Reply to the review of Anonymous Referee #1

We thank Reviewer #1 for his/her positive appreciation of this work. We especially appreciate his/her criticism against the evaporation experiment presented in this manuscript, which we have included in the revised manuscript.

Replies to his/her 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.

1. Major comment

The heart of this paper is the data shown in Figs 2 and 3 (and again in the supplement). This is a great dataset and I congratulate the authors on producing it. It really clarifies the extent of the phenomena being described. While I have detailed comments on various aspects of the paper, the major issue I have with the paper concerns the "laboratory" nitrate evaporation experiments and the conclusion from them that the evaporation fractionation is -8.5 permil. This result drives the conclusion that photochemistry dominates the loss process. While I think the conclusion may well be correct, I don't think this number is sound, and the authors should treat it very cautiously. I will therefore start by discussing section 3.2, Figure 8, and section 4.1.1.

We agree with reviewer #1: this value is not sound and we have changed the text to state this. Please see our detailed answers below. Especially, we invite you to note that the fractionation constant values associated with the evaporation experiments were revised.

Also, please see our comments to the review of Dr. Alexander. This experiment is not mimicking the field. However, this may not hamper our understanding of the nitrate isotopic effects associated with desorption processes.

It is first necessary to comment on their preconception (based on Frey et al 2009) that the fractionation constant for evaporation would be positive. It is not for this review to comment critically on an earlier paper, but this is a very surprising conclusion. One would naturally assume that the heavier isotope would have a lower vapor pressure and that the fractionation constant for evaporation would be negative. That this was not the conclusion in Frey et al (2009) arose from their decision that calculating the fractionation from the evaporation step was beyond their scope, so that they concentrated only on the fractionation arising from an ionization step. However that ionization step arises only if most of the nitric acid is dissociated. In practice, at a typical summer temperature of -30 degrees, and assuming HNO3 as the only impurity in the liquid, the equilibrium concentration in any liquid or liquid-like layer will be around 5 molar (and higher at lower temperatures), implying that a substantial percentage (I estimate of order 10%) of nitric acid is undissociated, and making it probable that the crucial step is the evaporation and not the ionization. In any case, whether they agree that this is the reason or not, the present authors need to comment on why the constant they derive from their experiments is of opposite sign to their colleagues' earlier deduction – at present this discrepancy is just ignored.

Yes indeed, Frey et al 2009 have simplified the calculation of the fractionation constant associated with nitrate evaporation by just considering the dissociation/protonation step (step 1 in their paper). This approach was dictated in part by the lack of literature data on vapor pressure of isotopically substituted HNO_3 at the time. To acknowledge this, we have changed a sentence in the introduction as follows : "Based on theoretical calculations, the same authors have estimated that the isotopic fractionation constant associated with the physical release of nitrate (in fact, with the dissociation/protonation step) should be positive, a result opposed to the large negative $^{15}\varepsilon_{app}$ value observed in the field."

In the revised version of the manuscript, we comment on the discrepancy of the $^{15}\varepsilon_{eva}$ value found in this study and that of Frey et al 2009. While the method and results sections were kept unchanged in this revised version, the discussion section was significantly rewritten.

In the current evaporation experiments, there are a number of issues. The experiments though interesting, are really not very similar to the real field situation, because they are done at a constant temperature (no vertical temperature gradient). In real life, the system is being driven by very strong temperature gradients. This difference is probably why no effect could be seen at the lower temperatures – precisely the relevant temperatures in the field.

Indeed, the evaporation experiment presented in this study does not intend to mimic the reality. However, we use approximately temperature and an open system (HNO_3 “sinks” by adsorption on the walls of the rooms) to force nitrate evaporation. The text was changed to acknowledge the exact nature of the experiments (not mimicking the reality) and the absence of neither temperature gradients nor wind pumping as noted by B. Alexander.

I am also not clear whether the experiment is in a closed system or whether the air above the snow is (as in real life) being replenished constantly.

The air above the snow was mostly nitrate-free given the wide area (> 40m^2 of walls) where nitrate could adsorb on. See our more detailed answer to Dr. Alexander.

The authors then state that they have corrected for snow sublimation (page 28566, line 17). The paper needs to explain what they mean by this. I am assuming the authors mean that they “diluted” the concentrations according to the water loss, but we need to have the details of this calculation explained as it is not at all obvious to me how a water sublimation, likely arising mainly from the top layers, is correctly allowed for in a bulk subsample. It is clearly important as my interpretation is that the nitrate concentration was actually higher at the end of the -30 experiment (more water mass loss than nitrate) than at the start, which makes the whole basis for the calculation very uncertain. Clearly this is not mimicking the field, where the nitrate concentration reduces with time.

As stated above, the aim of this experiment is not to mimic what happens in the field but to force nitrate loss through evaporation and to estimate a fractionation constant in these conditions.

Indeed, nitrate concentration at the end of the -10°C experiment was greater than at its beginning since snow mass loss was greater than nitrate mass loss in this experiment. Nitrate concentrations originally given in Fig. 8 (discussion paper) were concentrations corrected for snow sublimation, i.e. “diluted” as assumed by Reviewer #1. However, getting back to the data to better explicit the correction, we have found an error in the calculation of both the snow and nitrate mass fractions lost in each experiment.

For this reason, we are edited the text in sections 2.2 and 2.4 as well as later in the manuscript to update the correct values of $^{15}\varepsilon_{eva}$ as well as the method to obtain the remaining nitrate and snow mass from each sample. For this we have added two equations which we hope will clarify the calculation of the two quantities and therefore that of $^{15}\varepsilon_{eva}$.

The correct values of $^{15}\varepsilon_{eva}$ are : (-3,6 +/- 1,1)‰, (-0,3 +/- 1,2)‰ and (+0,9 +/- 1,5)‰ for the -10°C, -20°C and -30°C evaporation experiments. We note that these values are different than the values discussed in the discussion paper however the conclusions remain the same.

This is probably again down to the temperature: at -10 degrees there is substantial loss of water which will not be the case at field temperatures, and nitrate is likely to be lost as successive layers of water rapidly escape. At lower temperatures more representative of the field, the water loss is much reduced, while the nitrate loss may even be enhanced due to the higher concentrations in the remaining liquid at low temperature and the consequent reduced dissociation. My concern is therefore that we are left with a single experiment that is not really treating the field situation and mechanism, that is being calculated in an approximate way, and in which the slope can be calculated essentially from only a single data point (the one top left of Figure 8).

We agree with this but have tried to do our best to propose this simple experiment. We have acknowledged in the text that the experiment is not mimicking the field and that more lab research is required to derive a fractionation constant closer to reality with e.g. the control on the T gradients, wind pumping, nitrate vapor pressures in the air as well as the use of DC snow.

We do not agree with the reviewer comment. Tthe goal of this experiment is not to mimic all the processes occurring in the field. It is to quantify one and unique unidirectional process: sublimation of ice/desorption of nitric acid, and we think that in this strict context our experiment makes sense. At least we are sure that nitrate is where it should be located in ice and in the proper phase (because natural DC snow is used). We do not agree with the reviewer's QLL interpretation, at least at -30 °C and below. First the QLL at this temperature has to be demonstrated, not talking about -40, -50 °C. Moreover, liken a QLL to the same thermodynamical properties as a liquid is simply wrong. A 5M liquid solution at the DC temperature and P(HNO_3) (ca 10^{-8} mb) is simply thermodynamically impossible and way too far from equilibrium to exist (See Thibert and Domine, 1998). Futhermore, HNO_3 is essentially in the form of NO_3^- in ice at this low P(HNO_3) (See Pursell, et al, 2002) which is consistent with the increase of nitrate concentration in snow during its sublimation. Nevertheless, we have acknowledged in the text that the experiment is not mimicking the field and that more lab research is required to derive a fractionation constant closer to reality with e.g. the control on the T gradients, wind pumping, nitrate vapor pressures in the air as well as the use of DC snow.

Thibert, E., and F. Domine (1998), Thermodynamics and kinetics of the solid solution of HNO3 in ice, J Phys Chem B, 102(22), 4432-4439

Pursell, C. J., M. A. Everest, M. E. Falgout, and D. D. Sanchez (2002), Ionization of Nitric Acid on Ice, The Journal of Physical Chemistry A, 106(34), 7764-7768, doi: 10.1021/jp025697k

I do not have a brilliant solution to this, though I think it would be possible to estimate the fractionation constant for evaporation based on vapor pressures (which may exist in the literature), or from evaporation experiments simply based on bulk cooled solutions in which the water loss could be controlled better. It is also possible to buy H15NO3 as a pure compound on which experiments could be done. These are beyond the scope of this paper, but I nevertheless propose that the calculated fractionation constant needs to be treated with extreme caution, and that conclusions based on it must be heavily annotated with uncertainty.

The suggested theoretical calculations are beyond the scope of this paper. We don't understand the proposition of using $^{15}N\text{-}HNO_3$. Measuring the difference in P (which should be in the range of 10s of ‰) between $^{14}N\text{-}HNO_3$ and $^{15}N\text{-}HNO_3$ in equilibrium with the snow at 10^{-7} mbar level is well beyond the precision of any pressure gauge as sophisticated it can be (QMS, absorption spectroscopy etc).. Measuring the different vapor pressure of these pure isotopologues as function of temperature will be useless in the context of snow chemistry at low vapor pressure of HNO_3. We have to keep in mind to perform an isotopic measurement on the gas phase at the concentration found at DC; we need to pump air 5 days in a row at 1m^3/min. This gives the scale of the problem for laboratory experiment. Only the condensed phase will be accessible to isotopic analysis but then the snow will have to be considered as an infinite reservoir in comparison of the small gas phase that will possible to set up in a laboratory. For years these difficulties have occupied our mind but no practical solution has found so far except the sublimation performed in this study.

2. Other comments

Page 28560, line 15: I think it is misleading to give the fractionation constant for evaporation as having such a small error and the caveats around the experiment need to be mentioned here.

This sentence has been removed for clarity and also to shorten the abstract as suggested by Dr. Alexander.

Page 28563, line 25: I would suggest adding caveats about why the estimate of positive epsilon in Frey is dubious (as above). You will need this in order to avoid having to show extreme surprise when you find a negative value in the experiments.

For clarity, we mention the estimate of positive epsilon in Frey for the discussion section. However, in the introduction, we inform the reader that Frey et al clearly state that their theoretical estimate takes into account only the dissociation/protonation step ("ionization step"). The text of the introduction has been edited as follows: "Based on theoretical calculations, the same authors have estimated that the isotopic fractionation constant associated with the evaporation of nitrate (actually, with the dissociation/protonation step) should be positive, a result opposed to the large negative $^{15}\varepsilon_{app}$ value observed in the field.”

Page 28568, line 2 (and several other places, eg Fig 8, y-axis): there is a little carelessness about factors of 1000 here, you mean that you plotted 1 +delta/1000 if delta is in permil.

Anonymous Referee #1 is correct, the right y-axis in Figure 8 is wrong and it has been changed in the final ms to read d15N*10^3. However, the term ln(1 + delta) at Page 28568, Line 2, is correct. Indeed, our given definition of delta values (Page 28561, Line 27) does not have any 1000 factor in it so that the delta values can then be expressed in ‰ in the text. For instance, if a 0.087 value of d15N is calculated, the text will read 87‰. In the calculation of ln(1 + delta), we will obtain the 87‰ value.

Section 3.4 and Fig 11: I am not sure we learn anything from this figure and I’d be inclined to leave it out.

Figure 11 was moved to the Supplement.

Page 28574: Here is somewhere where more caution is needed about the role of evaporation. You should perhaps also mention that there is also evidence for loss of HCl from snow at Dome C (eg Rothlisberger et al 2003). As there is no obvious photochemical route for this, it suggests that evaporative loss can occur and maybe a scaling calculation (using vapour pressures) would allow an estimate to be made for nitric acid (though one would have to be cautious because of different ionization fractions). As a matter of interest did you measure chloride profiles in your snowpits?

We have not measured chloride profiles in our snow pits. We agree with Anonymous Referee #1: loss of HCl from snow occurs at Dome C as evidenced by Rothlisberger et al 2003. We have edited the text to add this information and to make our point clearer. At the end of 4.1.1. we now write : “We do not imply here that the evaporation of HNO_3 does not occur at all in Dome C snow since this statement would be in contradiction with observations of the loss from snow of other volatile species such as HCl (Röthlisberger et al., 2003), a compound which is not known to undergo any photolysis in DC conditions. Therefore, we remain cautious and acknowledge that nitrate may well be mobilized by evaporation at Dome C, however, the strength of UV-photolysis is such that it dominates the overall net loss from the snow” as supported also by flux measurements of nitrogen oxides (NO_x) and modelling (Frey et al 2012; France et al. , 2011).

Page 28579. If you believe that +24.7 is the fractionation constant for deposition to the snow, then doesn’t it follow that -24.7 is the constant for sublimation from the snow? This might be a more defendible value than the one from the evaporation experiments?

Page 28579, we do not provide a number for the fractionation constant associated with deposition of HNO_3 to the snow. However, we state that “our data suggest that […] (it) must be positive” which is consistent with the estimated negative value associated with the evaporation of HNO_3. Given that nitrate has a strong affinity for the condensed phase, a fractionation constant of a few ‰ above zero could be sufficient to explain the observed average +24.7‰ shift between the two reservoir. Indeed, using a fractionation constant of +4‰ and 1% of nitrate remaining in the atmosphere while 99% deposit to the snow gives a difference of more than +18‰ between the two reservoir when considering a Rayleigh type fractionation in an opened system.

Page 28580. I don’t think the explanation for the temporal offset really makes sense. Remember that the snow is the far larger reservoir, so it should be the concentration of nitrate in snow driving the air not the other way round. I have not calculated it but I would have thought a more likely explanation is that the lifetime of nitric acid in air (due to photolysis) decreases in midsummer, so that the atmospheric NOy is transferred much more into NOx rather than HNO3 during the snow peak. Unfortunately the Frey et al 2012 NOx data don’t extend early enough to assess this.

We agree with this reviewer that snow is a larger reservoir of nitrate than the atmosphere. But our study demonstrates that intense nitrate exchanges occur at the snow/air interface, so that even if snow remains the largest reservoir, the vertical profile of nitrate concentration, and thus the concentration of nitrate in the snow skin layer, can be influenced by atmospheric levels.

Our study shows that the atmospheric nitrate concentration peak occurs before that of the skin layer nitrate and this may indicate the preferential direction of the processes at play at the air-snow interface. Moreover, if nitrate concentrations in snow were controling those in the atmosphere, the latter should be much greater since skin layer concentrations are high. Therefore, a significant fraction of the nitrate reservoir in snow may well not take part in the exchanges with the atmosphere for reasons unknown yet. Therefore, atmospheric nitrate concentrations may not control skin layer nitrate concentrations.

Only numerical modeling including all components of the nitrate mass and nitrate isotopic mass balance in the atmosphere and snow compartments considered here would help elucidating this temporal offset. This is the purpose of a companion paper, currently in preparation, which will address such issues using a dedicated numerical model evaluated against all available field measurements.

Page 28583, line 6. Cage recombination deserves a longer explanation for the reader please.

Cage recombination has been better defined as a process which leads to the “reformation of nitrate from nitrate photo-products”. Because the two processes happen at the same time, we have changed the text and now refer to “the oxygen isotopic exchange and cage recombination effects undergone by nitrate photo-products” instead of only “cage recombination effects”.

Page 28584. There have been attempts to use the nitrate concentration in snow as a proxy for snow accumulation rate in the past (Wolff et al, 2010, QSR). Would you like to speculate on whether use of 15N might enhance this possible application?

This suggestion is interesting. However, the discussion of the use of isotope ratios in the interpretation of nitrate records in ice cores is the purpose of the companion paper.

Fig 9 caption. I don’t really understand what you mean by “the date when the data were composited”. Please explain what this means.

Each dataset plotted in Figures 9 and 10 do not start on January 1st. The vertical dashed line therefore locates the starting data of the datasets. The text was changed according to this explanation.

All other minor points or edits have been addressed.