

## ***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 #2**

Received and published: 21 January 2015

#### General comments:

This work is an interesting contribution in the growing body of work on nitrate, nitrate photolysis, and the isotopes of nitrate, particularly at Dome C. An experiment was done in the field at Dome C utilizing two snowpits with manually homogenized snow, with one pit covered with a plexiglass plate that allows UV light and another that limited UV exposure. The snowpits were then sampled over ~two months to characterize and compare the behavior and expected isotopic fractionation for  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of nitrate exposed and not exposed to UV light. The purpose of the experiment provides an interesting field test of the isotopic fractionation associated with photolytic loss to compare with the same groups laboratory experiments. The primary conclusion of the work is that photolysis is the primary driver of loss of nitrate based on comparison of derived

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apparent isotope fractionation factors in the field to that derived in the prior laboratory experiment (Berhanu et al., 2014) and in theoretical calculations (Frey et al., 2009). This conclusion is valid, but may be overstated based on the data and data reduction presented. The subject matter overall should be of interest to the ACP community. The manuscript needs a good deal of revision to be acceptable for publication.

The primary purpose of this work is to evaluate apparent isotope fractionation factors for photolytic loss of nitrate in the field. In the Data Reduction section of the paper, the authors use a Rayleigh-type formulation to calculate the isotope fractionations based upon the amount of loss of nitrate in experimental profiles that were exposed to UV light over time. The nitrate fraction, or fraction of nitrate remaining in the snow, is calculated from the ratio of the final nitrate concentration ( $C$ ) compared to the initial nitrate concentration in the snow ( $C_0$ ). The authors use the average concentration measured at 25-30 cm as  $C_0$  to compare with the concentrations at other depths in each profile. I do not understand this choice. The expectation would be that the amount of loss of nitrate would change with depth as the light is attenuated (and in fact they assume that 25-30 cm is sufficient to justify negligible loss but this is not entirely justified – see comments below). Why not use the profile collected at time zero, i.e. the first sampling and compare each sampling at the same depth to the original first profile to gauge the amount of loss of nitrate? They suggest that the depths of samples across different profiles may or cannot be exactly the same. In this case, it would make most sense to group the profiles based on depth intervals such as 0-5 cm, 5-10cm, 10-15cm, etc. In this case an average concentration value from the control and from UV#0 at each depth interval would be  $C_0$ , and measured concentration averaged over the number of samples collected in that interval could be compared (i.e. the 3 datapoints between 0-5cm in profile 1 would be compared against the average concentration in the control between 0-5cm). I do not see why it is relevant to calculate the amount of nitrate remaining near the surface or at 10 cm or at 15 cm against what is happening at 25-30 cm across all profiles at all times. In fact, there is a lot of heterogeneity across the profiles in each pit in terms of concentrations at 25-30 cm, suggesting that negligible loss is not

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necessarily accurate. Additionally, some of the profiles have higher concentrations than the control or UV#0 in the 25-30 cm interval. Finally, the conclusions regarding lack of change of the epsilon values with depth should be checked by verifying comparison of samples across similar depth intervals rather than comparing all profiles against a single depth interval.

The description of the data reduction does not appear to be true in the supplemental figures. There seems to be miscalculation and/or missing data, although admittedly the figures are hardly readable. First and foremost the data included in the figures should be reported somewhere (I thought this was a requirement of ACPD/ACP?). Second, the figures must be adjusted to be readable, the symbols and lines should be consistent and carried through all figures rather than changing with each figure (this again makes it very difficult to follow the discussion). It should be justified in the text as to why only the even profiles are chosen to be shown in the text while all data is shown in the supplement. (I believe that it should be possible to format the figures such that all profiles can be shown in a way that is readable.) From what I can tell there seems to be disagreement between figures S1 and S2 in terms of the calculations described in the Data Reduction section. For example UV#6 in Fig S1b nitrate concentration is reported to 23 cm, then in Fig S2b the UV#6 profile extends all the way to 30 cm. If the nitrate concentration only extends (or was only measured) to 23 cm how can the fraction of loss be calculated below this depth? In the control pit most profiles have concentrations higher than #0 (even at 25-30cm) but the f values are nearly equal – why? There are number of other inconsistencies between the supplementary figures and text figures of the concentration compared to fraction of nitrate suggesting the authors should recheck these calculations/figures/data.

At a few points in the manuscript the authors mention that “below 50 cm, the photolysis of nitrate becomes negligible. . .(France et al., 2011)” (p.33051). For the data reduction it is assumed that at 25-30cm negligible loss of nitrate would occur. There needs to be more discussion surrounding this point. (An additional side note here that the average

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concentration at 25-30 cm is near 1400 ppb while the original snow on p.33050 had a concentration of near 1600ppb; and there is considerable heterogeneity across concentrations in each pit at 25-30 cm suggesting that something may in fact be changing at this depth). The conclusion of the current manuscript (and previous work in the group) is that photolysis is the dominant control on changes in  $\delta^{15}\text{N}$  of nitrate. Yet, Frey et al., 2009 and Erbland et al., 2013 show changes in  $\delta^{15}\text{N}$  that occur below 50 cm. Between 30 and 60 cm one of the pits in Frey et al. shows a  $\delta^{15}\text{N}$  increase of more than 150 ‰. Several of the Erbland et al. inland pits show increasing  $\delta^{15}\text{N}$  over the entire depth range of 40cm. How is it possible that  $\delta^{15}\text{N}$  continues to show similar changes below 50 cm if photolysis is the main control and is negligible at this depth?

Consider too that the France et al. reference may not be entirely appropriate here. The e-folding depths (eFDs) from France et al. were measured at 350 and 400 nm only; as illustrated in Frey et al. 2009 the peak in the spectral absorption curve for nitrate is 305 nm and calculated  $j$  value is centered around 320 nm and is very low at 350 nm and above. The modeled eFD for 305 nm from Zatko et al. 2013 for remote Dome C snow is 18-22 cm, suggesting that about 37% of the light is left to penetrate below 22 cm. This distinction in the possibility of light reaching to 25-30 cm and possibly deeper than 50 cm is very important for the design of the data reduction in this paper.

It is unacceptable to mention an artifact in the data as part of the supplement and conclusions alone. The potential for the problem in the concentration data to affect all of the results needs to be better elucidated in the main text. In fact, in the methods section there is no mention of reproducibility for the concentration measurements based on the data shown here, only based on previous work. It should be directly addressed why and how there may be an artifact in concentration data. This should also then be considered in terms of the error associated with the calculation of the fractionation factors, which depend on the concentration measurements. Some type of error propagation should be possible to account for how much error this artifact in concentration data might introduce to the Rayleigh model based calculations. The use of standard

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deviation across the calculated results may not be a realistic measure of the range that is possible given the larger errors on concentration than is suggested in the main text.

Pre-concentration of samples appears to be a standard technique within this group. However, more discussion of the method should be included. Lines 20-25 p. 33052 suggest that standards were treated identically to samples, but it is not clear if they were also subjected to the pre-concentration method. Are the reference materials such as the USGS35, 34, 32 run through this method as well to verify that it does not change the isotopes? Is the same NaCl that was used for the pre-concentrating of samples used to make the matrix of the reference materials? The corrections for the isotope data say they are included the Supplement, but they are not.

I do appreciate that a field experiment of this type makes for many factors beyond one's control. But the manuscript fails to really put together a coherent picture and explanation for the data, yet in the abstract and conclusions are very firm about proof for photolytic loss of nitrate being the dominant process at Dome C. A few concerns surrounding this issue include that significant amounts of loss of nitrate in the top 10 cm take place in both pits – so in the case where UV light is allowed to penetrate and in the case when it is limited. While some of the explanations offered may account for this partly, it is really difficult to accept that a similar mass loss is seen in both pits that must be explained by photolytic loss in just one snowpit. The authors make the case that the isotopic fractionation is so different for the two pits, despite the similar mass loss, and this needs to be revisited based on the above suggestions regarding how to evaluate the fractionation factors relative to the control profiles at similar depths rather than by comparing with a single depth. It also would be important to consider changes in calculated epsilon with time for each pit. While both experimental pits show similar mass loss near the surface, over time differences in their behavior are very apparent and this likely could be made clear by looking at fractionation of  $^{15}\text{N}$  at a given depth interval and whether it changes in a consistent way over time that is different between the two pits. This may help to provide a better avenue for explaining the differences

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between the pits. Without a better understanding of what could have caused such similar loss, the importance of photolysis is overstated.

In the figures (but not the text), the authors suggest that they are ignoring the top 7 cm because the lack of an understanding for the big loss in the control pit but at the same time suggest that they only rule out some of the data based on  $\delta^{15}\text{N}$ . What data is ruled in (or out) and how? And why? This must be explained in the text.

The amount of loss observed in the field is very different than that calculated in Frey et al. 2009 and that found in the laboratory experiments. This should be discussed.

At several points in the manuscript the authors suggest that they cannot interpret the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data, but then do discuss it. The mentions of not discussing this data should be deleted since the data is shown and discussed, even if it is not yet understood. In several of the works by this group the possibility of “cage effects” that lead to re-oxidation of snow-sourced  $\text{NO}_x$  to nitrate in situ is invoked to explain the lowering of  $\delta^{18}\text{O}$  and (possibly)  $\Delta^{17}\text{O}$ . This is never connected to the understanding based on the  $\delta^{15}\text{N}$ . Comparison amongst the theoretical values (Frey), laboratory values (Berhanu) and the field values (this study) is used to suggest that this all speaks consistently to an understanding of the fractionation associated with photolysis as the primary driver of nitrate loss. Yet the theoretical values are calculated based on simple (one-way, single process) loss of nitrate alone, and no influence of secondary formation. In the laboratory experiments, nitrogen gas is specifically used to blow away photolysis products to limit secondary formation in the gas phase, but my guess is this would not necessarily limit the so-called cage effects. In the field, neither the secondary reformation in the gas phase nor the in situ “cage effect” is controlled for. So how does this all influence the fractionation for  $\delta^{15}\text{N}$  amongst the studies and why is this effect on  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  not important for  $\delta^{15}\text{N}$ ?

On page 33057, it is suggested that no real differences or trends are detected in the oxygen isotope data. I disagree. In Figure 5, the UV pit  $\Delta^{17}\text{O}$  is consistently lower for

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much of the profiles compared to #0 (especially below 10 cm). This is not the case in the control pit (all profiles overlap and there is no distinguishable pattern). This appears to be significant (especially when compared with the differences/patterns in  $\delta^{15}\text{N}$  that are invoked as truly significant and robust). While there is variability in  $\Delta^{17}\text{O}$  in the #0, only the values at the surface and 5 cm are not significantly different and the top 7 cm is largely being ignored in the manuscript anyhow. The lowering of  $\Delta^{17}\text{O}$  in the UV pit seems consistent with the hypothesis that re-oxidation of photolysis products in “the cage” leads to exchange with a low  $\Delta^{17}\text{O}$  (low  $\delta^{18}\text{O}$ ) source, does it not? It is not clear why this difference in  $\Delta^{17}\text{O}$  should be ignored.

Throughout the manuscript it should be consistently clear that the fractionation factors are apparent. In some cases the subscript “app” is used and this should be applied throughout the manuscript, including the abstract and supplement.

Specific comments:

-L17, p33046: would suggest using the subscript “app” to be clear that the fractionation values are derived as “apparent isotopic fractionations”

-L1, pp33048: SMOW = Standard Mean Ocean Water

-Methods section: I think the details regarding the potential artifact in the concentration data must be discussed in the methods section. The mention of the concentration methods, pre-concentration methods, etc. should be part of another or separate section – it doesn’t make sense to have this as part of the Experimental Design.

-For the Experimental Design it seems important to include more details about how the snowpit was sampled. If a hole was dug in order to sample “a wall” of snow, was this hole then backfilled? If it was left open this seems like it would radically change the wind-pumping, allow for a lot of drift, and/or allow for more radiation from the side – all of which could potentially contribute to the large changes seen near the surface in the experimental pits.

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If the snowpits were refilled between sampling time so there wasn't a large hole allowing for significantly more drift, wind-pumping or more radiation from the side, then how was snow added? By shoveling? Was density of the snow measured? This snow would likely be compacted and a significant change in density might explain some difference in the amounts of loss seen in the field compared to that in earlier work at Dome C or in the laboratory experiments. In other words, how might the change in density for the experimental pits influence the results seen?

In terms of density overall, the homogenizing of the snow is really important to consider as altering the conditions relative to the natural snow (this is also true for the laboratory experiment which are quoted here as being done on natural snow and that snow was also homogenized for the lab experiments). How might the compaction of the homogenized snow contribute to changes in the attenuation of light with depth for instance?

All of this is to say, more details are needed in how sampling was completed. It also might be worth moving Figure 11 and presenting it as part of the Methods section to fully explain the experimental setup and conditions to consider in understanding the results and discussion.

-p 33050: How was transmittance determined? Why is transmittance for the non-UV plate not shown for below 310 nm? It almost appears as if the values are increasing again below 330 nm and 305 nm is the peak in nitrate absorption so this could be really important.

-L9, p33051: why is data only shown to 30cm if samples were collected to 50cm? What does the data below 30 cm show?

-L19, p 33051: Does this reproducibility of concentration measurements from previous studies hold up based on replicates measurements in this study?

-L16, p33052: Is 900 degrees C correct here? Kaiser et al only use 780C and other

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studies report values closer to 800C.

-L20-25, p 33052: What is Dome C water? Is this melted snow that contains ions or is this melted snow that is purified or something else?

-p33052-33053: Were any replicate samples run? How do these standard deviations compare to that based upon the reference materials replicates that are run many times?

-L2, p33053: What is an average uncertainty?

-Data reduction section: In this section use of the “app” subscript is appropriate and useful. Please use this throughout the manuscript when referring to apparent isotope fractionation values.

-L18-20, p33054: I do not understand what this means –are these different days of collection? Or the same profile sub-sampled? If there are 4 samples averaged then why are there not error bars denoting the standard deviation associated with this averaging? Please better explain this.

-p33056: Throughout this section the language needs to be much more precise. In the figure it really looks like loss is only “significant” to 17 cm, yet here it says it is significant to 20cm, then below it’s not significant or ceases below 25 cm yet the difference between the UV#0 and UV#6 is as large here as the difference between UV#0 and other profiles at 20 cm. Then from 28-30cm all of the profiles show a decrease? why? What is “significant”? Please go through this section more carefully and quantitatively justify the choices of what is significant, what is robust, etc.

Why are only even #'s shown in these figures? (this needs to be justified in the text)

-L1, p33058: How is “robust” defined? Some type of table showing regressions, R2 values and significance (p values) for all samples sets should be shown somewhere (right now it is only shown for UV#6 in the figure). And R2 values should be included in Table 2.

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L20, p33058: The 18e and 17E data ARE presented in the manuscript! Rephrase this.

L20-23, p33060: This should lead to less loss, not more loss. And this should be true for only the experimental pits and not the natural surface snow (which is not the case shown in Figure 4 and Figure 6). This should be reconsidered.

L6-7, p33060: “tops of snow pits were covered with the plexi-plates” This seems a bit of an inconsistent statement with earlier comments in the paper. The plates were ~9 cm above the snow and snow is not necessarily perfectly vertical at all times. Also, is all of the deposition expected to be wet-only?

L15, p33061: This is a strange and incorrect title. Maybe “Nitrogen isotopic fractionation: 15<sup>eapp</sup>” (where the 15 is superscript and the app is subscript)

L5-8, p33062: Here and in the tables the Frey et al. values should be directly taken from the manuscript, not averaged or rounded.

L9-10, p33063: It is interesting however that the laboratory results were similar to the theoretical values in Frey et al. 2009, which used the TUV model that is very similar to the actual spectral actinic flux.

L6, p33064: “sample UV#3” – this is not really a sample, but a mean of samples or a profile or ?

L5-15, p33065: It seems important to note that the laboratory study was only a 12 cm column, and loss was only observed in the top 5 cm – so this is very different than what is observed in the field and not a big depth range to make such significant reaches in terms of conclusion in line 12-13.

p33065-33066: Again it is very important to label all of the epsilon values as apparent (i.e., “app”).

L26, p33066: you might consider including density in this list of physical properties as well.

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L5-8, p33067: see general comments, but this artifact needs to be clearly addressed in the manuscript and its potential influence on the calculated epsilon values needs to be quantified.

Overall the quality of the tables and figures is very poor.

Table 2: The text must explain how  $\delta^{15}\text{N}$  is used to identify “external processes” and therefore what data is excluded versus included. Why is sampling 1 not included here? It is not clear which columns belong to which headers.

Table 3: The values reported in the table are not the values reported in Frey et al. (e.g., -49.8 not -50.0, etc.). If reporting to one decimal place then this should be reported exactly and not rounded.

Table 4: again, these are not the exact values that appear in Frey et al. Here 6.0 +/-2.1 should be 8.8 +/- .2.1! Please copy both values correctly.

Figure 1: why is transmittance below 310 nm not included for the non-UV plate? Why are there values above 1 for transmittance?

Figure 2: It may be worth mentioning on the figure itself that the 2 nm shift has been applied for clarity.

Figure 3: Why is only some data shown and not all profiles? “unexposed to solar UV” is an overstatement as discussed in the manuscript (transmittance is not zero, some light comes in when the sun is low, etc.) – perhaps say “reduced UV exposure.” The shading in Figure 3 should be used consistently (i.e. in Figs 5, 7, and 8 as well).

Figure 4 and Figure 6: These data do not fit well with the overall explanations provided in the text. The surface snow in the experimental pits seems to have been largely influenced by “external processes” and unnatural drifting, scouring, sublimation. If these external factors are so important for explaining the top 7 cm behavior in the experiment pit, why does the surface snow in the experimental pits compare so well with natural snow?

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Figure 5: there is no top and bottom panels.

Can the formatting in Figure 3 and 5, be similar and consistent in Figure 7 and 8 (this includes the look of the plots and the symbols and lines).

Figure 9: This is an important figure/result. Some of the numbers are difficult to read. The relationships (including  $R^2$  and  $p$  values) shown in this example should be reported for all profiles, not just the one. This would work well as a table in the text or supplement.

Figure 10: The text emphasizes over and over that samples were not necessarily taken at the same depth in each sampling event, so why is that stated here? Please see general comments about the calculations. It would make much more sense to be using depth intervals and including all of the data within those depth intervals. Also the epsilon is not “measured” between -50 to -70 ‰ (this range includes theoretical and laboratory experiment).

Figure 11: Suggest moving this earlier. It would make the gray shading in the data plots make more sense and would set the stage for the discussion of results.

Figure 12: The text needs to explain what data points were identified and how based on the  $\delta^{15}\text{N}$ . Why is the dashed line a line and not individual points? The way that this figure and the text reads, it suggests that data was chosen to dismiss the observed trend in  $15\text{e}$ , which may in fact be real!

Figure 13: The text is very dismissive of the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data. And the  $R^2$  shown in Figure 9 for  $\Delta^{17}\text{O}$  is 0.07 (and what is the  $p$  value? Is this significant at all?), meaning that less than 7% of the variability is explained by this relationship. Thus, showing Figure 13 is not really appropriate or legitimate when the data is not treated or explained robustly.

Supplement.

The figures in the supplement overall are extremely poor. The symbols, colors, and

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lines (including the weight of individual profile lines) should all be used consistently. Figure 1 has an incomplete figure caption or no figure caption; Figure 3 does not even include numbers on the y-axis; using thicker lines for some profiles draws attention to only certain profiles, and should be avoided. The supplement does not include the isotope data corrections and description as suggested in the text.

The overall carelessness in the manuscript and supplement undermines the quality of the data and undermines the legitimacy of the manuscript overall.

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

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