Response to the Hastings lab group (Meredith Hastings, Aron Buffen, Katye Altieri, Dorothy Fibiger, and Rebecca Fahringer)

We thank Dr Hastings and her colleagues for their relevant comments which we have individually addressed below. Comments are in blue and italic and our response is in black font.

1. “Quantitative” collection of atmospheric nitrate

From manuscript (p 28,565): “Atmospheric samples were collected at DC during the same time period on glass fiber filters (20.3cm_25.4cm) using a high-volume air sampler (HVAS) which has been used during previous campaigns and has been shown to quantitatively trap both particulate nitrate and gaseous HNO3 (Frey et al., 2009).”

The methods employed here for atmospheric sampling have NOT been shown to quantitatively trap both particulate nitrate and gaseous HNO3. Nor have they been directly shown to quantitatively capture the isotopes of atmospheric nitrate. This is very important in terms of interpretation of the data herein. In particular, it should be directly justified, with evidence, that fractionation upon collection of nitrate cannot explain the difference between the atmospheric samples and the snow “skin” layer.

The present manuscript references Frey et al., 2009 and Frey et al., 2009 reference Morin et al., 2007 for the observation that HNO3 is trapped quantitatively (see the end of this comment for quoted material from these references). Morin et al., 2007 acknowledge the difficulty of collecting particulate and gaseous nitrate quantitatively and do not show any observations proving that both are in fact collected quantitatively. Furthermore, and of greater importance, the current manuscript and Frey et al., 2009 both use glass fiber filters as the substrate for collection, whereas the Morin et al., 2007 paper uses cellulose substrates for collection. Due to the importance of nitrate/nitric acid to air quality monitoring there is a litany of literature on method comparisons to capture both species (see for instance Huang et al., Atm Research, 2004; Chiwa et al., Env Ass Monitoring, 2008; Ames and Malm, Atm Env, 2001; Lavery et al., Air & Waste Management Ass, 2009; and EPA CASTNET methods papers). The ideal method depends on the time of deployment, how polluted or pristine the expected air masses are, temperature, flow rate, and location (marine atmosphere, coastal, or inland). According to EPA recommendations, a filter pack with a particle filter (Teflon, quartz, GF/F, etc.) and a cellulose backup filter impregnated with NaCl or Na2CO3 will quantitatively collect particulate nitrate and nitric acid in a large variety of sampling conditions. As the addition of NaCl improves the efficiency of collecting nitric acid (as Morin et al., 2009 points out), it is frequently assumed that both nitrate and nitric acid are collected with high efficiency in the marine boundary layer where there are high sea salt concentrations.

We are well aware of the difficulty to collect quantitatively particulate and gaseous nitrate. Indeed, this issue is abundantly discussed in the literature and, as Dr. Hastings pointed out appropriately, every sampling situation is unique and no universally approved method exists. We note that, to the best of our knowledge, the EPA method is not appropriate both for the collection of aerosols at high volume and the collection at temperatures such as those found at DC. Therefore, the EPA method cannot serve as a reference in our case.

As pointed out by M. Hastings, the filters used in the Morin et al 2007 and Frey et al 2009 studies are different : these were cellulose acetate filters (Whatman 41) and glass fiber filters (same as in Savarino et al 2007) respectively. In Frey et al 2009, tthe sampling efficiency is discussed by considering the nitrate concentrations measured on second-stage Whatman 41 filters. On those filters, nitrate concentrations are very low or below the detection limit of 0.5 ppbw. Thus, Frey et al 2009 conclude that no or very small loss of HNO3 from first-stage glass fiber filters occurs and that it is safe to assume near 100% sampling efficiency at Dome C.

To give additional support to the 100% collection of both particulate and gaseous nitrate at DC and using HVAS, we have compared the nitrate concentrations measured in this study and those obtained at DC and over the same period using annular denuder tubes coated with 10^{-2} M Na_2CO_3 (unpublished data, personal communication, B. Jourdain & S. Preunkert). Details on the sampling procedure with the denuders are found in Legrand et al 2012 (full reference below). Atmospheric HNO3 concentrations measured from the denuders at DC in 2009-2010 are in good agreement with the atmospheric nitrate concentrations measured using our setup (glass fiber filter and HVAS). The two curves match well and this is because aerosol nitrate concentrations are mostly found negligible (<10%) throughout the whole year (unpublished data from Legrand et al). The ratio NO_3^- denuder / NO_3^- HVAS is 0.97 on average for nitrate concentrations above 5 ng/m^3.

One reason to explain the efficient collection of atmospheric nitrate (and so that of gaseous HNO_3) on the bulk glass fiber filters used in this study is their high NaCl blanks. We have measured average chlorine amounts of more than 5 µmol on rinced glass fiber filters. Such high amounts may encourage the high collection efficiency and prevent loss of HNO_3 from our filters. Furthermore, the almost constant shift in d15N between the snow and the atmosphere does not militate in favor of a collection artifact. Finally, with more than 90% of nitrate in the gas phase, the concentration profile observed is consistent with such partitioning (maximum observed in summer in opposition to the sea salt aerosol which peaks in winter Jourdain et al., 2008) and thus strongly support the idea that the majority of HNO_3, if not all, is trapped on the filter.

For the reasons discussed above, we think that the collection efficiency of atmospheric nitrate in the "DC setup" is close to 100% thus preventing isotopic fractionation to affect the isotopic measurement obtain for the atmospheric data. For the sake of clarity, we add the following to the text in the Method part section 2.1 : "The efficient collection of both particulate and gaseous nitrate on glass fiber filters using the DC HVAS system is supported by the comparison of nitrate atmospheric concentrations measured in this study to HNO3 concentrations obtained from annular denuder tubes operated at DC over the same period of time. The data (unpublished, personal communication B. Jourdain and S. Preunkert, 2013) show a good agreement between the two collection procedures supporting the efficient collection of HNO_3 on glass fiber filters. Details on the sampling procedure with the denuders are found in Legrand et al 2012, a study which focuses on carboxylic acid but in which major inorganic ions such as NO3- were measured routinely.".
Last we add the following to the Discussion part section 4.2: "Isotopic fractionation occurring during atmospheric sampling cannot explain the average 25 ‰ shift in nitrogen-15 isotope observed between snow and atmospheric nitrate. Indeed,this would require that nitrate is not quantitatively collected on filter".

Legrand, M., V. Gros, S. Preunkert, R. Sarda-Estève, A.-M. Thierry, G. Pépy, and B. Jourdain (2012), A reassessment of the budget of formic and acetic acids in the boundary layer at Dumont d'Urville (coastal Antarctica): The role of penguin emissions on the budget of several oxygenated volatile organic compounds, J. Geophys. Res., 117, D06308, doi:10.1029/2011JD017102.

Jourdain, B., S. Preunkert, O. Cerri, H. Castebrunet, R. Udisti, and M. Legrand (2008), Year-round record of size-segregated aerosol composition in central Antarctica (Concordia station): Implications for the degree of fractionation of sea-salt particles, J Geophys Res, 113(D14), D14308, doi: 10.1029/2007jd009584.

2. "Skin layer" collection

It seems very difficult to accurately and precisely collect 1 kilogram of snow from only the top 3-4 millimeters. Please detail how this done to know that indeed only 3-4 mm is collected.

In fact, collecting accurately and precisely 300g of snow from only the top 3-4 mm is not so difficult, especially at Dome C where the rugosity of the surface is low. Very often, patchy flat surface of few m^2 are found, and using the appropriate tools make the exercise easy in absence of wind. Nevertheless, the uncertainty of few mm in the sampled thickness cannot is unavoidable be avoided given the fact that the softness of the uppermost snow layer is spatially, the quoted 3-4 mm range has to be seen as an average thickness given that a wide surface (ca 50 cm x 50 cm) has to be sampled to collect the targeted snow mass (300 g in the case of skin layer snow). We estimate an average skin layer thickness of 4 +/- 2 mm and have edited the text. For skilled and trained people, the sampling is in fact relatively easy, no more difficult than sampling a snow pit.

Moreover, Figure 11 in the discussion paper supports our hypothesis that the snow skin layer with a consistently constant thickness was sampled, because measurements in this compartment display a very low variability in terms of both concentrations and isotopic compositions argues for the sampling of a reproducible skin layer thickness as observed in the very small variability of nitrate concentrations and isotopic composition in this compartment. Last, we recall even if that the data presented in this paper were acquired over one single field season, the sampling technique was extensively tested over previous field experiments in the Arctic and the Antarctic.

3. Nitrate evaporation experiments.

Why not report δ18O and D17O data for the evaporation experiments and similarly quantify fractionation as done for δ15N? The D17O would be important since it should remain constant and provide confirmation that only mass-dependent processes are occurring. This data would also help support the supposition that there was no deposition of external HNO3.
Why not compare with the fractionation factor for evaporative loss calculated by Frey et al. 2009 for δ18O?

D17O and d18O data are not available for the evaporation experiments because two successive isotopic analyses failed in producing satisfactory calibrations for the oxygen isotope measurements. Given the small nitrate amounts obtained for this experiment, there are no sufficient nitrate amounts to re-analyze the entire dataset.

The amount of loss (due to sublimation only) reported in the -10C experiment seems implausibly large especially given that conditions were controlled, in a closed and dark room. From what is reported (28,565-28,566) we calculate an average snow density of 0.1875 g/cm3. Assuming a 0.72 lowering of the surface (how sublimation is usually assessed but not sure if the sides of the snow on the plates were exposed or not), lowering = 2.88 cm. Given the density above this yields a sublimation rate of 5.4 mm water equivalent day-1. This is roughly one order of magnitude greater than the rates measured at low-latitude, high elevation glaciers during the dry season (when sublimation is most significant and is promoted by strong radiation, clear skies, high wind speeds, low relative humidities and warm temperatures (Hastenrath, 1978; Ginot et al., 2001 and references therein; Wagnon et al., 2003; Favier et al., 2004). Some comparison or context for the rates of sublimation would be worth discussing.

We do not agree with this comparison and the reason is two-fold. First, the sides of the snow blocks were exposed. Second, the conditions in this experiment cannot be compared to high elevation glaciers at low-latitude sites even during the dry season. Indeed, while the room temperature was set to -10°C, the atmosphere in there was extremely dry, thereby enhancing sublimation.

Ambient air at Dome C is cold and dry, i.e. during 2009-10 mean Tair=-31.6ºC, RH = 68% and therefore water vapor pressure e=29.8 Pa. Undersaturation implies that sublimation will always occur. Ambient air warmed to -10ºC in the lab will be even more undersaturated with RH=15%.

4. Analytical reproducibility

The values of reference material corrected to should be reported. This is important for at least two reasons. First, in the future the accepted values may change (as has happened for IAEA-N3). Second, Bohlke et al., 2003, which is reference by Frey et al. 2009 for the isotopic reference values, does not use the linear definition for D17O and therefore the values reported in that reference should not be used when calculating D17O from the linear equation. If this has been taken into consideration then it should be said so, or at the very least report the isotopic reference values that are being corrected to so that other studies may directly compare.

The difference between the two definitions of D17O results in a small difference for USGS35 (21.1 versus 21.6‰, the last value accounting for the linear definition). In this paper we do not discuss such small differences. However, we follow the suggestion to report the D17O value used for USGS35 (21.6‰), USGS34 and 34. We also report the accepted d18O and d15N values used for the same material.

5. Data reduction

It is unclear how the best-fits are determined for the “asymptotic” functions. Further, the fits reported (e.g., Table 1) would benefit from some calculation of the significance of the “fit” (i.e. along the lines of r2).

Equation (2) (page 28568 in the discussion paper) gives the formulation assumed for the “asymptotic” functions of the quantity *X*. In the text, we explicitly report how the best fits are obtained : “the best set of parameters [X(0), X(as.), η(X)] was determined by minimizing the sum of squared residuals” (page 28568, line 17).

We already provide a metric for the significance of the fit since we calculate 1-σ uncertainties for the quantity *X* as the standard deviation of the residuals. We think that providing the value of r^2 for each quantity *X* of each snow pit would not benefit to the reader as it would overwhelm Table 1 with 3 additional columns and 69 additional values. One further support for the calculation of 1-σ uncertainties is their easy representation (under form of error bars) in Figures such as Figure 4 (and in all additional figures in the supplementary information) as well as in Figures 5, 6 and 7.

6. Continued changes in isotopes below several e-folding depths

How do you explain continued enrichment in d15N below 30 cm, indeed to 70cm?Could the recycling of nitrate within the firn and re-deposition potentially explain this? How can this be ruled out?

Indeed, changes in d15N are observed below 30cm and even sometimes below 70cm. These changes cannot be explained by nitrate UV photolysis using the 10cm e-folding depth value measured at Dome C and generally used as a baseline value in our study. We note that larger values for the e-folding depth up to 20 cm were however reported by France et al. (2011) in a hoar layer. In this case significant photolysis could occur down to 60 cm below the surface. However, we consider that non-photochemical effects must be invoked for variations exceeding a depth of 60 cm or been the remanant of a surface process (change in density, SSA, UV etc). Note that below the three e-folding depth, 15N is systematically enriched and thus precluding a systematic post depositional effect in the same direction.

7. Theoretical framework

On page 28,578 – why use the calculated fractionation factors in Frey et al. as opposed to the “observed” values found and reported in this work?

In this part of the discussion, we use the $^{15}N/^{14}N$ fractionation constant associated with nitrate UV-photolysis (denoted $^{15}\varepsilon_{pho}$ in the text) to discuss the signature of the NO_x emitted through this process. To this date, the best model for photolytic isotope fractionation of $15N(NO_3^-)$ in snow is that proposed by Frey et al. (2009) as it closely matches field observations. It is for the sake of clarity that we distinguish between a predicted value of a photolytic fractionation constant ($^{15}\varepsilon_{pho=}$ -48‰) and an apparent fraction constants ($^{15}\varepsilon_{app}$) which represent the “integrated isotopic effects” (page 28576, line 14) of nitrate recycling at the air-snow interface.

8. Isotopic offset between atmosphere and snow

Page 28,579 - why assume that deposition causes a fractionation? There are several other possible explanations that should be considered or ruled out: Can fractionation be caused by atmospheric sampling (see comment 1 above)? And can new deposition offset some the fractionation experienced by previously deposited HNO3?

Isotopic fractionation during atmospheric sampling cannot explain the different d15N values between skin layer and atmospheric nitrate in winter (see our response to comment 1). Considering the rate of snow accumulation at DC (ca. 10 cm/year), it is evident that this rate is not enough to “cover” the surface process effects. In fact, in summer it is very common to see the appearance of surface hoar which takes weeks to grow.

Furthermore, how does a constant offset indicate equilibrium? If it is at equilibrium shouldn't the D17O be equal between the atmospheric samples and the snow? If they are not does this not indicate mixing or exchange?

This comment refers to the discussion of D17O which was not correct in the discussion paper (paragraph 4, section 4.2). Therefore, it has been revisited in response to a comment by B. Alexander. In the revised version of the manuscript we show that the difference between D17O in skin layer and atmospheric nitrate decreases from mid-Oct (5 per mill difference) to January (difference within analytical error). In winter, D17O values in the two reservoirs are the same and indicate that atmospheric nitrate is then most probably of stratospheric origin. Then, when the sun rises and photochemistry starts in October, nitrate in the atmosphere mostly originates from the re-oxidation of snowpack emission of NO_x and then inherits a D17O signature from local oxidation processes. Because the skin layer reservoir is much larger than the atmospheric reservoir, it takes several weeks to the D17O in skin layer nitrate to be set to the local and summertime oxidative signature and the isotopic equilibrium is only found at this period of time. For this reason, we suggest to modify the title of the paper as follows: “Isotopic evidence for a photolytically driven dynamic equilibrium in summer”.

9. Application to Greenland glacial/interglacial record

The comments by the Hastings group show that a detailed discussion of the Greenland ice core record is beyond the scope of this paper. Therefore, the discussion on the Greenland ice core record is entirely removed from the revised version of this paper and kept for an upcoming article. We thank the Hastings group for constructive comments about this part of the work and will defer further discussion of this point to the upcoming publication currently in preparation.