

Interactive comment on “Isotopic effects of nitrate photochemistry in snow: a field study at Dome C, Antarctica” by T. A. Berhanu et al.

Anonymous Referee #1

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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
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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.

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. 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.

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 cm² 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 cm². 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/NO_x 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?

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. Was it possible

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to sample the profiles with the plexiglass plates in the frames, or did they need to be removed? 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)? 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 probably 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. 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.

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

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.

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. . .”

33047/24-27 confusing sentence, especially the part defining R (which is not anywhere

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else) Was an equation in an earlier draft that included R?

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

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.

33049/17 should "wider" be "wide"?

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)

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.

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.

33057/4-6 Sentence could be more precise. The 8-14 permil 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. 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).

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

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

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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.

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.

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 experimental 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.

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).

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 33045, 2014.

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