Changes brought to the TRANSITS model and additional changes brought to the manuscript after the review process

Diffusion calculation

Currently, the model runs at a time step (Δt) of one approx. one week and the diffusion routine runs at a time step (Δt_short) of 4 hours. In order to scale this routine to the main time step and allow the model to be used in different conditions, the ratio $\Delta t/\Delta t\_short = 50$ has been introduced in the model. In this case, $\Delta t\_short \approx 3.4$ hours. This modification does not change the results of our study. Indeed, the time step for the diffusion routine must be short enough to allow convergence.

We have edited the text which now writes: "Nitrate diffusion is assumed to occur in the snowpack and is solved at a time resolution 50 times shorter than the model main time resolution (i.e. approx. 3.4 hours)" and, later in the text "Equation (14) is solved at a time step of 3.4 hours".

Description of D17O(OH).

A number of errors have been made in the calculation of D17O(OH). First, a detailed reading of Kukui et al. (2014) indicates that HONO may contribute much less than 56% to the formation of OH because real HONO concentrations may be decreased by a factor 4 to provide a good match between modeled and measured HOx. Second, the calculation of D17O(OH) requires that of $\beta = \frac{\sum_i L_i}{\sum_i L_i + k_{HO+H_2O}\,[OH][H_2O]}$, a parameter which accounts for the competition of the isotopic exchange reaction with the OH sink reactions . Under the cold DC conditions, β is significantly different from 0 and D17O(OH) = β * D17O(OH, prod) shows that D17O(OH) will hold a fraction of the 17O-excess value set by its production channels.

In the frame of the OPALE campaign, D17O(OH) has been discussed in a submitted paper (Savarino et al., submitted to OPALE Special Issue, ACPD). The results of this study show that D17O(OH) varies in a narrow range, between 1 and 3 ‰, around summer solstice 2011-2012. We have changed the model to account for the changes described above. The text has been changed as follows:

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

Since the variable $\Delta^{17}O(OH)$ is introduced in the model, we will consider it for the sensitivity tests and when discussing the contributors to D17O(FA, corr.) (section 4).

Diffusion coefficient as an adjustment parameter

In the model version used for the ACPD version of the paper, we made a mistake in not converting units in cm² s^{-1} from (Thibert & Domine, 1998) into m² s^{-1} in the expression of the

diffusivity coefficient (D). As a result, a value of D four orders of magnitude higher than the Thibert & Domine value must be used in order to reproduce realistic nitrate profiles at depth. We note that this diffusion coefficient was measured on a single monocrystal of ice and thus do not take into account the complex polycrystalline nature of the snow, but most obviously the diffusion coefficient does not include the diffusivity of HNO3 in the interstitial air pack (see below).

In the current revised version of the TRANSITS model, we now use D, the HNO3 diffusion coefficient, as an adjustment parameter. Using a value of $D = 1.0 \times 10^{-11}$ m² s^{-1} allows to obtain smooth nitrate profiles consistently with the observations.

In section 3.3.1, we discuss the D value and compare it to the literature. The adjusted value is almost 4 orders of magnitude higher than the diffusion coefficient of solid solution of HNO3 in ice which is 2.6×10^{-15} m² s^{-1} for DC summertime conditions (T=244 K, Kukui et al., 2014) (Thibert et al., 1998).

HNO3 is a sticky gas and its effective diffusivity in snow (denoted D_eff) can be calculated as in Herbert et al. (2006) and by assuming that the snow layers are always under-saturated in nitrate. The D_eff coefficient is a function of the diffusivity of HNO3 in the interstitial air which depends on temperature and pressure (Massmann, 1998). Using a Surface Specific Area of snow of 38 m2 kg-1 (Gallet et al., 2011), a snow density of 300 kg m-3, median temperature and pressure for DC summer 2012 (Kukui et al., 2014) and a partition coefficient in the uptake of HNO3 on ice (Crowley et al., 2010), we find D_eff = 7.3×10^{-12} m² s^{-1}, a value close to the adjusted value.

The paper has been changed as follows:
-   D is now an adjustment parameter set to 1.0×10^{-11} m2 s-1 (Figure 3 and Table 3 are modified accordingly)
-   Sensitivity tests were modified (Figure 10 is changed)
-   We have added the following text in section 3.3.1 to discuss the choice of the value 1.0×10^{-11} m2 s-1 for D:

"Nitric acid is a sticky gas and its effective diffusivity in snow (denoted D_{eff}) can be calculated as in Herbert et al. (2006) and by assuming that the snow layers are always under-saturated in nitrate. The D_{eff} coefficient is a function of the diffusivity of HNO$_3$ in the interstitial air which depends on temperature and pressure (Massmann, 1998). Using a Surface Specific Area of snow of 38 m^2 kg^{-1} (Gallet et al., 2011), a snow density of 300 kg m^{-3}, median temperature and pressure for DC summer 2012 (Kukui et al., 2014) and a partition coefficient in the uptake of HNO$_3$ on ice (Crowley et al., 2010), we find $D_{eff} = 7.3 \times 10^{-12}$ m² s^{-1}, a value very close to our chosen value for D (1.0×10^{-11} m² s^{-1}) which means that the macroscopic mobility of nitrate in the snowpack is mostly the consequence of HNO$_3$ mobility. We recall that our description of nitrate diffusion in the snowpack is basic and that the picture may well be more complicated with, e.g. wind pumping effects."

On the use of the (Brizzi, et al., 2009) reference

In the ACPD version of the paper, we referred to (Brizzi, et al., 2009) in which atmospheric H15NO3/H14NO3 isotope ratio profiles were measured by the Earth observation instrument MIDAS operated onboard of the Environmental Satellite (ENVISAT). On the basis of that work, we attempted to provide an additional constrain on the d15N(FS) value.

We acknowledge that we have misread Figure 5h in (Brizzi, et al., 2009). Indeed, HNO3 at 15 km above South Pole at summer solstice has a d15N value of (210 ± 40) ‰ and not (21 ± 4) ‰.

It seems that (Brizzi, et al., 2009) cannot be directly used to constrain d15N(FS) and the reason is threefold. First, we note that uncertainties in the reported profiles are important even at altitudes where most HNO3 seems to be observed (from 15 to 25 km). Second, there is no winter profile reported. Third, further assumptions must be made to derive d15N values in the condensed nitric acid from the d15N values in the gaseous HNO3.

As a consequence, we decide not to refer to the work from (Brizzi, et al., 2009) in the final version of this paper. We recall that the reference to (Savarino, Kaiser, Morin, Sigman, & Thiemens, 2007) already allows us to provide a constrain on d15N(FS).

On the structure of the paper

In their quick reports, the reviewers suggested to reorganize the manuscript and to put information in appendixes. We acknowledge that the paper is long and that we should have wrote, ideally, two different papers (1. model description/validation, 2. Framework for the interpretation of ice cores). In this stage and given our schedule with this publication, we unfortunately won't be able to split the paper and we now have to live with its length.

Sadly, we do not see how to reorganize the paper without having the reader going back and forth from the main text to appendixes where some information would sit. Therefore, we would like to keep the main text as it is and not to move information to appendixes. However, we have worked on a better organization of Section 3 as advised by Anonymous Reviewer #1.

Below are most changes to the structure of the paper:

- 1. Introduction :
    o The sub-sections have been removed
    o Former section 1.3 has been removed. The important material has been moved to the appropriate parts of section 2 (model description)
    o Figure 1 has been removed
- 2. Description of the TRANSITS model
    o Structure unchanged
- 3. "Model setup, runs and evaluation" renamed to "Model evaluation"
    o 3.1 "Method" renamed to Method: observational constraints, model setup and runs
    o 3.3 "Evaluation and discussion" reorganized as follows:

- 3.3.1 "Validation of the mass loss, diffusion and 15N/14N fractionation process"
- 3.3.2 "Validation of the cage effects"
- 3.3.3 "Validation of the macroscopic fluxes"
- 3.3.4 "Validation of the residence time in the photic zone and calculation of the average number of recyclings"
- 3.3.5 "Validation of the nitrate mass in each compartment"
- 3.3.6 "Validation of the δ15N values in each compartment"
- 3.3.7 "Photolytically-driven dynamic equilibrium at the air-snow interface"
- 3.3.8 "On the discrepancies between simulated and observed Δ17O values"

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