rates. The interpretation framework described in this paper will be applicable to  
20 ice core records which display proofs of significant nitrate recycling, e. g. on the basis of  
21 elevated  $\delta^{15}\text{N}(\text{FA})$  values. In this case, sensitivity tests have shown that  $\delta^{15}\text{N}(\text{FA})$  is the result  
22 of a <sup>15</sup>N/<sup>14</sup>N fractionation constant which is set by the UV radiation spectrum (i.e. set by the  
23 ozone column above the site of interest). Indeed, the ozone column controls the slope in the  
24 “modified Rayleigh plot” introduced in this study. At a given ozone column,  $\delta^{15}\text{N}(\text{FA})$  is  
25 controlled by:

- 26 1. the nitrate trapping efficiency (i.e. the ratio of the archived flux versus the primary  
27 nitrate inputs,  $\text{FA}/\text{FPI}$ ) which determines the exposure time of nitrate and thus the  
28 intensity of nitrate recycling,
- 29 2. and, at a lesser extent, the  $\delta^{15}\text{N}$  of the primary sources of nitrate whose variations are  
30 negligible in comparison to the change produced by the photolysis loss.

1 We have observed that the major controls on  $FA/FPI$  are the photolytic quantum yield ( $\Phi$ ), the  
2 annual snow accumulation rate ( $A$ ), the snow density ( $\rho$ ), the photic zone compression factor  
3 ( $k$ ) and the actinic flux enhancement factor ( $q$ ), with equivalent relative impacts.

4 Given a constant actinic flux spectrum, the archived flux ( $FA$ ) is primarily controlled by the  
5 primary input flux and the trapping efficiency. Therefore, the plot of  $FA$  versus  $\delta^{15}N(FA)$  in the  
6 modified Rayleigh space is a good candidate to track modern or past changes in the spectral  
7 distribution of the UV received at ground, i.e. changes in the ozone column but also changes in  
8 the solar UV spectra. At a given spectral distribution of the actinic flux, past variations in  $FPI$   
9 can be reconstructed from  $FA$  and  $\delta^{15}N(FA)$  if  $\delta^{15}N(FPI)$  is known or assumed.

10 From the nitrate trapping efficiency ( $FA/FPI$ ), we have shown that we can deduce  $\Delta^{17}O(FA,$   
11 corr.) which represents the  $\Delta^{17}O$  value in the archived flux corrected from the cage  
12 recombination effects. To achieve this correction, the potential impact of nitrate speciation  
13 (association to  $H^+$  or, e.g.,  $Ca^{2+}$ ) on the cage effect should be considered (e.g. during glacial  
14 conditions). The variable  $\Delta^{17}O(FA, \text{corr.})$  is controlled by  $\Delta^{17}O(NO_2, \text{PSS}), \Delta^{17}O(\text{add. O}),$   
15  $\Delta^{17}O(FT)$  and  $\Delta^{17}O(FS)$  and the scaled contributions of each of these four variables has been  
16 determined as a function of  $FA/FPI$ . We have shown that these contributions are independent  
17 of the ozone column. Under the modern DC conditions, we have shown that the isotope mass  
18 balance of  $\Delta^{17}O(FA, \text{corr.})$  can be written as  $[52, 55] \% \times \Delta^{17}O(NO_2, \text{PSS}) + [26, 28] \% \times$   
19  $\Delta^{17}O(\text{add. O}) + [11, 13] \% \times \Delta^{17}O(FT) + [5, 9] \% \times \Delta^{17}O(FS)$ . These proportions result from  
20 the intense recycling cycles (on average, 4.0) present at low accumulation sites. As a  
21 consequence,  $\Delta^{17}O(FA, \text{corr.})$  is mostly driven by the  $\Delta^{17}O$  signature acquired during the  
22 summertime and local processing of  $NO_2$  in the DC atmosphere and only weakly by the  $\Delta^{17}O$   
23 signature of the primary nitrate fluxes ( $FT$  and  $FS$ ).

24 If the modern DC conditions applied to the past as well (i.e. important loss by photolysis  
25 followed by the local recycling of nitrate),  $\Delta^{17}O(FA, \text{corr.})$  obtained from ice cores drilled on  
26 the East Antarctic plateau is expected to deliver information about the oxidative chemistry  
27 occurring at the local and summertime scale rather than at the global scale. The reverse should  
28 therefore also be true. High accumulation sites with limited photolytic loss should deliver  
29 information about the oxidative chemistry of  $NO_x$  at the remote scale.

30

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1 **Tables**

2 Table 1. List of the acronyms used in this paper.

Compartment	Acronym	Unit	Definition
Atmosphere	$FS$	$\text{kgN m}^{-2} \text{a}^{-1}$	Stratospheric input flux
	$FT$	$\text{kgN m}^{-2} \text{a}^{-1}$	Tropospheric input flux
	$FPI$	$\text{kgN m}^{-2} \text{a}^{-1}$	Primary input flux ( $FPI = FS + FT$ )
	$FE$	$\text{kgN m}^{-2} \text{a}^{-1}$	Exported flux ( $FE = FPI - FA$ )
	$FA$	$\text{kgN m}^{-2} \text{a}^{-1}$	Archived flux
	$FD$	$\text{kgN m}^{-2} \text{a}^{-1}$	Deposited flux
	$FP$	$\text{kgN m}^{-2} \text{a}^{-1}$	Photolytic flux
	$\delta^{15}\text{N}(FX)$	‰	$\delta^{15}\text{N}$ in flux $FX$
	$\Delta^{17}\text{O}(FX)$	‰	$\Delta^{17}\text{O}$ in flux $FX$
	$\gamma(\text{NO}_3^-)$	$\text{ng m}^{-3}$	Atmospheric nitrate concentration
	$h_{AT}$	m	Height of the ABL
	$f_{\text{exp}}$	Adimensional	Exported fraction of the incoming fluxes to the atmospheric box
	$T$	K	Near ground atmospheric temperature
	$P$	mbar	Near ground atmospheric pressure
	$^{15}\epsilon_{\text{dep}}$	‰	$^{15}\text{N}/^{14}\text{N}$ fractionation constant associated with nitrate deposition
	$J(\text{NO}_2)$	$\text{s}^{-1}$	Photolytic rate constant of $\text{NO}_2$
	$\alpha$	Adimensional	Leighton cycle perturbation factor
	$\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}}$	‰	$^{17}\text{O}$ -excess in bulk ozone
	$\vartheta$	°	Solar zenith angle
	$I$	$\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$	Actinic flux
$q$	Adimensional	Actinic flux enhancement factor	
PSS	-	Photochemical Steady State	
Snow	$A$	$\text{kg m}^{-2} \text{a}^{-1}$	Annual snow accumulation rate
	$\rho$	$\text{kg m}^{-3}$	Snow density
	$f_{\text{cage}}$	Adimensional	Cage effect factor
	$D$	$\text{m}^2 \text{s}^{-1}$	Diffusion coefficient
	$\omega(\text{NO}_3^-)$	$\text{ng g}^{-1}$	Nitrate mass fraction
	$m_{50\text{cm}}(\text{NO}_3^-)$	$\text{mgN m}^{-2}$	Nitrate mass in the top 50 cm
	$\Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$	‰	$\Delta^{17}\text{O}$ <u>of nitrate</u> in the top 50 cm
	$\delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$	‰	$\delta^{15}\text{N}$ <u>of nitrate</u> in the top 50 cm
	$\Phi$	Adimensional	Quantum yield in nitrate photolysis
	$\sigma$	$\text{cm}^2$	Absorption cross section of $^{14}\text{NO}_3^-$
	$\sigma'$	$\text{cm}^2$	Absorption cross section of $^{15}\text{NO}_3^-$
	$k$	Adimensional	Photic zone compression factor
	$J$	$\text{s}^{-1}$	Photolytic rate constant of $^{14}\text{NO}_3^-$

Mis en forme : Exposant



$J'$	$s^{-1}$	Photolytic rate constant of $^{15}\text{NO}_3^-$
$\eta$	m	E-folding attenuation depth
$^{15}\epsilon_{\text{app}}$	‰	Apparent $^{15}\text{N}/^{14}\text{N}$ fractionation constant
$^{17}\epsilon_{\text{app}}$	‰	$^{17}\text{O}$ -excess apparent fractionation constant
$^{15}\epsilon_{\text{pho}}$	‰	$^{15}\text{N}/^{14}\text{N}$ fractionation constant associated with nitrate photolysis
<i>CYCL</i>	Adimensional	Average number of recyclings in a box
<del><math>\text{ANR}(FA)</math></del>	Adimensional	<del>Yearly</del> Average Number of Recyclings undergone by the archived nitrate

1  
2 Table 2. List of the physical and chemical processes included and excluded in TRANSITS.  
3 Physical and chemical processes are written in straight and italic font, respectively.

	Processes included	Processes excluded
Snow	Snow accumulation	Snow densification
	Macroscopic nitrate diffusion	Snow metamorphism (sublimation, melting)
		Snow erosion
		Snowpack ventilation
	<i>Nitrate UV-photolysis</i>	<i>Nitrate location changes</i>
	<i>Cage recombination effects</i>	<i>Nitrate saturation</i>
		<i>Physical release of <math>\text{HNO}_3</math></i>
		Variation of ABL
		<u>Change of actinic flux due to clouds and aerosol</u>
Atmosphere	Nitrate export	
	<i>Primary nitrate inputs (strato. and tropo.)</i>	
	<i><math>\text{HNO}_3</math> dry deposition</i>	
	<i>Local cycling of <math>\text{NO}_2</math> (conceptual)</i>	
	<i>Location oxidation of <math>\text{NO}_2</math> by OH (conceptual)</i>	
		<i>Nitrate wet deposition</i>
		<i>Formal atmospheric chemistry</i>

Mis en forme : Justifié

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5

1  
2 Table 3. Parameters and variables used for the realistic simulation of TRANSITS. Input time-  
3 variables and fixed parameters are written in bold.

Process		Realistic, DC	Realistic, EAP
Snow accumulation	$\rho$ / (kg m <sup>-3</sup> )		300
	$A$ / (kg m <sup>-2</sup> a <sup>-1</sup> )	28	[20 to 600]
HNO <sub>3</sub> deposition	Accu distribution	Uniform throughout the year	
	$10^3 \times \mathbf{^{15}E_{dep}}$		+10
Nitrate diffusion in snow	$D$ / (m <sup>2</sup> s <sup>-1</sup> )		$1.0 \times 10^{-11}$
TUV-snow parameters and variables	<b>Optical &amp; physical prop. snowpack</b>	DC snowpack, from France et al., 2011	
	O <sub>3</sub> column	DC observations 2000-2009	
Nitrate photolysis	$k$		1
	$\Phi$		0.026
	$\sigma$ and $\sigma'$	From Berhanu et al. (2014a)	
Cage effect	$q$		1
	$f_{cage}$		0.15
Cycling/oxidation of NO <sub>2</sub>	$10^3 \times \Delta^{17}\mathbf{O(H_2O)}$		0
	$[\mathbf{BrO}]$ / pptv	2.5 (Frey et al., 20154)	
	$[\mathbf{RO_2}]$ / (molecule m <sup>-3</sup> )	= $7.25 \times 10^{15} \times (J(\text{NO}_2) / \text{s}^{-1})$ (Kukui et al., 2014)	
	$[\mathbf{HO_2}]/[\mathbf{RO_2}]$	0.7 (Kukui et al., 2014)	
	$[\mathbf{O_3}]$ / ppbv	From Legrand et al. (2009)	
Atmospheric properties	$10^3 \times \Delta^{17}\mathbf{O(O_3)_{bulk}}$	25.2 (Savarino et al., submitted)	
	$10^3 \times \Delta^{17}\mathbf{O(OH)}$	3 (Savarino et al., submitted)	
Nitrate export	$T$ / K	Concordia AWS (8989) in 2009-2010	
	$P$ / mbar	Concordia AWS (8989) in 2009-2010	
Mass balance in the atmosphere	$f_{exp}$		20 %
	$FPI$ / (kgN m <sup>-2</sup> a <sup>-1</sup> )	$8.2 \times 10^{-6}$ (Muscari and de Zafra, 2003)	
	$FS/FPI$		50 %
	$FS$ distribution	Plateau from May 16 to October 18	
	$FT$ distribution	Uniform throughout the year	
	$h_{AT}$ / m		50
	$\gamma(\text{NO}_3^-)$		Idealized DC
	$10^3 \times \Delta^{17}\mathbf{O(FS)}$		42
	$10^3 \times \delta^{15}\mathbf{N(FS)}$		19
	$10^3 \times \Delta^{17}\mathbf{O(FT)}$		30
	$10^3 \times \delta^{15}\mathbf{N(FT)}$		0

1 Table 4. Simulated nitrate concentration and isotopic composition at the air-snow interface in  
 2 the case of the DC realistic simulation.

	Atmosphere			Skin layer		
	$\gamma(\text{NO}_3^-)$ / (ng m <sup>-3</sup> )	$10^3 \times \delta^{15}\text{N}$	$10^3 \times \Delta^{17}\text{O}$	$\omega(\text{NO}_3^-)$ / (ng g <sup>-1</sup> )	$10^3 \times \delta^{15}\text{N}$	$10^3 \times \Delta^{17}\text{O}$
average	31.9			3074		
weighted		0.2	23.7		34.9	25.5
average						
min	5.0	-17.0	20.8	707	10.1	20.5
max	110.0	19.4	39.3	5706	58.1	38.9

3

4 Table 5. Simulated nitrate mass, concentration and isotopic composition in the top 50 cm of  
 5 snow and in the archived flux as well as the apparent fractionation constants.

	Nitrate in top 50 cm			Nitrate in archived flux			Fractionation constants		
	$m_{50\text{cm}}(\text{NO}_3^-)$ / (mgN m <sup>-2</sup> )	$10^3 \times \delta^{15}\text{N}_{50\text{cm}}(\text{NO}_3^-)$	$10^3 \times \Delta^{17}\text{O}_{50\text{cm}}(\text{NO}_3^-)$	$\omega(\text{NO}_3^-)$ / (ng g <sup>-1</sup> )	$10^3 \times \delta^{15}\text{N}$	$10^3 \times \Delta^{17}\text{O}$	$10^3 \times {}^{15}\epsilon_{\text{app}}$	$10^3 \times {}^{17}\epsilon_{\text{app}}$	$10^3 \times {}^{15}\epsilon_{\text{pho}}$
average	8.1±1.6			23.0±0.0			-49.5±3.7	1.4±0.6	
weighted		100.5	23.3	317.7	17.8				-55.1
average									
min	6.2	77.4	20.0	22.9	317.6	17.8	-53.6	0.7	-78.8
max	11.0	127.5	27.4	23.0	317.8	17.8	-43.0	2.4	52.9

6

7 Table 6. Simulated nitrate mass fluxes and their isotopic composition in the case of the DC  
 8 realistic simulation.

Flux	Annual flux / (10 <sup>-6</sup> kgN m <sup>-2</sup> a <sup>-1</sup> )	Seasonal flux / (10 <sup>-12</sup> kgN m <sup>-2</sup> s <sup>-1</sup> )			Seasonal $10^3 \times \delta^{15}\text{N}$			Seasonal $10^3 \times \Delta^{17}\text{O}$		
		Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
FP	32.07	1.02	0.00	3.27	12.6	-23.8	29.3	21.7	20.4	25.0
FD	32.22	1.02	0.10	2.72	13.9	-7.0	29.4	24.8	20.8	39.3
FE	8.05	0.26	0.03	0.68	3.9	-17.0	19.4	24.8	20.8	39.3
FA	0.15	0.00	0.00	0.00	317.7	317.6	317.8	17.8	17.8	17.8
FS	4.10	0.13	0.00	0.45	19.0	19.0	19.0	42.0	42.0	42.0
FT	4.10	0.13	0.13	0.13	0.0	0.0	0.0	30.0	30.0	30.0

9

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1 Table 5. Overview of the TRANSITS results for the sensitivity tests.

2

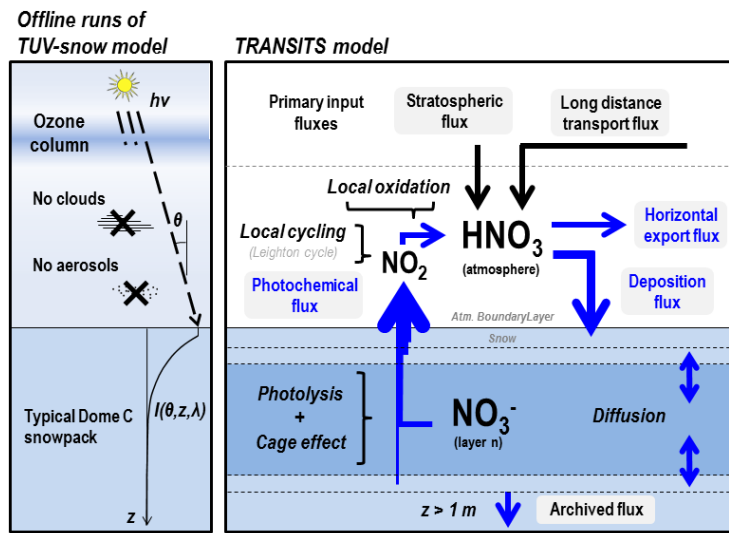
Tested variable	Tested values (reference value)	FA / ( $10^{-6}$ kgN m <sup>2</sup> a <sup>-1</sup> ) (abs. diff.)	FA/FPI in % (abs. diff.)	$10^3 \times \delta^{15}\text{N}(FA)$ (abs. diff.)	$10^3 \times \Delta^{17}\text{O}(FA)$ (abs. diff.)
<b>Realistic simulation</b>	<b>for DC (reference)</b>	<b>0.15</b>	<b>1.77</b>	<b>317.7</b>	<b>17.8</b>
$h_{AT}$ / m	500 ( <b>50</b> )	0.15 (=)	1.77 (=)	317.7 (=)	17.8 (=)
$\gamma(\text{NO}_3)$ / (ng m <sup>-3</sup> )	Real. ideal. DC $\times 10$ ( <b>Real. ideal. DC</b> )	0.15 (=)	1.77 (=)	317.7 (=)	17.8 (=)
$FPI$ / ( $10^{-6}$ kgN m <sup>2</sup> a <sup>-1</sup> )	82 ( <b>8.2</b> )	1.45 (+1.31)	1.77 (=)	317.7 (=)	17.8 (=)
$10^3 \times \delta^{15}\text{N}(FS)$	+119 ( <b>+19</b> )	0.15 (=)	1.77 (=)	376.0 (+58.4)	17.8 (=)
$10^3 \times \delta^{15}\text{N}(FT)$	+100 ( <b>0</b> )	0.15 (=)	1.77 (=)	388.5 (+70.9)	17.8 (=)
$10^3 \times {}^{15}\epsilon_{dep}$	0 ( <b>+10</b> )	0.15 (=)	1.77 (=)	303.5 (-14.2)	17.8 (=)
$10^3 \times \Delta^{17}\text{O}(FS)$	0 ( <b>42</b> )	0.15 (=)	1.77 (=)	317.7 (=)	16.0 (-1.8)
$10^3 \times \Delta^{17}\text{O}(FT)$	0 ( <b>30</b> )	0.15 (=)	1.77 (=)	317.7 (=)	15.1 (-2.7)
$10^3 \times \Delta^{17}\text{O}(\text{O}_3)_{bulk}$	0 ( <b>25.2</b> )	0.15 (=)	1.77 (=)	317.7 (=)	7.4 (-10.4)
$10^3 \times \Delta^{17}\text{O}(\text{OH})$	0 ( <b>3</b> )	0.15 (=)	1.77 (=)	317.7 (=)	17.2 (-0.6)
[BrO] / pptv	5.0 ( <b>2.5</b> )	0.15 (=)	1.77 (=)	317.7 (=)	18.2 (+0.4)
[HO <sub>2</sub> ]	Est. DC $\times 10$ ( <b>Est. DC</b> )	0.15 (=)	1.77 (=)	317.7 (=)	16.6 (-1.2)
[CH <sub>3</sub> O <sub>2</sub> ]	Est. DC $\times 10$ ( <b>Est. DC</b> )	0.15 (=)	1.77 (=)	317.7 (=)	17.3 (-0.5)
[O <sub>3</sub> ] / ppbv	Obs. DC $\times 10$ ( <b>Obs. DC</b> )	0.15 (=)	1.77 (=)	317.7 (=)	18.6 (+0.8)
$T$ / K	Obs. DC -10 ( <b>Obs. DC</b> )	0.15 (=)	1.77 (=)	317.7 (=)	17.5 (-0.3)
$FS/FPI$	0.6 ( <b>0.5</b> )	0.14 (-0.0)	1.73 (-0.04)	322.4 (+4.7)	17.8 (=)
$f_{cage}$	0.18 ( <b>0.15</b> )	0.17 (+0.03)	2.11 (+0.34)	305.5 (-12.2)	16.8 (-1.0)
$f_{exp}$	0.24 ( <b>0.2</b> )	0.11 (-0.03)	1.36 (-0.41)	322.1 (+4.5)	18.1 (+0.4)
$A$ / (kg m <sup>-2</sup> a <sup>-1</sup> )	33.6 ( <b>28</b> )	0.32 (+0.17)	3.90 (+2.13)	263.9 (-53.8)	18.6 (+0.8)
$\rho$ / (kg m <sup>-3</sup> )	360 ( <b>300</b> )	0.06 (-0.09)	0.72 (-1.05)	373.8 (+56.1)	17.0 (-0.8)
$k$	1.2 ( <b>1.0</b> )	0.35 (+0.21)	4.28 (+2.51)	252.0 (-65.6)	18.8 (+1.1)
$q$	1.2 ( <b>1.0</b> )	0.06 (-0.09)	0.70 (-1.07)	375.2 (+57.5)	16.9 (-0.9)
$\Phi$	0.0336 ( <b>0.026</b> )	0.06 (-0.09)	0.70 (-1.07)	375.2 (+57.5)	16.9 (-0.9)
$D$ / ( $10^{-11}$ m <sup>2</sup> s <sup>-1</sup> )	1.2 ( <b>1.0</b> )	0.16 (+0.01)	1.89 (+0.12)	309.4 (-8.2)	17.9 (+0.1)
Accumulation distribution	Winter = 2 $\times$ summer	0.16 (+0.02)	1.98 (+0.21)	306.1 (-11.6)	18.0 (+0.3)
	Summer = 2 $\times$ winter ( <b>flat</b> )	0.13 (-0.01)	1.64 (-0.13)	325.9 (+8.2)	17.6 (-0.2)
O <sub>3</sub> column	100 DU flat	0.01 (-0.14)	0.08 (-1.69)	344.1 (+26.4)	15.3 (-2.5)
	300 DU flat	0.19 (+0.05)	2.33 (+0.56)	309.1 (-8.6)	18.1 (+0.3)
	500 DU flat	0.70 (+0.56)	8.58 (+6.81)	252.1 (-65.5)	19.6 (+1.8)
	300 DU / 100 DU hole ( <b>real. DC</b> )	0.06 (-0.08)	0.76 (-1.01)	328.3 (+10.6)	16.9 (-0.9)

3

4

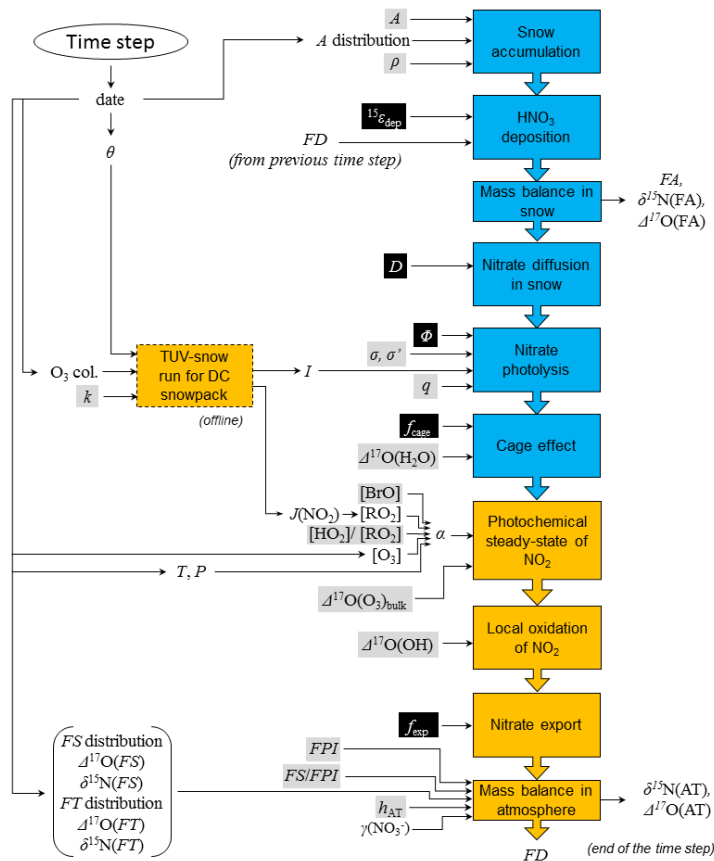
1 **Figures**

2

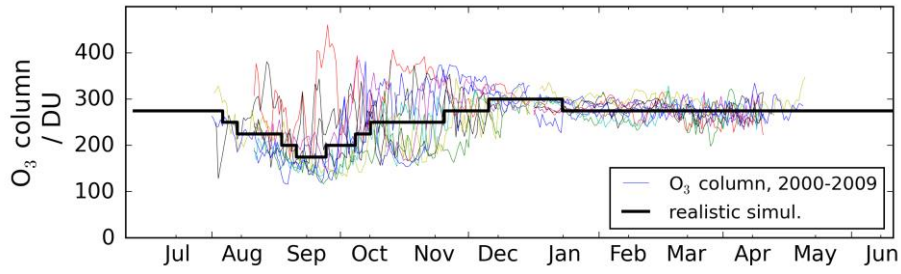


3

4 Figure 1. Overview of the TRANSITS model.

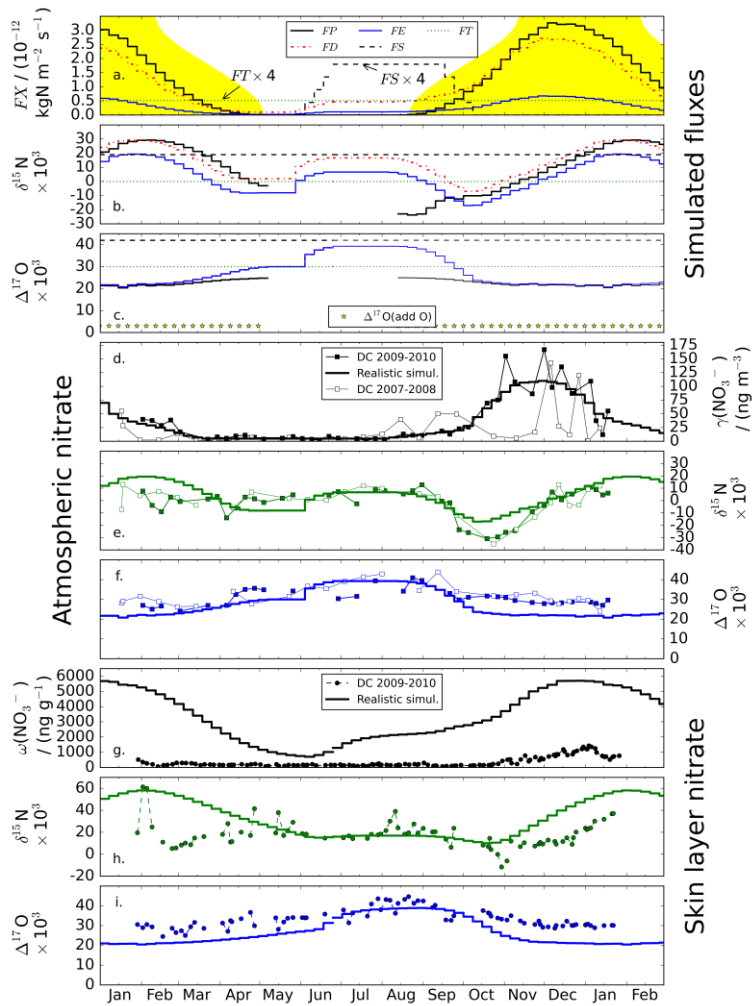


1  
 2 Figure 2. Schematic view of the processes included in TRANSITS (one time step is shown).  
 3 The orange and blue boxes represent processes occurring in the atmosphere and the snowpack,  
 4 respectively. Arrows entering from left and leaving to right represent inputs and outputs for  
 5 each process. Arrows entering from left and right sides of each box represent required inputs to  
 6 the calculation of each process. For the sake of clarity, we only display the input time-variables  
 7 (black font on white background), the fixed parameters (black on grey) and the adjustment  
 8 parameters (white on black).



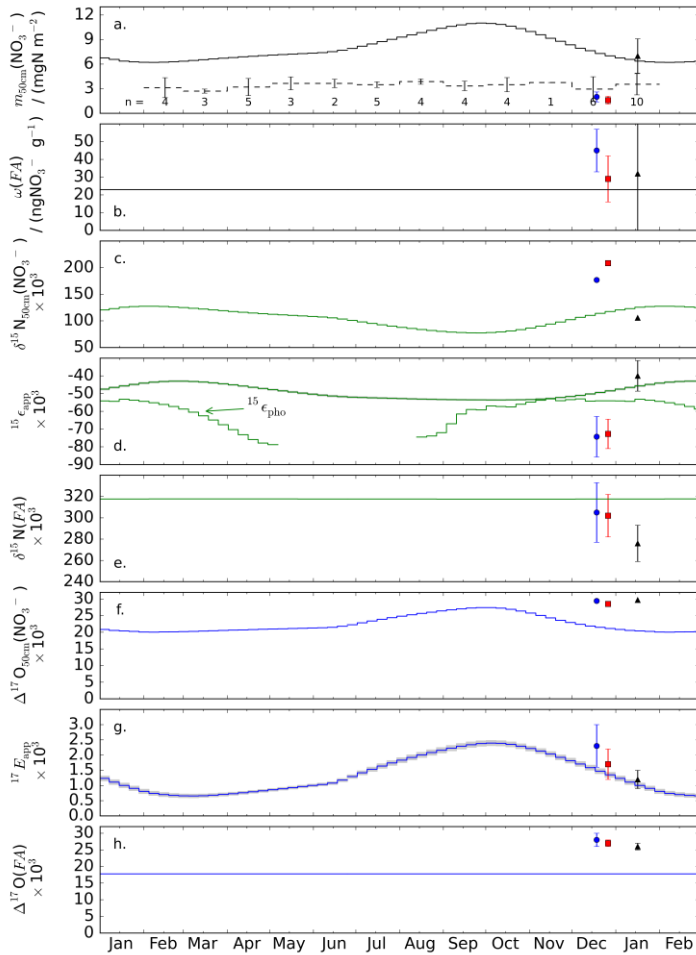
1  
2 Figure 3. Driving ozone column data for the DC realistic simulation versus observed annual  
3 time series for years over the 2000-2009.

4

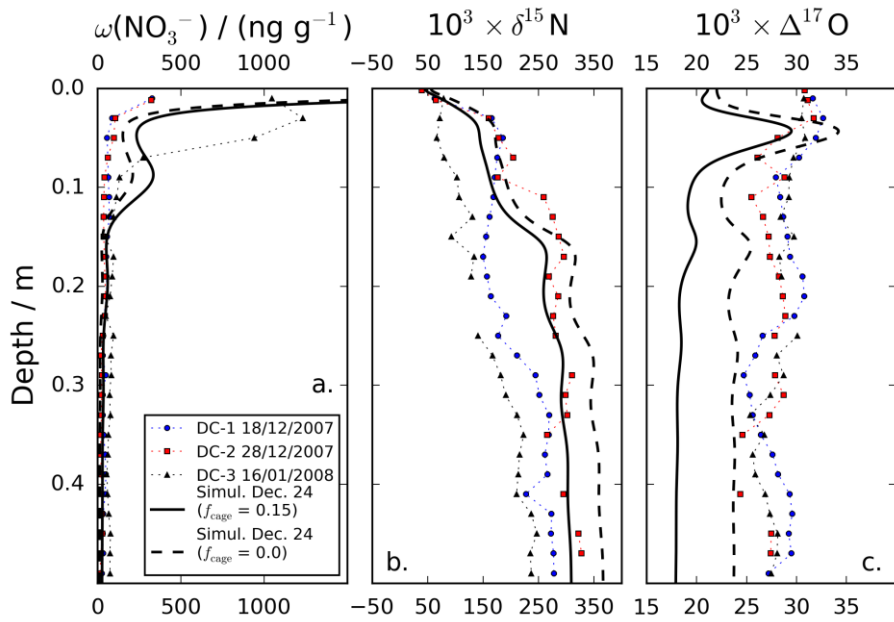


1  
 2 Figure 4. Realistic simulation results and comparison to the observations at Dome C. (a–c)  
 3 simulated fluxes (mass and isotopic composition) and  $\Delta^{17}\text{O}$  in the additional O atom (panel c).  
 4 The legend in panel a also applies to panels b and c. The yellow filled curve in panel a.  
 5 represents the day length at Dome C. Note that  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  in *FE* and *FD* are equal. (d–f)  
 6 simulated and observed concentrations,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  in atmospheric nitrate. (g–i) simulated  
 7 and observed mass fractions,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  in skin layer nitrate. The 2007–2008 and 2009–  
 8 2010 observed data originate from Frey et al. (2009) and Erbland et al. (2013) respectively.

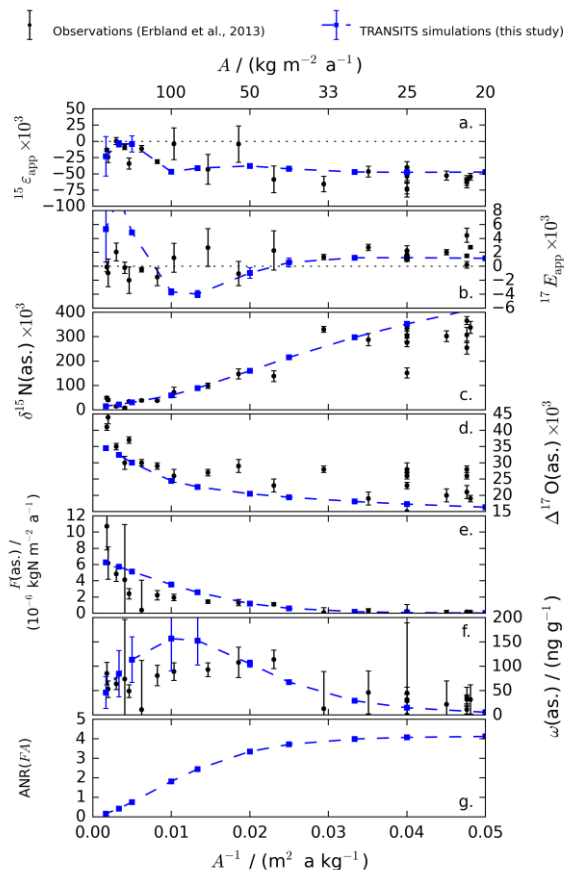




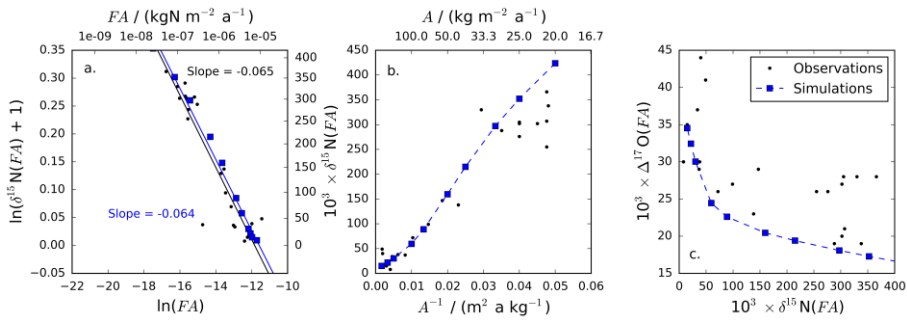
1  
 2 Figure 5. Realistic simulation results for the snowpack and comparison to the observations at  
 3 Dome C. (a) nitrate mass in the top 50 cm (the dashed curve represents the observed monthly  
 4 values), (b) archived nitrate mass fractions, (c)  $\delta^{15}\text{N}$  of nitrate in the top 50 cm, (d) apparent  
 5 and photolytic  $^{15}\epsilon$  fractionation constants (in grey, the range  $\pm 1\sigma$ ), (e)  $\delta^{15}\text{N}$  in the archived  
 6 nitrate, (f)  $\Delta^{17}\text{O}$  of nitrate in the top 50 cm, (g) apparent  $^{17}E$  fractionation constant (in grey, the  
 7 range  $\pm 1\sigma$ ) and (h)  $\Delta^{17}\text{O}$  in the archived nitrate. In each panels, the observed data from the  
 8 three DC snowpits (Frey et al., 2009; Erbland et al., 2013) are represented by the same symbols  
 9 as in Fig. 6).



1  
 2 Figure 6. Realistic simulation results: nitrate in the 50 top cm of the snowpack on 24 December  
 3 and comparison to the three observed profiles at Dome C in summer 2007-2008 (Frey et al.  
 4 (2009) and Erbland et al. (2013)). (a) nitrate mass fractions, (b)  $\delta^{15}\text{N}$  in nitrate and (c)  $\Delta^{17}\text{O}$  in  
 5 nitrate.

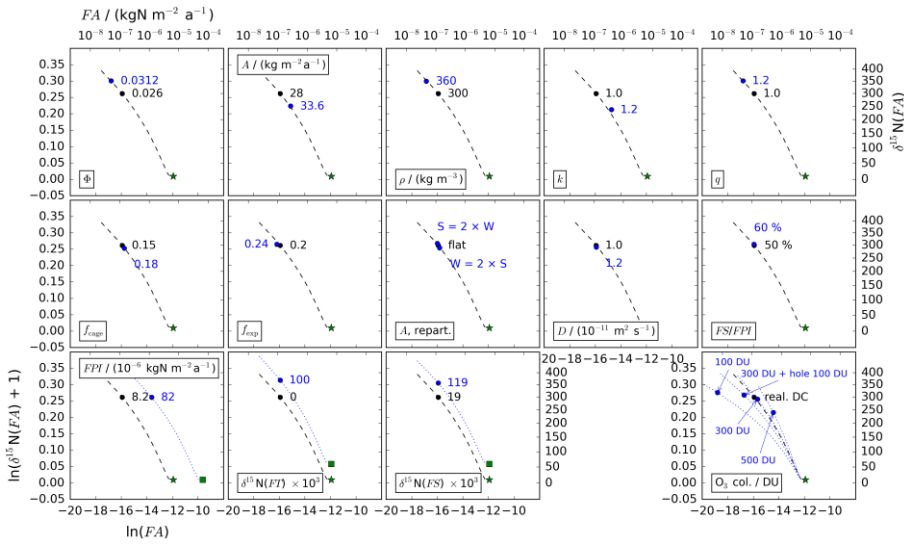


1  
2 Figure 7. Reduced data in the TRANSITS simulations across East Antarctica and in the  
3 observations (Erbland et al., 2013) as a function of the snow accumulation rates (top x-axis)  
4 and their inverse (bottom x-axis). (a–b)  $^{15}\text{N}/^{14}\text{N}$  and  $^{17}\text{O}$ -excess apparent fractionation constants  
5 (simulated dots and errors bars represent the mean and standard deviation values over the  
6 December/January period), (c–d) Asymptotic (observed) and archived (simulated)  $\delta^{15}\text{N}$  and  
7  $\Delta^{17}\text{O}$  values (simulated dots represent annual average values), (e) Asymptotic and archived  
8 nitrate mass, (f) Asymptotic and archived nitrate mass fractions (simulated dots and errors bars  
9 represent the mean and standard deviation values over the whole year), (g) ~~Yearly~~-Average  
10 Number of Recyclings in the archived nitrate (~~Y~~ANR(FA)).



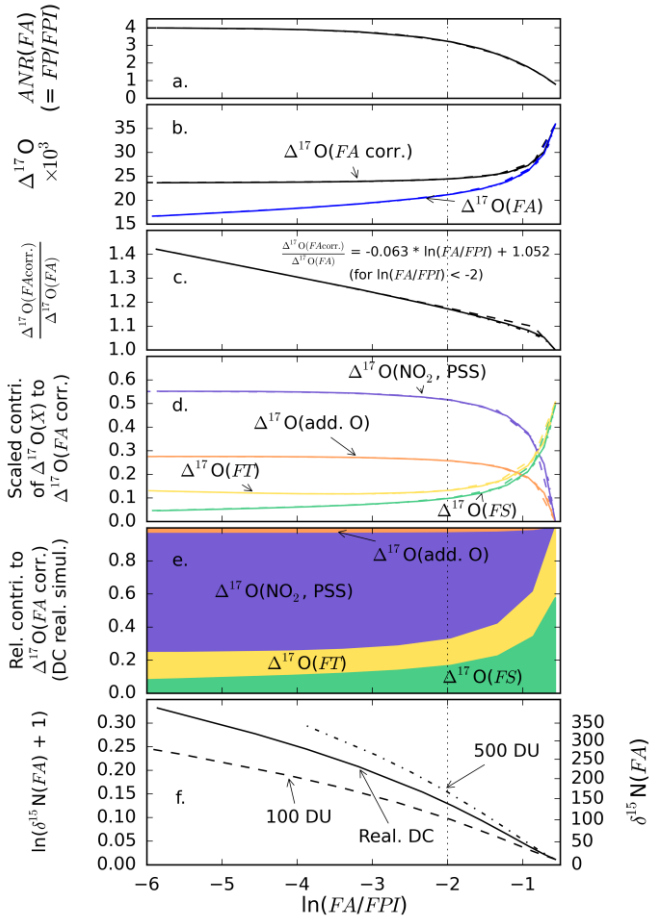
1  
 2 Figure 8. Realistic simulation with varying snow accumulation rates (blue squares) versus  
 3 observations along the D10–Dome C–Vostok route (black dots). (a) modified Rayleigh plot.  
 4 The two lines are linear fit to the data and the slopes are given in the respective colors. (b)  
 5  $\delta^{15}\text{N}(FA)$  versus the inverse of the snow accumulation rates, (c)  $\Delta^{17}\text{O}(FA)$  versus  $\delta^{15}\text{N}(FA)$ .  
 6

1

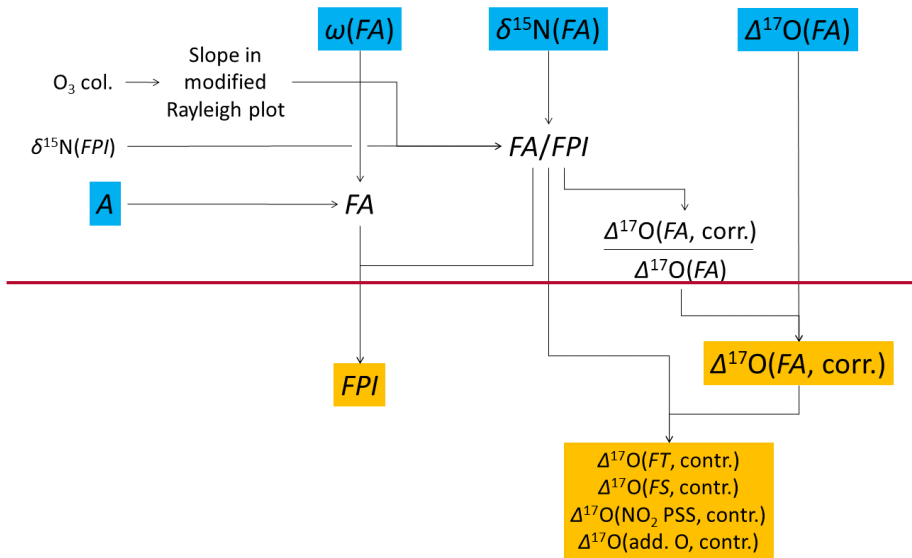


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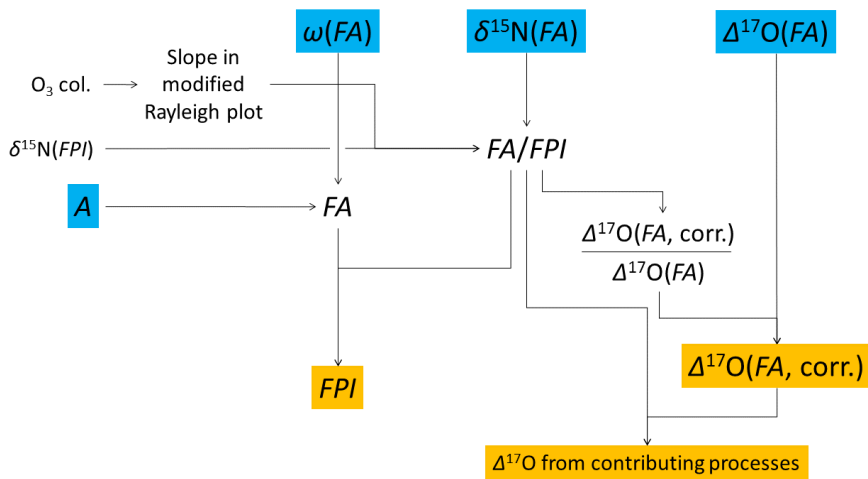
3 Figure 9. Modified Rayleigh plots of the sensitivity tests to the TRANSITS model. Only the  
 4 tests which imply significant changes in  $FA$  and  $\delta^{15}N(FA)$  are shown. The green star represents  
 5 the starting point whose coordinates are  $(\ln(FPI), \ln(\delta^{15}N(FA) + 1))$  and thick dashed lines  
 6 represent the curve which is obtained for the realistic DC simulation ( $\Phi$  varied). The other blue  
 7 dashed curves represent the consequences of a change in the starting point (squares) or in the  
 8 ozone column.



1  
2 Figure 10. TRANSITS simulations of the reduction in  $\Delta^{17}\text{O}(\text{FA})$  under the cage recombination  
3 effects and scaled contributions to  $\Delta^{17}\text{O}(\text{FA, corr.})$  as a function of nitrate trapping efficiency  
4 ( $\ln(\text{FA}/\text{FPI})$ ). (a) average number of recyclings undergone by the archived nitrate ( $\overline{ANR}(\text{FA})$ ),  
5 (c)  $\Delta^{17}\text{O}(\text{FA})$  with and without cage effect and (d) the associated  $\Delta^{17}\text{O}(\text{FA, corr.})/\Delta^{17}\text{O}(\text{FA})$   
6 ratio, (e) the scaled contributions of  $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS})$ ,  $\Delta^{17}\text{O}(\text{add. O})$ ,  $\Delta^{17}\text{O}(\text{FT})$  and  $\Delta^{17}\text{O}(\text{FS})$ ,  
7 (f) the relative contributions to  $\Delta^{17}\text{O}(\text{FA, corr.})$  in the DC case ( $\Delta^{17}\text{O}(\text{NO}_2, \text{PSS}) = 31.3\%$ ,  
8  $\Delta^{17}\text{O}(\text{add. O}) = 3\%$ ,  $\Delta^{17}\text{O}(\text{FT}) = 30\%$  and  $\Delta^{17}\text{O}(\text{FS}) = 42\%$ ), and (g) the  $\delta^{15}\text{N}(\text{FA})$  as a  
9 function of the ozone column. Note that for the (a-e) panels, the curves for the three  $\text{O}_3$  column  
10 case almost superimpose. The vertical dashed line at  $\ln(\text{FA}/\text{FPI}) = -2$  represents a threshold  
11 value below which  $\Delta^{17}\text{O}(\text{FA, corr.})/\Delta^{17}\text{O}(\text{FA})$  ratio is linear with  $\ln(\text{FA}/\text{FPI})$ .



1



2

- 1 Figure 11. Schematic of the suggested method to retrieve information about the variables in the
- 2 orange boxes using the measurement of  $\omega(FA)$ ,  $\delta^{15}\text{N}(FA)$ ,  $\Delta^{17}\text{O}(FA)$  and the annual snow
- 3 accumulation rates accessible in ice cores.