Reply to the review of Eric Wolff

We thank Prof. Eric Wolff for his positive review of this work.

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.

This paper presents a model that aims to trace the mass and isotopic changes of nitrate in the air and snow of the East Antarctic plateau. It builds on the insights obtained in a string of fieldwork by various of the authors, as well as some recent lab work (which has provided some essential parameters for the model). The paper provides a useful overall description of the processes that determine the processing and archiving of nitrate (and its isotopic values), with all the many factors that may be involved, and this is in itself useful. It provides a way of assessing the validity of some of the ideas that have been deduced from the fieldwork (generally with success). Finally the authors argue that it provides a framework for interpreting deep ice core records: I agree that it does although I am less confident than the authors that it will be possible to derive unique interpretations from the data using the model.

Overall the paper and the modelling effort are an impressive and fairly comprehensive attempt on the problem, and this will be a valuable contribution that should be published. The structure of the paper is logical, and the conclusions seem valid. I have one conceptual issue, regarding the number of recyclings that I would like to discuss. The paper is hard work to read: in fact I defy anyone to read it through at a single sitting. This is perhaps inevitable in a paper with so many parameters that have to be described: I will in any case suggest a couple of places where the reader might be given more help through summary paragraphs that would allow them to skip some of the more convoluted sections. I am also a little concerned about some of the figures: some of the multipart figures appear very small in the way they print as pdf (and in some cases coloured lines are hard to distinguish or not fully defined). While I realise readers can stretch them on screen, the authors should try and persuade the publishers to give some of them full pages in the print pdf format to help the reader who prints their papers.

We thank Prof. Wolff for his appreciation of this work. Indeed, it is difficult to make the paper more concise given the different goals we want to reach. This is to say: describing the model, comparing it to observations for DC conditions, comparing it to observations for EAIS conditions and providing a framework for the interpretation of ice cores.

We will attempt to add summary paragraphs in order to help the reader skipping some parts of the text.

We will ask the publisher to print figures 5 and 6 in full page or, at least, the two on one full page.

The paper should certainly be published in ACP, after revisions that are relatively minor, though important. (See below).

Abstract: last few lines. I think this gives an impression that is more positive than the reality about the likelihood of deriving particular changes from the ice core record. At least as presented later there are far more unknowns than measurements and for example it is not clear to me that it will be possible to infer any particular change in local processes from del17O. Please reassess the wording.

Please see our answers to your comments below.

Page 6892, last few lines. I commented at pre-discussion stage about the figure (now revised to 120) for the average cycling of an archived nitrate. This recurs in various ways numerous times throughout the text (page 6936, line 7; page 6938, line 2 page 6940, line 11 – although it is often cited as 150). Presumably it is calculated as tau_arch/tau_photo, perhaps with a correction for seasonality in tau_photo. 120 seems very high but I think I have argued myself into agreeing with you. I am less sure about tau_arch itself though.

To address this comment, we refer to our answer to the second comment of Prof. Wolff: "Reply to the "Conceptual issue with the age of nitrate and number of recyclings" by Eric Wolff".

Tau_arch denotes the time it takes for the amount of nitrate in the top 50 cm to be archived. Putting some numbers in: with the values (for m_50cm and FA) in Tables 6 and 5, tau_arch is 52 years. The time taken for snow to reach 50 cm is less than 6 years, so this number implies that nitrate molecules in the surface skin are already typically nearly 50 years old on average. Later on (section 3.3.3) you argue that the model converges after 20 years, which seems inconsistent with this number, so please think about that. In addition, later in the paper you will show that you get FA about right, but are almost a factor 3 low for m_50cm. This implies that an experimental value for tau_arch is perhaps a factor 3 lower than you would infer. While obviously you have to run with your modelled values for now, I think it would be worthwhile to say that the real number might be lower, so as not to get weird numbers embedded in the literature.

Here as well, to address this comment, we refer to our answer to the second comment of Prof. Wolff: "Reply to the "Conceptual issue with the age of nitrate and number of recyclings" by Eric Wolff".

Moving on to more detailed issues:

Page 6898, line 5. Be careful here. Almost all parameters in the tables are in units of meters (m) but now you introduce terms with cm. Please be sure you have correctly accounted for such unit changes.

Unit changes in this equation have been checked. There is no mistake in the conversion.

However, the reader should read "$m^{-3}\ s^{-1}$" for the unit of P_i and L_j (and not $cm^{-3}\ s^{-1}$). In the text, the information about the unit of P_i and L_j has been removed to avoid any further

confusion. Indeed, providing this information only makes sense if the unit of *X* is provided as well.

Also, for the sake of clarity, units for the atmospheric mixing ratios of RO₂ and OH have changed to molecule m⁻³ and the unit for the diffusion coefficient has been changed to m² s⁻¹.

Page 6908, line 23. I realise this is partly addressed later but why was 20% chosen. Was this a tuned parameter, ie 20% gives the best answer?

The parameter f_exp is tuned (adjusted) and the value 20% gives realistic results. As mentioned in the text, setting f_exp to 0 (no export) would lead to unrealistic results: "d15N values in [the atmosphere and skin layer] become highly negative (< -120 ‰) which is clearly not realistic when compared to the observations ". Also, in such conditions, the model does not converge within a reasonable time and nitrate endlessly builds up in the photic zone.

However, f_exp can be related to physical variables. Indeed, f_exp represents the competition between the export of NO_y (NO_2 or HNO_3) and the deposition of (to make it simple) HNO_3.

Let us consider the schematic below where NO2 and HNO3 are considered at steady-state. The deposition of NO_2 is neglected because the deposition of HNO_3 is a factor 8.0 ± 3.2 faster than that of NO_2 (Zhang, et al., 2009). Also, oxidation by OH is considered to be the only channel of NO_2 oxidation (an assumption valid in summer).
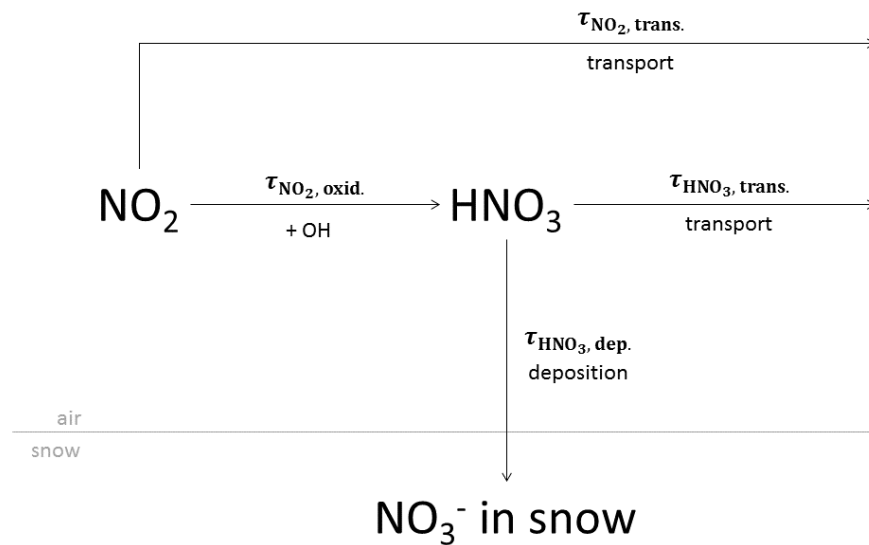
The overall residence time of atmospheric NOy (= NO2 + HNO3) against deposition is expressed as follows:

$$\tau_{dep} = \tau_{NO_2, oxi.+ dep.} = \tau_{NO_2, oxi.} + \tau_{HNO_3, dep.}$$ (dry deposition of NO₂ is neglected)

The residence time of atmospheric NOy against horizontal export is expressed as follows:

$$\tau_{exp} = \frac{1}{\frac{1}{\tau_{NO_2, trans.}} + \frac{1}{\tau_{NO_2, oxi.+ trans.}}}$$

with $\tau_{\mathrm{NO_2,oxi.+ trans.}} = \tau_{\mathrm{NO_2,oxi.}} + \tau_{\mathrm{HNO_3,trans.}}$

$$\tau_{\mathrm{NO_2,oxi.}} = \tau_{\mathrm{NO_2+OH}} = \frac{1}{k_{\mathrm{NO_2+OH}}(T,P) \times [\mathrm{OH}]} = 3.5\ 10^3 \text{ s.}$$

We use kinetic rate constants from (Atkinson, et al., 2004) and *T, P* and [OH] for mean summertime conditions at DC (Kukui, et al., 2014).

For the calculation of $\tau_{\mathrm{HNO_3,dep.}}$, we use *v*_dep = 0.8 cm s^{-1} (Huey, et al., 2004) and assume an average boundary layer height of *H* = 100 m representative of the 2011-2012 summer at DC (Gallée, et al., 2014). $\tau_{\mathrm{HNO_3,dep.}}$ = *H* / *v*_dep = 1.3 10^4 s (Jacob, 1999).

For the calculation of $\tau_{\mathrm{NO_2,trans.}}$ and $\tau_{\mathrm{HNO_3,trans.}}$, we consider a characteristic horizontal length of *L* = 400 km which represents the width of the East Antarctic plateau. We also consider the mean summertime wind speed at Dome C (*v*_wind = 3.1 m s^{-1}, (Kukui, et al., 2014)). $\tau_{\mathrm{NO_2,trans.}}$ = $\tau_{\mathrm{HNO_3,trans.}}$ = *L* / *v*_wind = 1.3 10^5 s.

We then obtain $f_{\mathrm{exp}} = \frac{1}{1+\frac{\tau_{\mathrm{exp}}}{\tau_{\mathrm{dep}}}} = 0.20$ in accordance to the chosen value of f_exp used to adjust the model.

We suggest to add the following sentences in section 3.1.1 where we discuss the choice of the "adjustment parameters": "Following the approach of Jacob (1999), a summertime value for f_exp can be approached by considering the chemical lifetime of NO2 in its oxidation by OH and the residence times of NO2 and HNO3 in the atmosphere and against the deposition and horizontal export processes. Using kinetic rate constants from (Atkinson et al., 2004), *T, P*, wind speeds and OH mixing ratios for mean summertime conditions at DC (Kukui, et al., 2014), HNO3 dry deposition velocity from Huey et al. (2004), and vertical and horizontal characteristic dimensions of 100 m (average summertime boundary layer height, Gallée et al., 2004) and 400 km (Antarctic plateau width), respectively, we obtain f_exp = 0.20, in accordance with the chosen value used to adjust the model."

In a future version of the TRANSITS model, the f_exp parameter (or the deposition of HNO3 and the export of atmospheric nitrate) could be explicitly calculated at each time step.

Page 6912, line 23. I don't understand this sentence since the figure shows a 1 year period starting in January not June.

This is an error: this sentence referred to an earlier version of Figure 5. The sentence has been removed.

Page 6914, line 9. This discrepancy between modelled and measured values in the skin layer needs more discussion. Later on, you say it may be an artefact of the discrete measurements (ie the data don't really show the skin layer), and this may be true, surely does not apply to the

We agree, errors in sampling the skin layer cannot entirely explain the discrepancies between simulated and observed m_50cm values as shown on Fig. 7a. From the experiment where FPI has been multiplied by a factor 10, we have shown that the effect on m_50cm last for more than 10 years (actually 21 years) and this means that observations in 2007-2008 or 2009-2010 at Dome C could be sensitive to past changes in FPI.

Also, it is likely that a missing process in TRANSITS could explain the observed discrepancy. For example, the model does not include snow erosion, a process which could blow away a fraction of the skin layer and which may explain our observations in the field around 10 January 2010. Around this date, we observed a decrease of factor 2 in skin layer concentrations which was concurrent with an increase in wind speed (Erbland, et al., 2013).

The following sentence has been added to the text in section 3.3.3.: "It is also likely that missing processes in TRANSITS could explain the observed discrepancy. For example, the model does not include snow erosion, a process which could blow away a significant fraction of the skin layer and thus lead to a rapid decrease in $m_{50cm}(NO_3^-)$".

This is not exactly true. Indeed, not only f_exp controls the FA/FPI ratio. As discussed in section 4.1.1, parameters and variables controlling nitrate photolysis (f_cage, A, ρ, k, q, Φ and the ozone column) also control this ratio (see also Table 7).

We think that Prof. Wolff is mistaking here. Indeed, here is how the horizontal export flux is calculated in the model (FE = f_exp * (FS + FT + FP)). As a consequence, f_exp is bounded at the high end by f_exp = 1 and greater values would lead to a net export of nitrate from the simulated combined atmosphere/snow box.

Indeed, we are mistaking here. Showing that the model takes 20 years to reach equilibrium means that the slowest nitrate ions take 20 years to get through the top 1 m of snow. However, the residence time of nitrate in the top 1 m of snow is calculated as $1/(A/\rho)$ and represents the average time that nitrate ions take to get though the top 1 m of snow (as

demonstrated in "Reply to the "Conceptual issue with the age of nitrate and number of recyclings" by Eric Wolff".). For DC conditions (as presented in this paper), the residence time is 10.7 years.

We have removed the reference to "more than 20 years" in sentence page 6922, line 23.

Page 6932, line 20. Thank you for introducing this. However note that the speciation would also affect the cage effects (surely?). I think this issue needs to be mentioned also in the conclusions as it might strongly affect your interpretation of LGM data.

We do not yet have a clue on how nitrate speciation would affect the cage effects. Would it directly affect them? Or would it be by affecting the ability to photolyze nitrate? Anyway, this is an important point and the following sentence has been added to the last paragraph of the conclusion: "To achieve this correction, the potential impact of nitrate speciation (association to H^+ or, e.g., Ca^{2+}) on the cage effect will have to be taken into account (say, e.g. in the case of glacial conditions)".

Page 6934-5. This section is really hard to read (step back and look how much of it is symbols!). I suggest: (1) PSS needs to be listed in table 1 or somewhere, it took me ages to find where you had defined it, (2) Please give a summary paragraph explaining the outcome of section 4.2.2. You might consider this for other difficult sections.

Good idea. We have added the acronym "PSS" in Table 1.

A summary paragraph explaining the outcome of section 4.2.2 has been written.

Page 6936, line 7. 150 or 120?

Our original calculation was wrong. The number of recyclings has been updated in light of our calculation in "Reply to the "Conceptual issue with the age of nitrate and number of recyclings" by Eric Wolff"". The number is now 3-4 cycles for DC conditions.

Page 6938, line 22, ditto.

Idem.

Page 6938, line 3, not sure what you mean by "transcripts".

We meant "means". The sentence now is: "Under the DC realistic simulation conditions, the quantum yield value which is necessary to reproduce the observations (0.026) means that nitrate lies in two different domains in or on the snow ice matrix (Meusinger et al., 2014)"

Section 4.1 and 5. My problem with your optimism is that you have too many unknowns. For example if we consider Figure 10 and think about the LGM. We know accumulation rate will have changed, but under a different climate we can reasonably expect changes in O3 and FPI, (not to mention speciation with Ca). There will always be more than on combination, even if we can discriminate changes, that can move us to a new location on these diagrams. Similarly for 17O (page 6937, line 8): just what aspect of local atmospheric chemistry would we deduce had changed. I don't disagree with what is written but feel its presented in a too optimistic way at this stage.

Yes, indeed, various parameters and variables could have changed under LGM conditions. However, it seems important to us to provide a tool which can classify the impacts of each parameter and variable in terms of mass and isotopic composition in the archived nitrate. Indeed, only d15N(FA) and [NO3-](FA) (and d18O(FA) and D17O(FA)) can be measured from ice cores and the ways to discriminate changes in A, O3 or FPI (not to mention all the parameters and variables) is limited.

Regarding D17O, we state in the text that, if DC modern conditions prevail on the Antarctic plateau during, say, the LGM, then D17O(FA) must be mostly seen as harboring information about the past <u>local and summertime oxidative conditions of NO and NO2</u>. As it is written it seems, indeed, optimistic. However, what we mean is that, in such conditions, most of the potential global information (on D17O(FS) and D17O(FT)) is mostly lost. Rather, D17O(FA) holds local information. The sentence in the paper now reads "However, in such conditions, $\Delta^{17}O(FA$, corr.) would rather hold information about the local and summertime atmospheric oxidation above the East Antarctic plateau.".

However having said that, it's an important statement that we cannot deduce changes in atmospheric oxidation at global scale and that should be highlighted.

Yes. The last sentence in the conclusion now reads: "Therefore, if the modern DC conditions applied in the past as well (i.e. important loss by photolysis followed by the local recycling of nitrate), the determination of $\Delta^{17}O(FA$, corr.) from ice cores drilled on the East Antarctic plateau are expected to deliver information about the oxidative chemistry occurring at the local and summertime scale rather than at the global scale".

Table 1. m_50cm is a mass not a mass fraction.

We agree. The text has been changed accordingly.

Table 6. m_50cm should be in units of mgN ˆ-2.

We guess Prof. Wolff meant mgN m^{-2}. We agree that this unit should be the unit of m_50cm. Table 6 and the entire text have been changed accordingly.

Fig 4. Part a must be wrong, with 52 timesteps this would give 7.8 kg mˆ-2 aˆ-1, which is a factor 3 too high. Anyway this flat line is pointless, just leave it out, after checking the accumulation is correct in your model.

We agree that the representation of the snow accumulation rates in this figure is wrong: the flat line must be at a value of 0.54 kg m^{-2} Δt^{-1}. The figure has been updated and this panel has been removed.

Fig 5, parts b and c, what are the different coloured lines. Please improve the caption.

The different colored lines refer to the same caption as in panel a. The caption has been changed to avoid such confusion.

Fig 5g. Please replot without the factor 4 scaling. This is confusing and unnecessary.

Figure 5g has been updated accordingly.

A number of additional changes have been made to the model and the main text. The reviewers can refer to our other uploaded file.

References

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