Response to the Editor's comments

We thank Dr Kaiser for his helpful comments at all stages of the reviewing process. Replies to this round of comments are given below in black font.

Editor's comments:

In the abstract, the authors suggest that the "However, the overall fractionation in D(17O) is small thus allowing the preservation of an atmospheric signal." Overall fractionation might be understood to mean the difference between the D(17O) of asymptotic nitrate and atmospheric nitrate. Perhaps the term "apparent D(17O) fractionation constant" would be more appropriate, to be consistent with the remainder of the paper. Also, the sentence might be understood to mean that the atmospheric D(17O) signature is preserved in ice core nitrate on the plateau. However, as Fig. 8 shows D(17O) in asymptotic nitrate is up to 5-13‰ lower than D(17O) in the top 2 cm, so this suggestion does not appear to hold water.

We agree that the term "apparent fractionation in D(17O)" is more appropriate. Also, we agree that only a portion of the atmospheric D(17O) signature is preserved. The abstract sentence now reads : "However, the apparent fractionation in D(17O) is small thus allowing the preservation of a portion of the atmospheric signal".

Referee #1 suggested measuring the isotope effect during nitric acid evaporation using H15NO3. The authors replied to the reviewer that the equilibrium vapor pressure at in situ conditions would be too low to do this. They also cited thermodynamic calculations that discount the existence of a possible quasi-liquid layer below -30°C. Notwithstanding that any thermodynamic calculations would need to be verified by observations for a concentrated brine-nitrate-water mixture, their evaporation experiments were done at temperatures of -30°C and above. In any case, the approach suggested by referee #1 would seem to be a sensible as a first step, this would seem to be viable and feasible approach to measure any associated isotopic fractionation, given the significant vapor pressure of nitric acid. Of course, the isotopic fractionation might vary with temperature and there may be secondary effects due to the interaction between HNO3 and water in a mixture. However, such effects may be taken into account using thermodynamic calculations using the Gibbs-Duhem equation (Janco and Van Hook (1974), Chem. Rev. 74, 689-750).

We thank both the referee and the editor for suggesting this experiment but again we think that the proposed experiment is inadequate in the context of our experiment. Firstly snow at DC cannot be compared to a brine-nitrate-water mixture like frozen seawater. Regarding the Quasi-Liquid Layer, notwithstanding its thickness as function of temperature, the main issue is that properties of this layer cannot be approximated by a liquid layer and there is now a consensus that such wording should actually be avoided [1] to limit confusion between a disordered layer and a liquid layer.

In order to clarify the reasons why we think such an experiment may pose more questions than solutions we reproduce below the diagram phase of HNO3/H2O mixture [2]

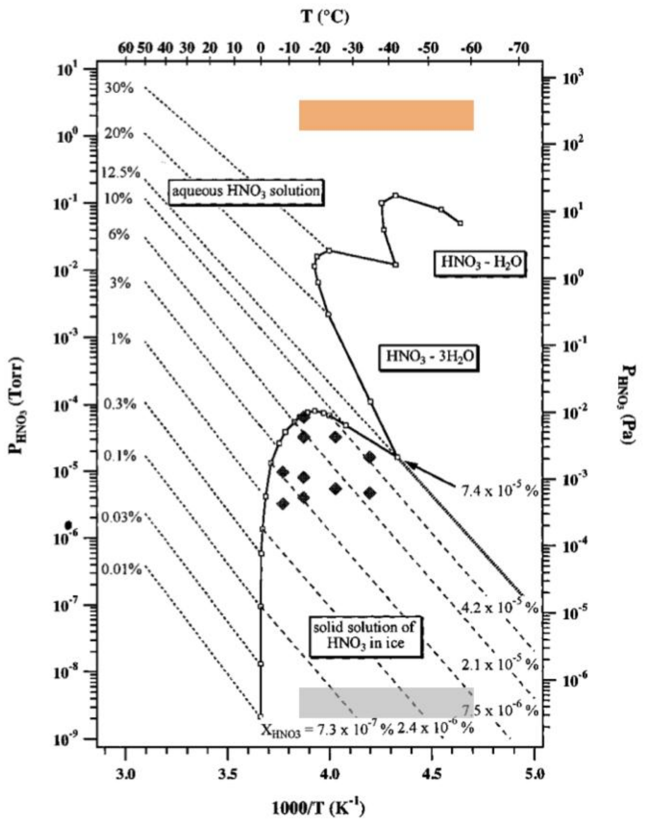

Figure 4. Isosolubility curves in mole fraction for HNO_3 in ice (calculated from eq 6) and in aqueous solutions (calculated from Jaecker-Voirol et al.[33]) as a function of P_{HNO_3} and inverse temperature. The symbol ◆ indicates our experimental conditions. The solid line is the ice−water boundary from Ji and Petit.[21] The dotted line is the ice-trihydrate boundary from Wooldridge et al. 1995.

The orange box symbolizes the experimental conditions proposed by the referee (fixed by a vapor pressure of HNO3 in a range of Torr which allows a possible comparison between P(H14NO3) and P(H15NO3) at a reasonable precision, estimated to be in range of few mTorr, using a good capacitance pressure gauge with enough precision). Note that in this range of pressure values, adsorption of the sticky HNO3 gas can cause serious problems for the pressure measurements but has been ignored here for simplicity. The grey box represents the range of conditions found in the field (few pptv of HNO3 at -15 to -40°C).

It seems to us that the “referee” and DC situations are very different. The difference between the 2 situations covers more than 9 orders of magnitude in pressure, 4 in concentration, two different phases with HNO_3 form dominating the “referee” case and NO_3^- the DC case [3, 4], two different situations that we think cannot be reconciled by the disordered layer [1] at temperature prevailing at DC (-15 to -50 °C).

However, it remains true that experimental investigations are needed to increase our knowledge of the physical, chemical and isotopic characteristics of the snow/nitrate interactions with and without solar illumination. Work is in progress in our laboratory and elsewhere to further address these issues.

NOx and nitric acid and/or nitrate readily exchange nitrogen isotopes, leading to substantial enrichment of 15N in the more oxidized phase (Brown and Begun (1959), Journal of Chemical Physics 30, 1206-1209), e.g. +(64±1) ‰ for 1 M HNO3 solutions. Isotopic exchange rates may be lower at lower concentrations, but the isotopic fractionation will presumably be similar, if not larger. Such nitrate concentrations do not appear to be unattainable and just as there are "cage effects" for oxygen isotopes, local conditions in the snow might be conducive to isotope exchange between nitrogen species. Intermediate species generated by nitrate photolysis might catalyze this exchange. Such equilibrium isotopic fractionation would add to any kinetic isotopic fractionation, which may be attributed to absorption cross section difference between nitric acid isotopologues. Have the authors undertaken any calculations or modeling to establish the potential significance of equilibrium isotope fractionation? They only seem to have considered equilibrium fractionation between HNO3 and NO3-. This would seem to be a potentially relevant process, especially if, as stated by the authors, photoproducts undergo oxygen isotope exchange and NOx has a longer lifetime than HNO3.

We thank Dr Kaiser for drawing our attention to the isotopic exchange occurring between nitrogen species. We did not undertake any calculation or modeling to establish the potential significance of this equilibrium isotope fractionation. However, we can explain why we believe that the isotopic fractionation is dominated by the photolytic process and not some isotopic equilibrium between nitrate and its photo-products.

In the case of photolysis, it is expected that the fractionation factor will vary depending on the light spectra. The isotopic fractionation of N atoms by nitrate photolysis is believed to occur because the two isotopologues (14NO3- and 15NO3-) should have slightly different absorption cross sections as discussed in Frey et al, 2009 [5] and thus the fractionation factor (i.e. the ratio of the photolysis rates) will directly depend on the light spectra. In Blunier et al 2005 [6], the use of a pure Xe lamp to photolyze nitrate in snow leads to fractionation constants of (-11.7±1.4)‰ a value contrasting with the -54‰ apparent fractionation constant measured from DC snow pits. Frey et al, 2009 were able to reconcile the laboratory and in situ observations by considering the photolysis as the primary process, something not possible with the exchange process. We have conducted photolysis experiments in the field [7] as well as in the lab [8] by varying the output spectra of the incident light using different UV filters and results are again consistent with the photolysis and not an isotopic exchange, (variation of fractionation factor observed at constant T but varying wavelength). These works, available to the editor, are currently reviewed by the authors and soon will be submitted. To conclude, we have good evidence that N isotopic fractionation occurs at the stage of the production of NOx under the effect of nitrate UV-photolysis. N isotopic equilibrium occurring between the NOx photo-products and nitrate ions is less likely to occur although it cannot be entirely ruled out as a secondary effect on top of the photolysis effect, adding its effect to the apparent fractionation factor observed but as now observations seem to indicate that this effect is minor. Work is in progress to test this idea.

[1] Bartels-Rausch, T., et al. (2012), Relationship between snow microstructure and physical and chemical processes, *Atmos. Chem. Phys. Discuss.*, *12*(11), 30409-30541, doi: 10.5194/acpd-12-30409-2012.
[2] 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.
[3] Marchand, P., G. Marcotte, and P. Ayotte (2012), Spectroscopic Study of HNO3 Dissociation on Ice, *The Journal of Physical Chemistry A*, *116*(49), 12112-12122, doi: 10.1021/jp309533f.

[4] Lewis, T., B. Winter, A. C. Stern, M. D. Baer, C. J. Mundy, D. J. Tobias, and J. C. Hemminger (2011), Does Nitric Acid Dissociate at the Aqueous Solution Surface?, *The Journal of Physical Chemistry C*, *115*(43), 21183-21190, doi: 10.1021/jp205842w.
[5] Frey, M. M., J. Savarino, S. Morin, J. Erbland, and J. M. F. Martins (2009), Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, *Atmos Chem Phys*, *9*, 8681–8696, doi: doi:10.5194/acp-9-8681-2009.
[6] Blunier, T., G. L. Floch, H.-W. Jacobi, and E. Quansah (2005), Isotopic view on nitrate loss in Antarctica surface snow, *Geophys Res Lett*, *32*, L13501, doi:13510.11029/12005GL023011.
[7] Berhanu, T. A., J. Erbland, and J. Savarino (2012), Isotopic effects of nitrate photochemistry in snow: A field study at Dome C, Antarctica, paper presented at AGU Fall Meeting, Eos Transaction, San Francisco.
[8] Meusinger, C., T. A. Berhanu, J. Erbland, F. Dominé, J. Savarino, and M. Johnson (2012), Photochemical isotope effect in snowpack nitrate, paper presented at 5th International Symposium on Isotopomers, Washington, DC.