Response to the review of B. Alexander

We thank Dr Becky Alexander for her positive review of this work.

As for Reviewer #1, replies to Dr Alexander’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.

1. General comment

The only significant comment that I have is related to the evaporation experiments. I found myself wondering exactly how to interpret the reported fractionation constant, as I wasn’t sure whether or not to think of it as an open or closed system and how closely this experiment mimics the real world. For example, how much does potential redeposition of HNO3 influence the fractionation constant?

The evaporation experiment setup can be seen as an open system. As stated at lines 19-21 Page 28574 in the Discussion Paper, “all of the experiments were conducted in closed spaces where atmospheric HNO3 is more likely to stick on walls rather than on snow”. Indeed, the walls have a wide area of more than 40m² to be compared to the small surface of the snow used for the experiments (40x20cm, 4cm thick). Therefore any redeposition must have been very limited thus not influencing the fractionation constant. We agree that this does not mimic the field since the atmospheric reservoir would be constantly replenished with nitrate as pointed out by Reviewer #1.

The goal was to get an estimate of the evaporative fractionation constant using natural snow from the study site, a basic quantity needed for modeling; so an open system & diffusion only would give you that. The real world shows the net effect of many processes, which we are trying to deconvolute, Wind pumping & redeposition play a role. It is neither possible nor needed to recreate all aspects of the natural system.

The idea behind this experiment is to isolate a given unidirectional process not to reproduce the field apparent fractionation. As crude as it is, it is better than doping a artificial snow and doing the same kind of experiment in an lab environment where P(HNO3) can easily exceeds orders of magnitude the P(HNO3) of DC.

Two types of transport within the firm exist (diffusion and wind pumping), while in the experiments it will only be diffusion. How important is this in determining the amount of redeposition in the firm, given that the lifetime in the snowpack interstitial air may be longer than in the real world?

We do not understand what Dr Alexander exactly means here. We agree that the only transport process in the experiments is diffusion. However, since any redeposition is prevented in the experiment (because of the wide wall surfaces), we do not think we can learn anything about the amount of redeposition of nitrate in the firm.

The residence time of air in the open pore space of the lab snow (assuming that any air movement from fans or heaters was small) might be longer than in the natural snow pack a Dome C if indeed wind pumping was an important process at the study location. At Dome C wind speeds in summer are low with a mean of ~2.6 m/s during Dec-2009 to Jan-2010. Previously, calculated diffusion time scales due to molecular diffusion of a trace gas in firm air and due to wind pumping in Antarctic snow were compared. The comparison reveals that at low wind speeds, i.e. <5m/s, molecular diffusion is 4-10 times faster than wind pumping, thus the dominating transport process (details in Frey et al., 2005). But again the main point of this experiment is to “scale” the desorption effect which depends intrinsically on only two parameters, the temperature and P(HNO3), assuming solid diffusion in ice lattice << gas diffusion. Thus pumping or passive diffusion is not what is at stake. Furthermore, the surface loss of nitric acid on ice surface is certainly more controlled by sublimation of water molecule than by a pure langmuir desorption process. Again it is not the apparent effect that we are researching here but the unidirectional loss from the ice surface.

2. Other comments
Minor points are addressed below.

Abstract: It is not clear at this point what an apparent fractionation factor is. Also, the abstract is long and has too many details. Just focus on main points, and leave the details to the text.

Indeed, the term “apparent” is not clear and has been removed from the abstract since we define it in the introduction only. We have shortened the abstract as suggested.

Page 28560 Line 6: Be specific upfront on what you mean by nitrate loss. Loss by what process?

We have added the words “(either by physical release or UV-photolysis of nitrate)".

Page 28564 Line 10-11: What does “isotopic transfer function of nitrate at the air-snow interface” mean? Be specific as to process or processes at this early stage in the manuscript.

We have edited the text as follows: “Last, we study the isotopic transfer function of nitrate at the air-snow interface, i.e. how d15N, D17O and d18O values in atmospheric nitrate are transferred to the skin layer snow nitrate.

Page 28568 Line 26: My memory of the France et al paper is that the e-folding depth ranges from 10-20 cm, not just 10 cm. You can also use calculations in Zatko et al., ACPD, 2012 of the e-folding depth at 305 nm, which is the more relevant wavelength for nitrate photolysis than 350 or 400 nm.

Yes, indeed, the e-folding depth ranges from 10 to 20 cm in the France et al paper. However, we kept referring to the 10 cm value since it applies to the soft and hard windpack snow layers which are found in the top 20-25 cm of snow at DC (Fig. 1 (b) in France et al). We changed the text to mention the 10-20 cm range instead of 10 cm only.

We were unaware of the recent Zatko et al paper. We therefore included the following sentence to the main text: “A recent study has calculated e-folding depths in the range 18-22 cm in snow remote from the DC station and at 305 nm, the peak wavelength of nitrate photolysis in the snowpack”.

Page 28570 Lines 23-24 and Figure 7a: What is the asymptotic nitrate flux? Flux up? Flux down? Net flux? This should be explained in section 2.4, and it is not mentioned here.

Indeed, the information is missing there. We have added the following sentence: “F(as.) represents the downward nitrate mass flux which escapes the photic zone towards the deeper snow layers”. The caption of Fig. 7a has also been edited.

Page 28572 Line 18: d15N(NO3-) of nitrate in the atmosphere or in the snow?

We mean d15N in atmospheric nitrate. The text was changed accordingly.

Page 28574 Line 6 and elsewhere: Don’t refer to -8.5 to be “near zero”. Although closer to zero than the photolysis fractionation factor, it is not near zero. This is confusing.

The text was changed and we preferred the adjective “small”.

Page 28578 Line 13: Does HNO3 have a shorter lifetime than NOx? If so, why?

The cited references indicate that HNO3 has a shorter lifetime than NOx. The lifetime of HNO3 is short because of dry deposition (0.8 cm/s) while the lifetime of NOx depends mostly on sink reactions and conversion to HNO3.

Page 28582 Line 5: MIF occurs during deposition? I think this would be mass-dependent, and thus not impact the D17O.

The discussion concerning the difference between D17O in skin layer and atmospheric nitrate has been revised. We note that the difference between the two is greater at the end of the winter (5‰ in
Mid-Oct) than in summer (almost no difference in January). The text in the result section was changed accordingly.

Therefore the discussion in Section 4.2 (paragraph 4) has been revisited and the variation of the D17O difference between the two reservoirs is only attributed to reservoir effects: the skin layer being a bigger nitrate reservoir than is the atmosphere, its oxygen isotopic composition gets only slowly set to a purely summertime value. The text in this paragraph has been significantly rewritten.

MIF during deposition is no longer invoked since it would be very unlikely that a deposition process could cause such a fractionation. Moreover, one would expect d18O to be more sensitive than D17O to a fractionation occurring during deposition. Such an effect is not observed (Figure 10c in the discussion paper, Fig. 6e in the revised version).

Page 28582 Line 6: Define what you mean by "reservoir effects".

The sentence was rephrased as follows: “The difference between the two series decreases during spring and summer most likely because the nitrate reservoir in the skin layer is on average a factor 100 larger than the atmospheric reservoir thus evolving with a greater inertia”.

Section 5: What about a discussion of the impact of “light”HNO3 derived from the photolysis of snow nitrate depositing downwind of its emission? Wouldn’t this impact (lower?) the apparent fractionation factor?

This discussion is interesting and beyond the scope of the current paper. We keep it for the companion paper.

Last 2 sentences of 2nd to last paragraph (beginning with “Nitrate recorded in ice cores…”): I do not know what you are saying in these 2 sentences, especially the second one. I think it’s just too vague. Be more specific about your implications.

The last two paragraphs have been edited and the two sentences mentioned have been completely rephrased as follows: “For the two reasons above, the isotopic composition of nitrate below the photic zone may well be archived and remain identical until nitrate is retrieved from ice cores and isotopic ratios are measured in it. Nitrate isotopic ratios measured in ice (e.g. on the Antarctic plateau) could therefore record past changes in isotopic ratios in nitrate escaping the photic zone, i.e. a few 10s of cm below the surface. Obtaining a record of past changes in the isotopic composition of atmospheric nitrate (i.e. potential changes in the oxidative state of the atmosphere using D17O) using isotopic ratios measured in ice cores requires to deconvolute the integrated effects of nitrate recycling and cage recombination on nitrate isotopic ratios measured in modern Antarctic plateau snow pits.”

Figure 9 caption: I don’t understand what the last sentence means.

See response to Anonymous Referee #1.

Combine Figures 9 and 10.

Figures 9 and 10 are recombined in the final ACP paper (ACP version required the portioning of the big figures). The same will be done with unification of Figures 2-3 and Figures 5-6-7 in two big figures.

All other minor points or edits have been addressed.