Reply to the review of Anonymous Referee #1

We would like to thank Reviewer #1 for his/her useful suggestions and comments which we have addressed briefly below. For clarity, we keep the reviewer's comments in black while our response is in red font.

This manuscript presents an interesting attempt to better understand the impact of UV light on the preservation, and isotopic modification, of nitrate in snow at Dome C. A pair of experimental snow pits was created from drifted snow that was manually homogenized, then a plexiglass filter was used to largely exclude UV from one of the pits, with a transparent plexiglass plate above the other pit to replicate any impacts due to wind pumping, greenhouse effect, etc. Both pits were sampled about every 10 days (7 times total), yielding depth profiles of both the concentration of nitrate and its isotopic composition. Analysis focuses primarily on the loss of nitrate mass and the enrichment of N-15 in the nitrate remaining in the snow over the 2-month long experiment.

The main conclusions are that UV photolysis of nitrate is the primary factor causing both loss of nitrate mass and strong preferential release of N-14 from the snow at low accumulation sites in east Antarctica like Dome C. Of particular interest is the derived "apparent N-15 fractionation" of -68 =/- 12 permil in the pit exposed to UV compared to -12 +/- 2 permil in the pit where most of the UV photons were excluded. The authors suggest that this fractionation may be a better value to use in models than previously published estimates based on both field and lab studies. This may be correct, or it may be a matter to be debated by the experts, but I agree that the isolation study clearly demonstrates that UV photolysis is the dominant process changing the N isotopic composition of nitrate lingering in the photic zone of snow at Dome C.

On the other hand, it is far less clear that photolysis is the main process causing loss of nitrate from the snow. In both of the pits most of the nitrate that is lost comes from the near surface layers (0-5 cm in some cases, more like 0-12 in others, authors suggest 0- 7 cm as the zone where non-photolytic processes may have complicated their results). The authors state that "In general, the loss of nitrate in the top 7 cm was comparable for both the control and UV samples;" (pg 33056, lines 10 and 11) and based on Figure 3 in the manuscript and Figure 2 in the supplemental material I fully agree. However, the sentence quoted above continues: "the loss was larger for those samples exposed to solar UV relative to the control samples." This assertion seems to reflect what they hoped to see, rather than what the data revealed. The authors also suggest that in the pit exposed to UV there is continued minor loss (up to 25 %) between 7 and 20 cm while in the control pit no more than 20% is lost from any layer below 5 cm. But, Figure 2 in the supplemental material shows that for the profiles sampled 20 Jan in the pit not exposed to UV about 60% of the nitrate appears to have been lost from sample plotted at 6 cm and about 50% from the one just below, with > 20% lost as deep as 12 cm.

As already mentioned in our replies to the other reviewers, strong indications (unrealistic "mass loss" with corresponding isotope fractionation, convergence of the surface concentration and isotope values to the surrounding snow, observed drifted snow on each field with variable pattern (up to 20 cm thick), impossible to stop gaseous dry deposition, etc.) show that the first 7 cm should be viewed as a mixed layer between the experimental snow and surrounding snow, through both wet and dry mixing. Because surrounding snow has a lower nitrate concentration, mixing gives the false impression of an apparent mass loss. Thus this layer should be treated with caution, and the observed decrease in concentrations is not necessarily the consequence of mass loss. We agree that the original manuscript was not enough clear on this point. We hope that it is clear in the new version. Our reply regarding the excess nitrate in the UV pit follows below.

Note that mine are "eyeball" estimates that could be refined if I had the data. If the authors want to assert that there truly is more nitrate lost from the UV pit (overall, or in certain depth ranges) they should quantify such statements.

We think that the figures plotting *f* vs isotopic values, the level of ^{15}N fractionation between the two fields, even the concentration profiles taking into account the hiatus in standard are clear enough to show a significant difference in mass loss between the two experiments (e.g. no *f* change in the control at 20 cm depth, more than 10 % for the UV). The Rayleigh treatment of the data is another way of showing this difference. Again here we are mainly talking about observations below the 7 cm threshold. Saying that, it does not mean that there is no change in the control field but the change is significantly different than the UV pit.

Granted, given the surprising variability in measured nitrate concentrations near the bottom of both pits (which should have been, and in fact is assumed to be, constant) (see Figure 1 in supplement) it will be hard to show statistically significant differences. Bottom line, I urge the authors to stick with claiming that UV photolysis causes most of the change in N-15/N-14, and back off the mass loss claim.

Given the experimental complexity and caveats in the field study, indeed it is difficult to show a significant mass loss at the deepest levels of these pits without taking account the hiatus in the concentration measurements. In our effort to show the original data, we did not choose to display the corrected concentration profiles. Saying that, we agree with the reviewer that mass loss is more blurry than the isotope data. In fact, the isotope profiles clearly show that the control pit is not subjected to radical isotope change, an indication that either the concomitant variation of concentration should be minimum or that the fractionation associated this variation is small; basically the conclusion of the manuscript.

This is probably the most important example, but I find that the authors are kind of sloppy throughout the manuscript, making poorly substantiated claims, and sometimes making mildly contradictory claims in different passages. In the list of minor edits below further examples will be noted. First, I will raise an example where I feel important details are just omitted.

Given that there is a section 2.4 on Experimental precautions, I was very surprised that so few details were provided in section 2.1 regarding how the sample profiles were collected 7 different times from a 200 x 100 cmˆ2 area without disturbing the snow left behind. It is stated that each sample included 500-1000 g of snow, and near the surface the sampling depth interval appeared to be 2 cm. Assuming density of 0.3 g/cc, the surface area of the top several samples would have to be a little more than 800 cmˆ2. Noting that 7 such profiles were collected from each of the experimental pits, by the end of the season nearly 30% of the homogenized snow would have been removed (at least in the near surface layers). (It also seems likely that the act of sampling would disturb snow around the profile to some extent, so how was this minimized and/or mitigated?) The vertical pipes created by each profile would seem likely to modify air/heat/NOx exchange if left open, so I assume they were backfilled, but what was the source of the fill? Clearly, it would be fortuitous if the fill material closely matched what was removed (in terms of the evolving depth profiles of microphysics and also nitrate concentrations and isotopes), so what precautions were taken to ensure that subsequent profiles were not modified by earlier sampling events?

The reviewer has raised some very important points which requires clarification in the manuscript.

We have now reorganized sections 2.1 and 2.4. To answer the reviewer’s questions samples were collected 7 times at a 10-day frequency. Mostly, we have sampled 300-600 g snow and in a few cases about 1 kg of snow was sampled. A gap of 10 cm undisturbed snow was left in between each sampling location so that the nearby snow profiles remain unaffected. Every time after sampling, the vertical pipes were filled with natural snow (Note that this natural snow is not same as the homogenized drifted snow). In our protocol, we opted for open fields to minimize other perturbations (heat, accumulation of NOx, not allowing air snow exchange etc), the limitation of this strategy is a possible exchange of matter with the surrounding area by wind pumping, drifted snow, dry deposition etc. Thus even if we had refilled the vertical pipe with initial snow, exchange, wind pumping dry deposition would not have stopped, as it occurs in a natural field. Observing is disturbing, something unavoidable. The question is if the perturbation is large enough to disturb the photodinitrification. We took all possible precautions to limit these perturbations. As noted by the reviewer, the % of surface sampling was small, we refilled the sample volume. The distance between sample locations (10 cm) is believed to be sufficient to limit light backscattering change but ultimately what should be viewed is the different behavior between the two fields, as it can reasonably be assumed that at the statistical level both fields are disturbed by the same processes except that UV photolysis is magnified in one of the two fields.

A couple of additional minor quibbles in this section: given Figure 1 in the supplement, do you really think that the precision of the nitrate concentration measurements was better than 3% (pg 33051, line 19)? I think that would imply that the 1450 ppb in the bottom 5 cm should always have been in the range 1400 – 1500 ppb.

After reviewing all the replicates of the standard measurements, the stdev is actually closer to 5 %. This has been corrected in the new manuscript. We would like also to mention that 5 % is precision not accuracy and thus does not take into account any offset as mentioned before. In fact, for a given profile, the variation of concentration of the last 10 cm is in the precision range.

Was it possible to sample the profiles with the plexiglass plates in the frames, or did they need to be re- moved? If the latter, how long was the control pit exposed to full sun each time (and was it near mid day and peak actinic flux)?

The plexi plates were removed from their frames for the length of sampling (1h maximum) mostly in the morning (10 a.m. local time). Considering the characteristic time of the photolysis process (week if not months, note that after two months of experiment, the isotope composition were still far from reaching the observed natural field isotope fractionation at 10 cm 20 ‰ vs 150 ‰ for artificial and natural respectively) so that just time of sampling is very short in comparison of the characteristic time.

I note that a 1000 g snow sample will not fit into a 2-L Whirl-Pack bag unless the density is greater than 0.5, which seems implausibly high for depths < 30 cm, especially for experimental snow that was ground just before the experiment. I am also confused by the need for such large samples, given the complications noted in paragraph above (i.e., it would have seemed desirable to collect smaller samples to minimize disturbance). Authors state that they wanted to ensure > 100 nmol nitrate per sample for the full isotope analyses, but the lowest concentration in any single sample (Fig 1 in supplement) was > 3 nmol/g, suggesting samples of 35 g would have been adequate (vast majority of samples had concentrations > 6 and prob- ably 2/3 were over 16 nmol/g). Not sure what the authors are talking about when they mention some of the samples had “initial nitrate concentrations of about 1.5 nmol/ml” but even such clean snow would have > 100 nmol in a 70 g sample.

We needed to collect enough samples for replicate isotopic measurements in case of failure during the process. Our procedure is scaled for a few hundreds of ml of samples (as most of the time it is natural snow that we are processing). We agree that we could have sampled less snow, but could not have reduced disrupting the snow as a minimum size for a snow pit is required to sample comfortably (size of tools and hands, width to reach the bottom, etc.).

Here are a list of additional, mostly minor, comments keyed to page/line #.

33046/14-15 as noted above, if you want to claim more mass loss in the UV pit, need to make the comparison more quantitative. Based on current text, I would not put this statement in the abstract.

This sentence is now removed from the abstract

33046/23-24 related comment, not sure that photolysis established as dominant for mass loss, so suggest just claiming it dominates N fractionation.

Corrected accordingly.

33047/10 Mayewski and Legrand, 1990 is not a great citation given context of this sentence. They claimed that nitrate at South Pole was not impacted by post-depositional processing.

We have changed this reference to Legrand, M. R., and S. Kirchner (1990), Origins and variations of nitrate in south polar precipitation, *J Geophys Res*, *95*(D4), 3493-3507.

33047/14 Not sure the Summit references belong in a sentence talking about low accumulation sites. Maybe change the early part to say "is problematic at most sites on the polar ice sheets, where…"

The sentence has been modified as suggested by the reviewer.

33047/24-27 confusing sentence, especially the part defining R (which is not anywhere else) Was an equation in an earlier draft that included R?

This comment is correct; indeed a sentence was missing which has now been added to the manuscript:
"Stable isotope ratios (R) ($n(^{18}\mathrm{O})/n(^{16}\mathrm{O})$, $n(^{17}\mathrm{O})/n(^{16}\mathrm{O})$ and $n(^{15}\mathrm{N})/n(^{14}\mathrm{N})$) are expressed as isotopic enrichments/depletion ($\delta^{18}\mathrm{O}$, $\Delta^{17}\mathrm{O}$ and $\delta^{15}\mathrm{N}$) relative to a reference where $\delta = (R_{\mathrm{spl}}/R_{\mathrm{ref}}) - 1$, and R represents the elemental $^{17}\mathrm{O}/^{16}\mathrm{O}$, $^{18}\mathrm{O}/^{16}\mathrm{O}$, or $^{15}\mathrm{N}/^{14}\mathrm{N}$ ratio in the sample or reference material.".

33047/27 don't need both "in for" here

Corrected.

33048/19-22 Confused by this sentence, and how it relates to suggestion that Blunier et al., 2005 measured too low a fractionation in lab study using broad band light source. Seems that the fractionation would need to get more negative in UV to reconcile with field estimates (including yours in this paper) but I think sentence implies opposite.

The reason why Blunier et al., 2005 measured too low fractionations is due to exposing the snow to short wavelength UV (down to 200 nm). This will lead to less negative or even positive fractionations. In the laboratory study (Berhanu et al., 2014) we have shown this case, and stated that with filters appropriate to Dome C, the laboratory shows close agreement with the field.

33049/17 should “wider” be “wide”?

It is now corrected

33050/5 on page 33055 state that the mean nitrate in the two pits was 1431 and 1478 ppb, so I would say 1450 here (rather than 1600)

It is now corrected.

33053/19 delta in this line should not be the fractionation factor, since you are already using delta for the isotope ratio values in Eqn 1. Blunier et al. used alpha, so perhaps that is a good precedent.

We don’t understand the reviewers point here. The Rayleigh fractionation line can be given either as a power law of α or ε since α-1 = ε. The Rayleigh equation written R/R0 = f^(α -1), the ln of this law gives our equation 1 and the slope, α -1 or ε.

33054/15-21 Not clear how you use the natural pits to estimate fractionation. If same analysis as above, how is initial concentration constrained (needed for f)? In fact, as noted later (in sections 3.4 and 4.1.3), I am not sure if you do end up using natural pits.

This section is modified and as noted by the reviewer it was meant to be from the two snow pits (not natural snow pits).

33057/4-6 Sentence could be more precise. The 8-14 ‰ values are always in the top sample (0-2 cm, not 0-7) and for UV2 this is the max (it is not decreasing to this value). Could add UV1 also if the range was 5-14 permil.

The turn towards the surface value took place within the top 0-7 cm but the value 8-14 ‰ is at the surface. Even UV#2 showed a turn from a δ^{15}N value of 14.9 ‰ to 12.5 ‰. We have changed the surface level to 0-2 cm from 0-7 cm.

33058/section 3.4 Not clear how the values in Fig 10 were derived. Are they based on Rayleigh plots for each depth, with points for sampling events 1-6? Note, here it seems that Fig 10 is based on the UV pit (not natural pits).

Yes, figure 10 is based on the UV exposed pit. By using f and δ^{15}N obtained from samples collected at similar depth, we have derived fractionations using Rayleigh plots for that depth.

33059/6 Again, not convinced by claim for more loss in UV pits.

Please refer to previous comments as well as comments to other reviewers.

33061-62/first paragraph of 4.1.1 If you want to subjectively pick which samples to include and which to leave out, you need to explicitly tell the reader which ones stayed for each pit. Also, if you are going to do this for the UV pit, seems you may be obliged to also do it for the control. I do not think this will change the overall story, but including the region where f and the isotopes are changing fast will probably give larger fractionation for that pit as well. Would be better if you could define objective criteria to identify near surface samples that do not fit assumptions, and apply to both pits.

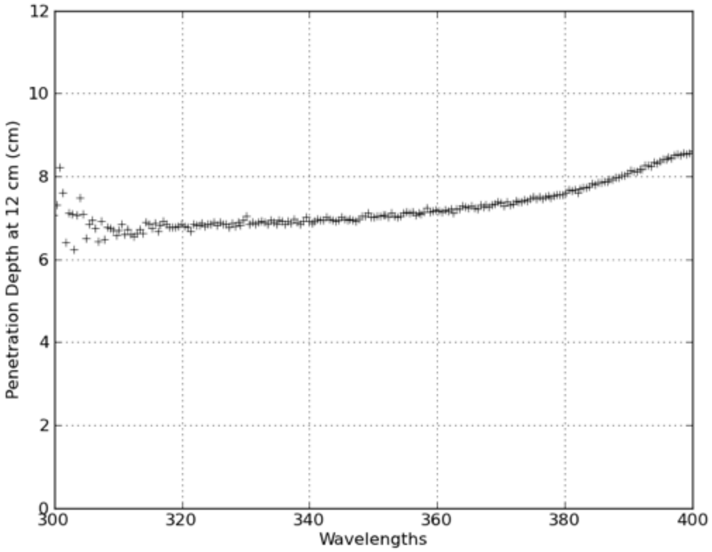
In section 4.1 we stated that some of the surface snow samples were excluded due to the strange profile in the δ^{15}N pattern opposite to what is observed below 7 cm depth. As simply disregarding values below 7 cm depth will introduce an artefact, we have used the change in δ^{15}N as a tracer so that any data point within 0-7 cm depth with δ^{15}N shifting to lower values than its following depth was excluded. In case of UV#4-UV#6, this is the region where non-photolytic processes are taking part significantly and all samples between 0-7 cm were excluded. In case of UV#0 to UV#3, only samples at 0-2 cm depth were excluded. This is in agreement with an increase of mixing (with surrounding environment) with time. As time passes, the top layers are increasingly impacted by the mixing effect. The only rational criteria to eliminate layers (we should keep in mind that drifted snow was not evenly distributed on the field) are therefore based on the isotopic composition trends which should always increase with time, the opposite is a sign of mixing with local nitrate that possesses, like our starting isotope composition, always a relatively low value.
This procedure is applied for both control and UV-exposed samples. In section 4.1.1 we have stated that samples from the surface to where δ^{15}N starts to shift to more negative values were excluded. In the conclusion section 33067/3-5, we have also stated that there might be an error introduced while excluding some of the top layer points where the photolysis effect is significant.

33062/20 What do you mean about comparisons between center and edge? Does this mean that even more profiles than 7 were collected (see long comment about sampling details above)? Even if you just mean that some of the 7 profiles were close to the edge of both the experimental snow and plexiglass while others were near center, this should have been detailed in section 2.1.

As we have repeatedly stated we had 7 sampling events. However, the total field size is much bigger than for only 7 samplings. Some samples were at the edge of the plate and some at the center. During high solar zenith angle, a portion of UV might directly find the control pits and we expect more direct contact with the edge samples than center samples. But we have not observed any systematic bias associated with the location of sampling, an indication that the residual photolysis had a minor effect. We now believe that most of the change observed on the control experiment is probably the result of physical processes.

33064-33065/section 4.1.3 Where does the -60 value come from? Is this not the average of the points in Fig 10? Confusing to compare this value to -68 “from the ex- perimental UV exposed pit” since Fig 10 is from that pit. My impression was that the -68 came from adjusted values based on each profile (Fig 12 and third column in Table 2) while Fig 10 came from looking at constant depth bins over time from UV1-6. Any case, this is confusing.

Yes, as stated by the reviewer the value -59.9 ± 24.7 ‰ is calculated as the average of the points in Fig 10. The value -67.9 ± 12.0 ‰ is the average of the individual samplings (UV#0 to UV#6). The comparison was made to show that the isotopic fractionations are both time and depth independent because as demonstrated in the laboratory experiment (Berhanu, et al., 2014), the only important parameter to change the fractionation factor (as cross section are intrinsic properties of the molecule and quantum yield is assumed to be the same) is the spectral distribution of the radiation and how it convolves with the cross section. In other words, reducing or increasing the spectral distribution of the incoming light by the same factor for all wavelengths does not change the fractionation factor. For UVs in the range of interest, energy is reduced by a factor almost independent of wavelength (Warren et al., 2006; France et al., 2011) which can also be seen from the figure below (Libois Q., personal communication). Therefore it is logical to see no dependence with time or depth. This is the same argument used to say that only physical processes or a mix of physical and photolysis processes impact the control experiment but can’t be only a photolysis effect.



33065/7-8 you say that Berha al closely

matched

33065/7-8 here you say that Berhanu et al closely matched Dome C irradiance, but on 33063/8-11 and again just below (33066/7) you say that the lab study could not match natural light field. Suspect the filtered lab light was pretty close, maybe close enough (probably not the main reason for disagreement).

The lab study closely matched the field light conditions. But there are many other issues including snow optical properties and non-photolytic processes which are also different in both studies. Complication in the top layer sample measurements from multiple processes may have also impacted the determined isotopic fractionations in the field.

33066/16-18 Not sure I saw where the results from the natural pits were shown and described before this. See comment above from 33064-33065.

This is now corrected.

References

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