1 Reviewer comments on "Investigation of post-depositional processing of nitrate in East Antarctic snow: isotopic constraints on photolytitc loss, re-oxidation and source inputs" by Shi et al.

Shi et al. report in their study snow pit measurements of nitrate and its stable isotopes from an overland traverse in East Antarctica and discuss potential contributions of post-depositional processing and the atmospheric source signal to the isotope ratios observed in the snow. The main findings are:

Nitrate concentrations and isotope ratios at low-accumulation sites in the interior of the continent ($<$55 kg m^{-2}yr^{-1}) are found to be affected by post-depositional processing, i.e. nitrate concentrations decrease in the top few 10s of cm of snow, concurrent with enrichment in δ^{15}N(NO$_3^-$) and depletion in δ^{18}O(NO$_3^-$). The negative correlation between δ^{15}N and δ^{18}O in NO$_3^-$ is consistent with the current understanding of post-depositional isotopic fractionation from nitrate photolysis, i.e. enrichment in δ^{15}N(NO$_3^-$) and depletion in δ^{18}O(NO$_3^-$). The latter is attributed to isotope exchange with a reservoir of small or negative oxygen isotope ratios during formation of secondary nitrate. However some of the low-accumulation sites show at depth a positive correlation between δ^{15}N and δ^{18}O in NO$_3^-$, which lead the authors to raise caution when interpreting the preserved isotope signal as a tracer of a single process, i.e. inversion of the preserved nitrate isotope signal to an atmospheric signal may be more complicated than only assuming nitrate photolysis and associated isotopic fractionation.

Sites with higher accumulation rates closer to the coast (91-172 kg m^{-2}yr^{-1}) appear to preserve the atmospheric signal, as indicated by generally lower δ^{15}N(NO$_3^-$) and higher δ^{18}O(NO$_3^-$) values when compared to sites in the interior, and preservation of the seasonal variability in nitrate concentration and stable isotope ratios. The authors interpret the winter signal as a result of a stratospheric source, and the summer signal originating from a both tropospheric sources and chemical reactions.

Overall, the main merit of this study consists in reporting new spatially distributed data of nitrate and its stable isotopes in Antarctic surface snow, which is important to work towards a quantitative understanding of the Antarctic ice core signal of nitrate stable isotopes. Most findings and their interpretation are not really new, but rather confirm previous comprehensive (traverse) studies carried out in another sector of East Antarctica (Erbland et al., 2013; Frey et al., 2009; Savarino et al., 2007). Thus it's a bit disappointing that not more effort was undertaken to quantitatively compare the data to the existing literature, for example the dependence of the isotope ratios on site-specific accumulation rates or using an isotope fractionation model including recent progress in the lab (Berhanu et al., 2014). A more detailed and critical discussion of the data may well yield more insight into the complex topic of post-depositional processing of nitrate. The presentation of the material I find at times inaccurate (typos in table or equations) or lacking detail to follow the reasoning. Suggestions to rework the manuscript are included in the more detailed comments below.

We appreciate the time and attention to detail by referee 2. His/her constructive comments improve the manuscript in important ways. Please see below for point-by-point responses in blue following the referee's comments.

2 Detailed Comments

p31945/l9: or halogen radicals (XO)

Fixed, thank you.

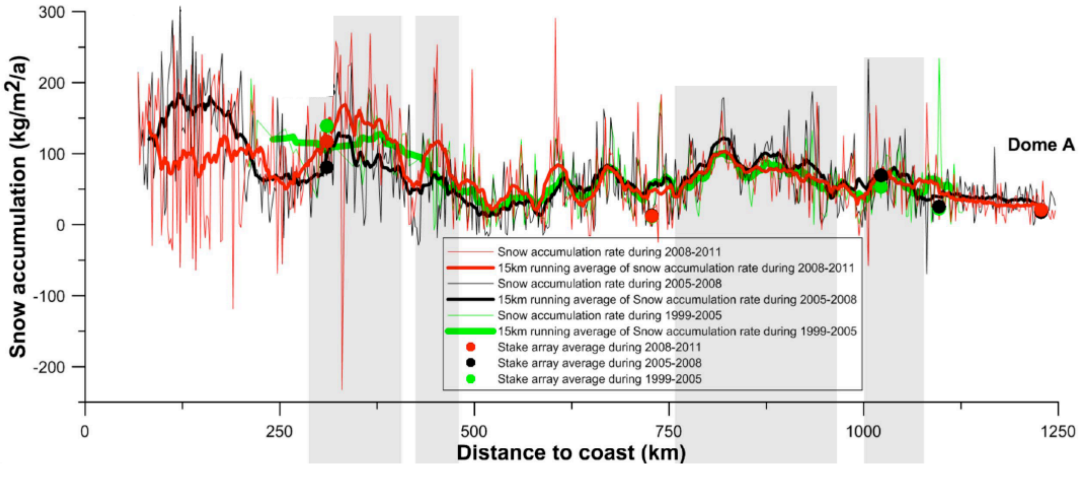
p31945/l28: Cite here previous work, which found and discussed the relationship between isotope ratios and accumulation rate, as summarised in Fig.4 of Erbland et al. (2013).

This has been updated and a figure similar to that of Erbland et al. (2013) Figure 4 will now be included in the manuscript.

p31948/l2: The snow pit information given in Table S1 is very relevant to the discussion, e.g. accumulation rates, one of the key parameter for preservation of nitrate (e.g. Röthlisberger et al., 2002) as well as sampling depth resolution, and therefore needs to be moved from the Supporting Material section to the main manuscript. The method section needs also more detail from Ding et al. (2011) on the site-specific annual accumulation rate A: how was A determined? As the time series are likely too short to detect a trend state at least the inter-annual variability (standard deviation). Is there any information on the seasonality of A in the region?

The snow accumulation rates were determined using the standard stake technique, where changes in snow height over time are measured relative to fixed stakes, and density was measured using a density scoop with volume of 1000ml. For the details regarding the stake measurements, please refer to Ding et al. (Ding et al., 2011. Spatial variability of surface mass balance along a traverse route from Zhongshan station to Dome A, Antarctica. *Journal of Glaciology* 57, 658-666.). There are not significant trends in the annual accumulation rates, and we considered this in terms of explaining the change in behavior in the isotopes over time/depth. Wang et al. (2013) (Wang, Y., H. Sodemann, S. Hou, V. Masson-Delmotte, J. Jouzel, and H. Pang (2013), Snow accumulation and its moisture origin over Dome Argus, Antarctica, Climate Dynamics, 40(3-4), 731-742, doi:10.1007/s00382-012-1398-9) have compiled existing stake and snowpit accumulation measurements from Dome A and show 1) little spatial variability (surrounding 50 km) and 2) stable accumulation rates over recent decades and since 1260 AD (1965-2009 = 21 kg m^2 m^{-1}; 2005-2008 = 18 kg m^2 m^{-1}; 2005-2009 = 19 kg m^2 m^{-1}; 2008-2009 = 21 kg m^2 m^{-1}; and 1260-2005 = 21.6 to 23 kg m^2 m^{-1}). Automatic weather station measurements presented in the same work show somewhat higher accumulation in the spring and summer (roughly 6-7 mm per month) vs. fall and winter (roughly 3-6 mm per month) with fairly stable values in the warmer months.

The following figure show the accumulation rates on the traverse from the coast to Dome A during the three periods, 1998-2005, 2005-2008 and 2008-2011 (unpublished data, Ding et al., 2015, personal communication). Although this information is limited in time compared to some our snowpits, it also speaks to the idea that no significant trend in recent snow accumulation is apparent in the study region over the time period covered by the snowpits.



The CHINARE (Chinese National Antarctic Research Expedition) and ANARE ((Australian National Antarctica Research Expedition) have measured the annual average temperature using borehole (a well-established recorder of mean annual surface air temperature) or automatic weather station observations on the Zhongshan-Dome A traverse (Ding, M., et al., 2010. Distribution of δ^{18}O in surface snow along a transect from Zhongshan Station to Dome A, East Antarctica. *Chinese Science Bulletin* 55, 2709-2714.). The multiple regression plus Kriging was used to interpolate these data on this traverse at a 10^{-5} degree spatial resolution (about 4e-3 km^2), to estimate annual average temperature at different sampling sites, and there is good consistency between the observed and estimated values (Xiao, C., et al., 2013. Stable isotopes in surface snow along a traverse route from Zhongshan station to Dome A, East Antarctica. *Climate Dynamics* 41, 2427-2438.).

The information on the date of snowpit collection is provided in the updated table below and this will be moved into the revised manuscript.

Table - Summary information for the seven snowpits presented in this study.

Snowpit	Location	Elevation (m)	Distance from coast (km)	Mean annual accumulation (kg m^{-2} a^{-1}) 1)	Mean annual air temperature (°C) 2)	Depth (cm)	Sample resolution (cm)	Sampling date (DD.MM.YYYY)
P1	71.13°S 77.31°E	2037	200	172.0	-29.1	150	3.0	18.12.2012
P2	71.81°S 77.89°S	2295	283	99.4	-32.9	200	5.0	20.12.2012
P3	73.40°S 77.00°E	2545	462	90.7	-35.7	200	5.0	22.12.2012
P4	76.29°S 77.03°E	2843	787	54.8	-41.3	200	2.0	28.12.2012
P5	77.91°S 77.13°E	3154	968	33.3	-46.4	200	2.0	30.12.2012
P6	79.02°S 76.98°E	3738	1092	25.4	-53.1	200	2.5	02.01.2013
P7	80.42°S 77.12°E	4093	1256	23.5	-58.5	300	2.5	06.01.2013

1) Mean annual snow accumulation rates are obtained from stake height field measurements, updated to 2013 from Ding et al. (2011).

2) Mean annual surface air temperatures are derived from 10m borehole temperatures and automatic weather station observations (Ding et al., 2010; Xiao et al., 2013).

p31948/l7: what was the diameter of the vials?

We will include this detail as part of a more extended methodological discussion (the 20 mL vials are 23 mm in outer diameter and the 60 mL vials are 43 mm in outer diameter). All three comments (2 review + comments by Dr. Erbland) make clear that we need to provide more information regarding the ability to measure only 5 nmol of nitrate. For compelteness, here is the information provided in response to the comments by Dr. Erbland as well:
The denitrifying bacteria are prepared as described in the original methods paper by Sigman et al., 2001 (and this can be re-described/added to the manuscript). Indeed, the maximum injection volumes are near 55 mL for the method at Brown University (see the figure below). The autosampler carousel is designed to fit either 20 mL vials or 60 mL vials – both vials have the same size septa caps (see the figure below), and the purging needle is designed such that the carrier gas and sample outflow into the rest of the system near the very top of the vial (such that a volume near 60 mL can be achieved). We have tested the addition of high volume samples extensively, and will include additional information on this in the supplemental material. Below is an example table of data obtained from a 5 nmol run. It is critically important when running very low concentrations to include standards/reference materials that are very close in concentration to the samples (i.e. there

is a small “volume” effect that is accounted for by using samples and standards of the same volume which yields similar area peaks on the mass spectrometer). Below is also two additional tables of data obtained on internal working standards. The first is a mix of USGS 35+USGS 34, and the second is KNO3. Both are used as internal standards for quality control purposes (they are treated as samples and corrected to reference materials in each run). Each has been injected for different volumes in different runs and its isotope values corrected to reference materials in each run that are close in concentration (i.e. close in injection volume). As you can see this also shows excellent reproducibility over a variety of runs and range in (low) concentrations for Δ^{17}O, δ^{15}N, and δ^{18}O.

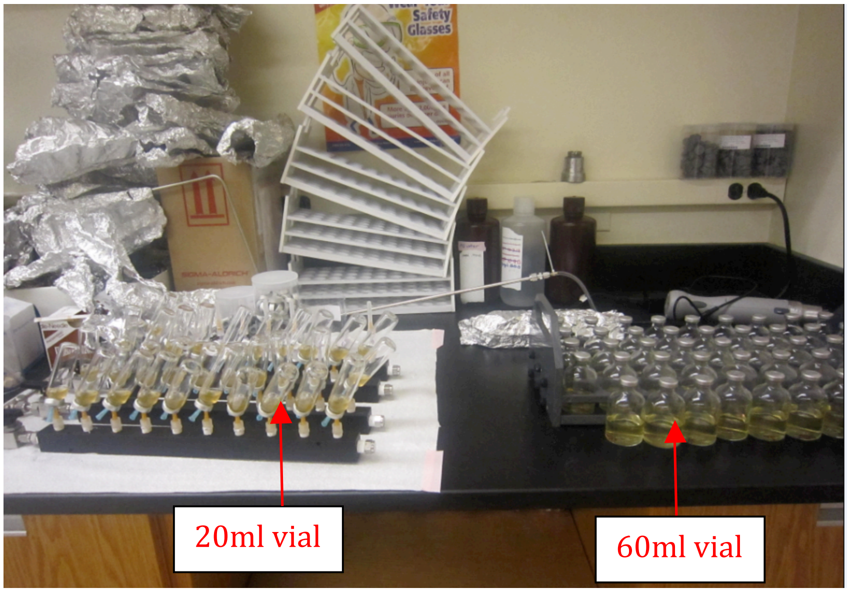


Figure: The two types of injection vials (e.g., 20ml and 60ml) used at Brown University.

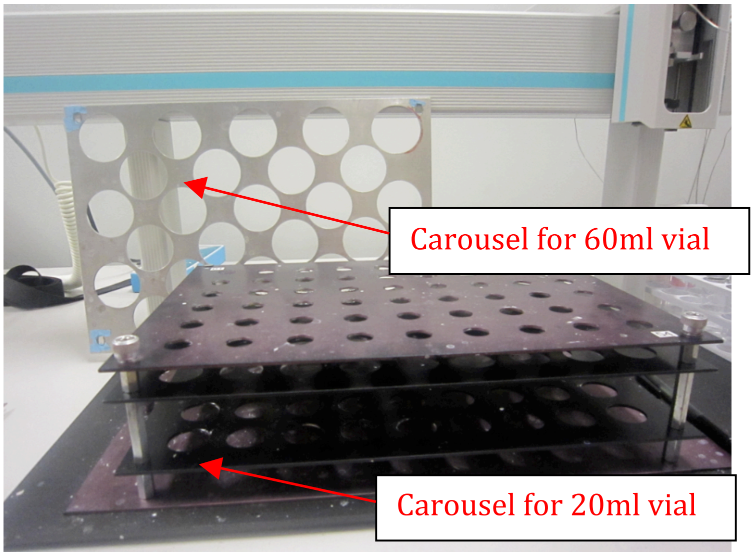


Figure: The autosampler carousel designed to fit either 20 mL vials or 60 mL vials

Table: Example raw data using 5nmol injections. Note that the “flush vial N2O” is a vial filled with reference gas that serves as an additional quality check on the system prior to and after completing a sample run.

Sample/Standard	Injection volume, ml	Peak area, Vs	rd ^{15}N uncorrected	rd ^{18}O uncorrected
flush vial N_2O		22.1	-0.7	-0.2
flush vial N_2O		23.6	-0.9	-0.5
Blank		<0.2		
USGS 35	25.0	3.7	3.7	44.9
USGS 32	25.0	4.3	156.9	20.3
USGS 34	25.0	4.0	-3.5	-28.6
IAEA N3	25.0	4.2	3.7	17.7
Sample-2	24.5	3.8	271.6	40.2
Sample-4	24.5	4.4	299.1	35.8
Sample-7	25.1	4.5	323.3	35.2
Sample-8	22.1	4.3	299.0	36.5
Sample-9	23.6	4.2	290.3	37.2
IAEA N3	25.0	4.2	3.9	17.6
USGS 35	25.0	4.0	3.5	44.2
USGS 34	25.0	4.1	-3.0	-28.2
USGS 32	25.0	4.2	155.5	20.3
Sample-12	24.6	4.3	346.2	33.0
Sample-13	29.0	3.7	318.2	34.6
Sample-15	27.3	3.9	323.2	37.3
Sample-16	29.3	3.7	308.9	38.9
Sample-17	26.4	3.4	284.1	42.8
Sample-18	24.4	3.9	289.5	40.2
Sample-19	28.0	4.0	269.7	42.4
USGS 32	25.0	4.2	155.3	20.4
IAEA N3	25.0	4.4	3.9	17.4
USGS 35	25.0	3.9	3.4	44.7
USGS 34	25.0	4.0	-3.2	-28.8
flush vial N_2O		25.5	-1.1	-1.0

Δ^{17}O for a USGS 35/34 mix internal standard. Mix is not quite 50/50.

Mean = 11.45 +/- 0.44‰. Range = 10.88 - 12.21‰.

Δ^{17}O (‰)	Amount (nmol)	Concentration (uM)	Injected volume (mL)
11.26	50.00	5.00	10.00
10.89	50.00	5.00	10.00
10.88	50.00	3.00	16.67
11.06	50.00	3.00	16.67
11.78	50.00	2.00	25.00
10.94	50.00	2.00	25.00
11.62	50.00	1.50	33.33
11.71	50.00	1.00	50.00
12.21	50.00	1.00	50.00
11.83	50.00	1.00	50.00
11.59	45.00	3.00	15.00
11.37	45.00	2.00	22.50
11.23	40.00	1.00	40.00
11.20	40.00	1.00	40.00
12.20	40.00	1.00	40.00

KNO3 internal standard.

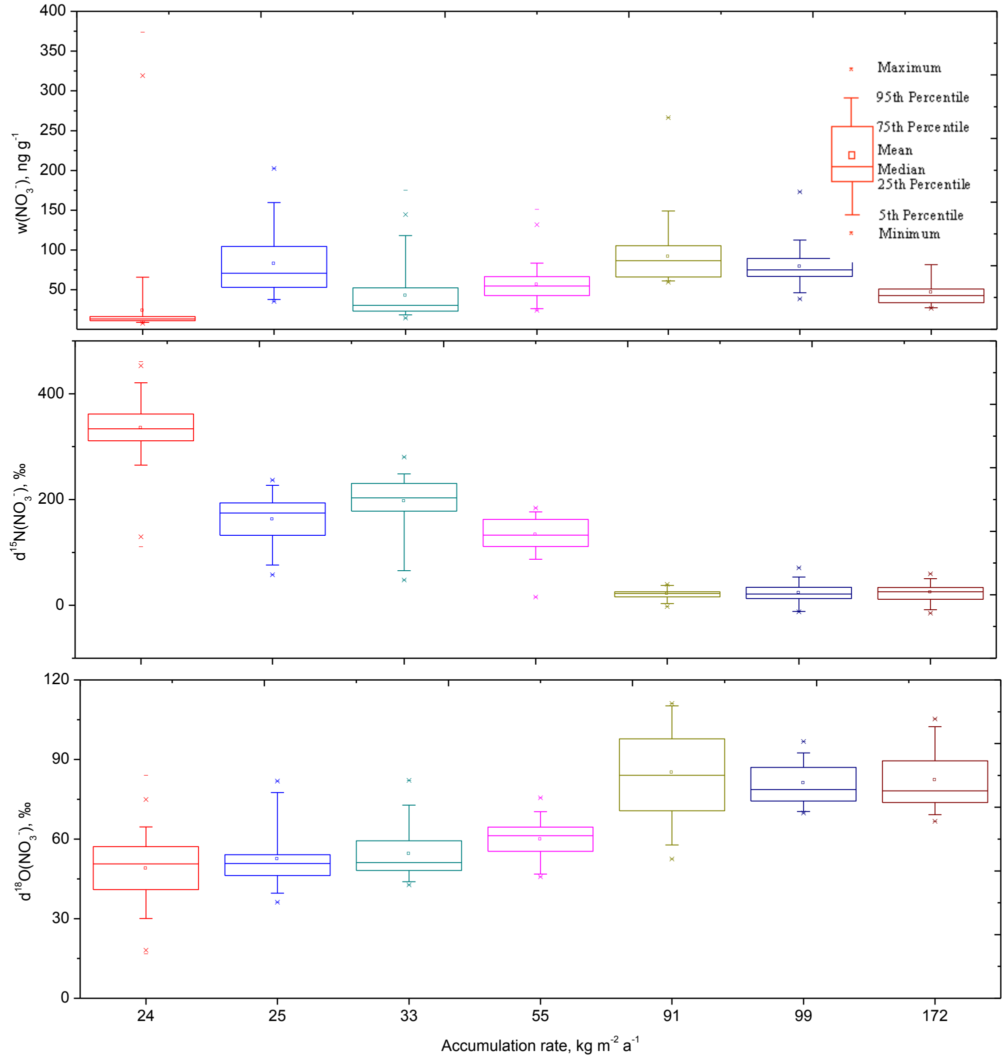
δ^{15}N: Mean = 58.37 +/- 0.62‰. Range = 57.52 - 59.59‰.

δ^{18}O: Mean = 30.65 +/- 0.52‰. Range = 29.55 - 31.50‰.

δ^{15}N	δ^{18}O	Injected volume (mL)	Concentration (uM)
59.39	30.43	20.00	0.50
58.19	30.85	20.00	0.50
58.37	30.80	20.00	0.50
57.52	31.13	16.67	0.60
58.77	30.62	16.67	0.60
58.12	30.59	13.33	0.75
57.66	31.50	13.33	0.75
58.73	30.16	13.33	0.75
58.39	31.31	10.31	0.97
57.71	31.00	10.00	1.00
58.26	31.01	10.00	1.00
58.48	30.82	10.00	1.00
57.70	30.45	10.00	1.00
57.57	31.04	10.00	1.00
58.96	29.93	10.00	1.00
59.59	29.77	10.00	1.00
59.31	30.16	10.00	1.00
58.70	30.88	10.00	1.00
58.27	29.55	10.00	1.00
57.76	31.01	6.67	1.50

p31951/l20: A comparison of the snow pit statistics given in Table 1 is only meaningful if the parameters (mean, σ etc.) are calculated over the same snow depth interval, which is apparently not the case. For example, it would be interesting to see how the snow top layer (uppermost sample), the top 3-5 e-folding depths (e.g. 30-50cm) or top 150cm vary across sites; a graph (whisker plot) is even warranted to illustrate site variability e.g. as a function of A or distance from coast.

We agree with the referee that there should be a better way to capture a "picture" of the large amount of data included in this study. As suggested, a box and whisker plot is shown below, displaying the mass fraction and isotope results, including the maximum, minimum, percentiles (5th, 25th, 75th, and 95th), mean and median plotted as a function of accumulation rate. This would be included in the manuscript in place of (instead of) Table 1.



p31954/l11: But Table 2 states for P6 a $^{15}\varepsilon$ value of -54.0‰. which one is correct?

This was a typo. The depths for which the apparent fractionation values were calculated have been updated based on the referee comments, and the new Table 2 and updated text is included in the revised manuscript.

p31954/l24-5: For completeness add also reactions of NO_2^- producing NO_x (photolysis and rxn with OH).

This has been added.

> p31955/l8 ...: The theory of how to model ε values needs to be introduced properly in the method section, explaining advantages and limitations, as well as including the latest progress from lab experiments (e.g. Frey et al., 2009; Berhanu et al., 2014). For instance, the approach by Frey et al. (2009) is based on the Zero Point Energy shift (ΔZPE) model, a general modelling framework developed originally to explain isotopic enrichment in stratospheric gas phase N_2O (Miller and Yung, 2000). A ΔZPE of -44.8 cm is applied to the $\sigma_{^{14}NO_3^-}$ spectrum (measured in lab experiments) to obtain the unknown $\sigma_{^{15}NO_3^-}$ spectrum. While model predictions of $^{15}\varepsilon$ match field observations reasonably well, Berhanu et al. (2014) suggest an improved model based on their lab experiments. I suggest to update your calculation following these authors recommendations: use $\sigma_{^{14}NO_3^-}$ in the aqueous phase at 278 K (Chu and Anastasio, 2003) and model the ^{14}N to ^{15}N substitution by applying a four parameter analytical model (i.e. asymmetry factor 0.9, ΔC=-32.5 cm, width reduction factor 1%) (Berhanu et al., 2014). In addition state also boundary conditions for your TUV model runs, namely elevation, albedo and column ozone.

The ZPE model is an important choice for us as it allows us to calculate both $^{15}\varepsilon$ and $^{18}\varepsilon$. We will updated the text to make clear the assumptions behind using it (e.g. that the isotopologues retain equal quantum yields and similar absorption curves (shape, peak), etc.) We contacted T. Berhanu and now provide comparison with the calculations using the Chu and Anastasio cross sections. Using the C/A data as discussed in the paper, $^{15}\varepsilon$ was calculated to be −45.3 ‰ at P1 and −48.0 ‰ at P7. Using the Berhanu 243K cross sections, $^{15}\varepsilon$ is calculated to be -48.9‰ at P1 and -52.8‰ at P7 (therefore, not changing any of our conclusions). For the TUV calculations, the elevations are those listed in the site descriptions table, which we now note in the text. We assumed clear sky conditions and no overhead SO_2 or NO_2. Total overhead ozone was set to 300 DU for both sites. Albedo was set to 0.97 following Grenfell et al. (1004 (Grenfell, T. C., S. G. Warren, and P. C. Mullen (1994), Reflection of solar radiation by the Antarctic snow surface at ultraviolet, visible, and near-infrared wavelengths, J. Geophys. Res., 99(D9), 18669-18684, doi:10.1029/94jd01484).

> p31955/l12: φ? also it should be dλ

These were errors associated with file transfer and have been fixed.

> p31955/l13: $\Phi_{NO_3^-}$; note that the quantum yield of nitrate photolysis on ice or in the natural snow pack can be 10-100 times larger than the value based on the Chu and Anastasio (2003) experiments. Please comment in the context of the Meusinger et al. (2014) lab study.

The Meusinger et al. and Berhanu et al. studies had only recently been published when we submitted out study. We will update the text to better reflect these studies. The quantum yield, however, will not change the calculated fractionation factors as long as it is equal for the isotopologue pairs.

> p31956/l10: as first observed in Dome C snow (Frey et al., 2009)

The observation of this decrease and its previous interpretation are discussed a few lines below in the original text.

> p31957/l5: I suggest to introduce the Rayleigh model and equations under methods, i.e. using general equations as developed in Blunier et al. (2005).

We will take this suggestion into account as we clarify and reorganize the manuscript

> p31957/l8-15: This is an interesting detail: how does the extent of post-depositional O-exchange vary (in time and in between sites)? And does available information on the depositional environment yield an explanation? While there may be no definitive answer, I suggest to repeat the calculation done for P7 for the other sites (at least on the Plateau), making use of the concurrent δ^{18}O(H_2O) measurements, and evaluate how much accumulative exchange of O atoms is needed to explain observations.

Indeed, the extent of post-depositional O-exchange varied among different sites. We use the discussion here as a "back of the envelope" type approach to hone in on the point we are making. The referee suggests estimating the amount of oxygen required to account for the changes in δ^{18}O across all of the inland snowpits. This is a complicated but important point from the perspective of understanding nitrate photolysis in snow, and to be accurate the initially deposited values prior to any post-depositional processing must be known. For a simple mass balance approach where photolysis alone is assumed to be responsible for NO_3^- loss and isotopic alteration, a $\delta^{18}O(NO_3^-)$ is expected to be 161‰ at 25cm for P7 and thus an observed δ^{18}O of 38.4‰ requires that 55% of the O atoms in the remaining NO_3^- are derived from H_2O (if assumed to the be the oxidant oxygen pool) for a $\delta^{18}O(H_2O)$ of -60‰. For P4, P5 and P6, this exchange is estimated to be 48%, 36% and 2%, respectively. (It is noted that the exchange percent in P6 is rather small, associated with the small difference in concentrations and δ^{18}O of NO_3^- between the surface snow ($w(NO_3^-)$=203 ng g^{-1}, $\delta^{18}O(NO_3^-)$=70‰) and the snow at depth of 25cm ($w(NO_3^-)$=155 ng g^{-1}, $\delta^{18}O(NO_3^-)$=78‰)). Overall, though, this would indicate that re-oxidation plays a very significant role in determining how the δ^{18}O of NO_3^- evolves in the snow. But this also raises a number of other difficult questions. For instance, using the exchange calculated at P7 would imply that, using a hypothetical starting Δ^{17}O of 32‰ (roughly similar to the top snowpit samples in Frey et al. and Erbland et al.) and $\Delta^{17}O(H_2O)$ of 0‰, a Δ^{17}O of ~14‰ is predicted at 25 cm, which is far lower than what is observed previous work. A more complete assessment of this is the subject of current and future work in our group.

> p31959/l4: If there was only a single process driving isotopic fractionation in snow ...

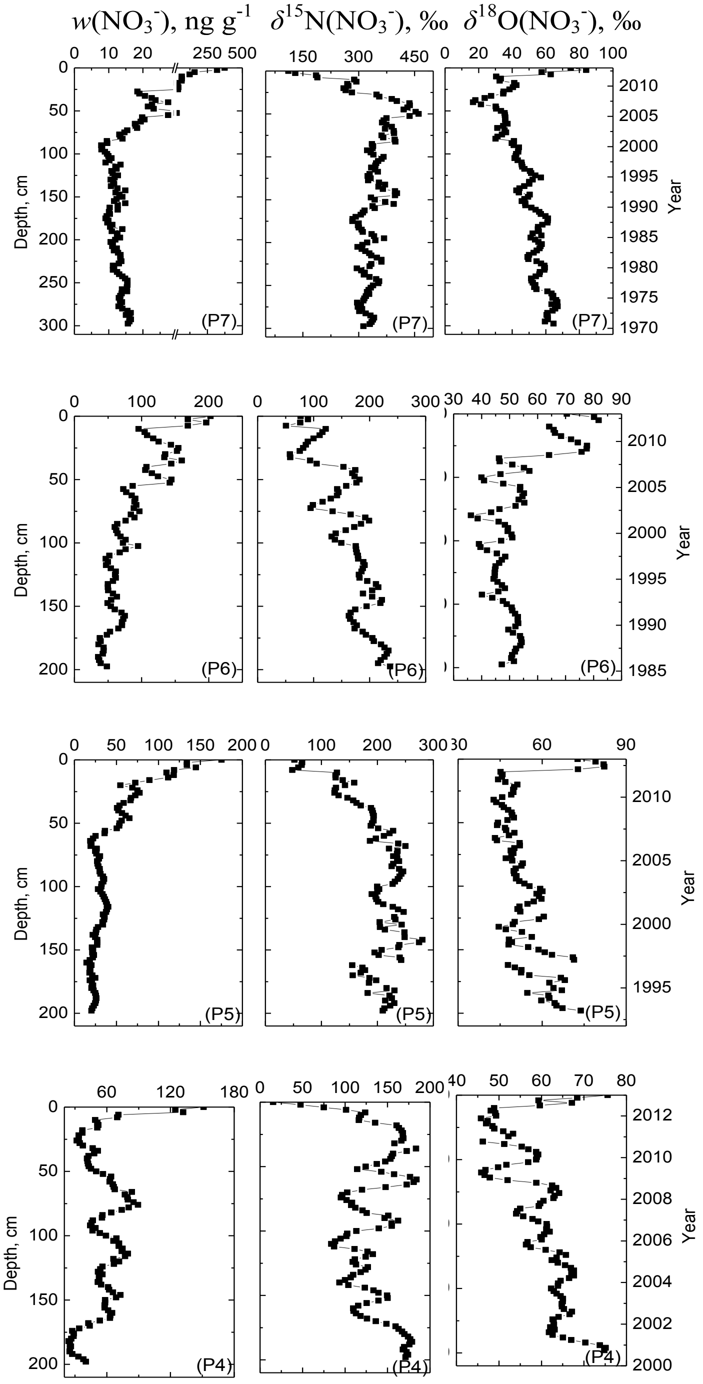
Thank you, fixed.

> p31959/l4-22: I disagree with your interpretation. Changes at depth may not reflect ongoing change but rather changes in past deposition conditions, notably accumulation rates (see above, what is the variability/trend?) and recent changes in column ozone. Associated changes in spectrum and seasonal dose of incident UV in turn impact ε values as well as total nitrate loss from snow. Detailed modelling of your pit profiles is beyond the scope of this paper but at least comment. Adding to the pit profiles a 2nd y-axis with approximate snow age would help to discuss this aspect.

Thank you for pointing this out. Our purpose was to first consider changes based on the current understanding of the impact of photolysis on both δ^{15}N and δ^{18}O; then consider how this varies with depth (i.e. time or additional in situ processes). This could be better framed in the manuscript. The changes in δ^{18}O with depth are different than would be expected, and intriguing. Even with "less" photolytic loss at some time point earlier, we cannot explain such higher values in δ^{18}O, especially across snowpits with differing accumulation rates and therefore representation of this signal at different times in history. In other words, if a significant change occurred in say, stratospheric chemistry this should influence the plateau around a similar time – not several years apart. It is a good suggestion to consider adding snow age to the y-axis, and we have added *approximate* timescales based on the accumulation rates (see below). There is little to suggest significant trends in accumulation at the inland sites (described above) and the discussion below could be added to the text to clarify this. We do consider changes in the ozone layer as a way to assess changes in incident UV. The text can be re-organized to better address the different hypotheses for explaining the trends in $\delta^{18}O$, and being clear which hypotheses have some evidence in their favor (and which do not).

Regarding the dating of P7 (the longest record) based on accumulation rate, the snow pit dug at Dome A in 2005 showed that accumulation was 2.3cm w.eq. a^{-1} during ~1965-2005 (pit dated with the aid of β-radioactivity peaks in 1964; Hou, et al., 2007)(Hou, S., Li, Y., Xiao, C., Ren, J., 2007. Recent accumulation rate at Dome A, Antarctica. Chinese Science Bulletin 52, 428-431.). The Dome A snow pit dug in 2010 showed that the accumulation rate was 2.37cm w.eq. a^{-1} during 1992-2010 (unpublished data, dated from the Pinatubo eruption $nssSO_4^{2-}$ peak in 1992). The stake array observations showed that the snow accumulation at Dome A was 2.35cm w.eq. a^{-1} during 2009-2013. Combined with the discussion above, there is little to support any recent trend in snow accumulation at Dome A. This also speaks to why it is unlikely that the changes in $^{18}\varepsilon_{app}$ can be explained by variation in snow accumulation.

If it is *assumed* that the snow accumulation is constant for 4 inland sites (also see the figure above lending confidence to this assumption), then the snowpit could be dated roughly following the measured accumulation and snow density, as shown below in the figure. We can add this to manuscript, and make clear both the assumption of constant accumulation and the existing data that would indicate this.



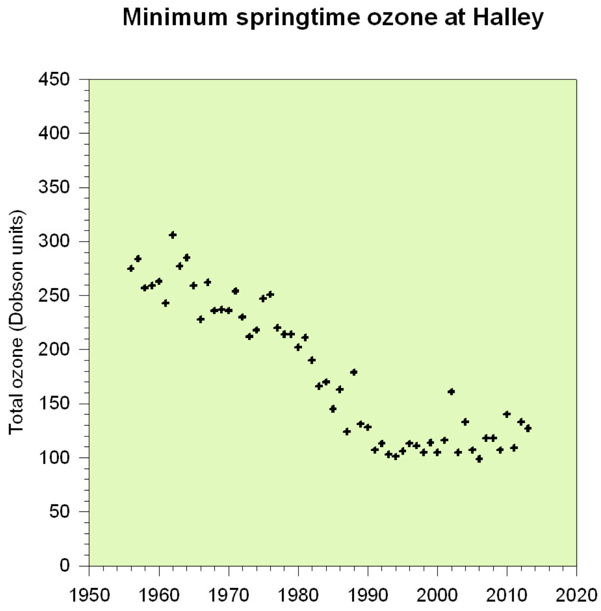
p31960/l2: "This can explain ... " is redundant with p31959/l26-7

Changed to "This is consistent with…"

p31960/l3-9 and below: Your suggestion to explain negative correlations between $w(\mathrm{NO}_3^-)$ and $\delta^{18}\mathrm{O}(\mathrm{NO}_3^-)$ at 100-200cm depth through the dark reaction NO_2+O_3 needs a more critical evaluation. (i) this process depends on O_3 and NO_2 mixing ratios in firn air at a particular snow depth. One would expect this process to occur at all sites, but why do you observe it only at P4-P7? Comparing the respective snow age with estimates of re-oxidation rates might yield further insight. (ii) in general the gas phase oxidation of NO_x contributes only small amounts of nitrate, and thus must be going on for quite some time to make a significant change in the isotope signature of a very large nitrate reservoir; e.g. taking Dome C firn air observations from the top meter of snow (as an upper limit) for NO_x ($\sim$4ppbv) and O_3 ($\sim$16ppbv) (Frey et al., 2014), along with typical snow density of 0.3 g cm^{-3} and assuming that the O_3 would oxidise all NO_2 then one obtains roughly 0.4 nmol $\mathrm{L}^{-1}_{H_2O}$ additional nitrate, contributing only a few ‰ to snow nitrate (typically a few tens of ng g^{-1}). While not impossible, it requires downward redistribution of nitrate, thus in the opposite direction of what is commonly assumed during snow denitrification. (iii) At the driest sites snow at 100-200 cm depth and below may have been deposited during the pre-O3 hole era, when boundary conditions for photolysis were different (see above). Please comment.

This is a very good point regarding the firn air measurements and we will incorporate this in the revision. As we noted in the text, these types of measurements are critical but have been very limited to date, and the Frey et al. (2014) OPALE paper was not yet published when we submitted our manuscript. As for why the correlations are more apparent in the plateau pits, the photolytic imprint is much less pronounced in the coastal pits due to the higher accumulation (shorter residence time in the photic zone), thus allowing for greater expression of seasonality which obscures a (more limited) post-depositional signature in the isotopic relationships at these sites.

As for changes in the ozone hole, we will more clearly address changing boundary conditions, but a connection to recent ozone depletion is not straightforward. Below are stratospheric ozone plots that help illustrate this. Based on the approximate dating in plots above, P7 overlaps with the pre-ozone hole era (generally considered prior to ~1980), but there is no obvious change in the nitrate isotope observations. Also, the shift at which δ^{18}O starts increasing with depth and changes in its relationship with δ^{15}N occurs roughly between 2005 and 2011 depending on the pit, yet there is also no clear correspondence to a change in ozone. Nor is there a signal reflecting when the ozone hole plateaus in the mid/early 1990s (for pits which overlap). This is not to say that the observed changes aren't related to changing boundary conditions (influence on photolysis or source), but that a link to ozone is not obvious based on a simple comparison. Also, it is notable that the DC07 and DC04 pits from Frey et al. (2009) cover 8-10 years and thus overlap with our observations, yet they do not show any increasing δ^{18}O with depth (or decreasing δ^{15}N in P7). The depths at which we observe this are also covered by the DC04 and DC07 pits (~70 cm). Given the large spatial influence of stratospheric ozone on surface irradiance in Antarctica, it seems unlikely that Dome A and its surrounding region would be affected by this process and not Dome C. So something clearly more regional, or local, is at play in our observations. One suggestion was different in situ chemistry. We will revisit our explanation, however, and consider other factors, such as possible changes in source. For ozone, the changes in the boundary conditions should be most influential, and mostly confined, to spring, despite the majority of photolysis occurring in summer. We will include a measure of sensitivity in the rate constant and fractionation factors to varying ozone concentrations.



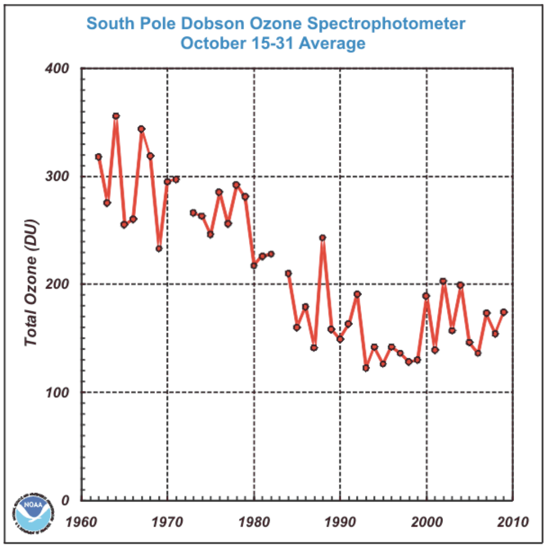
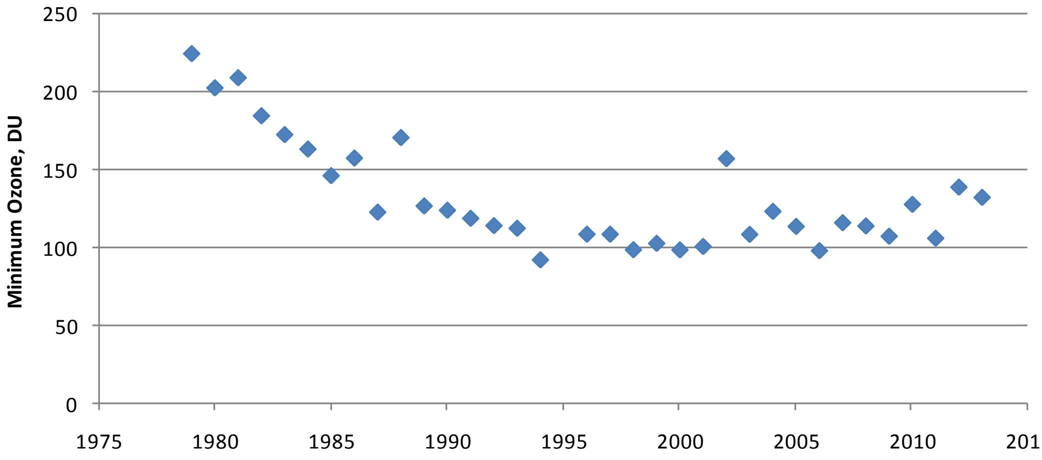


Figure 17. Mean total ozone amount between October 15-31 measured by the Dobson spectrophotometer at the NOAA South Pole station.

Sources: http://www.antarctica.ac.uk/met/jds/ozone/graphs.html; http://www.cpc.noaa.gov/products/stratosphere/winter_bulletins/sh_09/



Minimum daily Southern Hemisphere total overhead ozone from TOMS/OMI measurements. Data from: http://ozonewatch.gsfc.nasa.gov/statistics/annual_data.html.

> p31961/l5-8: An important assumption is also that the boundary conditions of deposition (i.e. for photolysis) remain constant.

Agreed, and based on the comments here and in the other reviews we need to clearly state earlier in the manuscript what assumptions are made in order to use these relationships.

> p31963/l3-5: Note that photolytic loss (or redistribution) is expected to occur throughout the sunlit season, while deposition of nitrate spikes may depend also on other factors such as the timing of snow fall.

Noted.

> p31963/l21: describe dating of the snow pit(s) (along with the accumulation rate measurement) in the method section

This will be added to the methods section.

> p31964/l4: Nitrate profiles in snow and firn show occasionally also winter spikes; for a discussion see Wolff et al. (2008).

In general, the nitrate peaks in surface snow at Halley were present in summertime (Wolff et al., 2008). However, there was also *one prominent peak* in snow concentration of nitrate observed in winter 2004 (see the figure below). Wolff et al. argued that the high concentrations in winter surface snow appear to have been associated with an enhancement of partitioning of nitrate to aerosol, without definitively attributing a cause. In comparison with summertime nitrate peaks, the winter peak was small. Overall, the results in Wolff et al. (2008) are consistent with our findings and we can re-phrase this point, possibly as “Previous observations at Antarctic coastal sites suggested that NO_3^- concentrations were generally higher in summer and lower in winter (Mulvaney et al., 1998; Wagenbach et al., 1998; Wolff et al., 2008), which is consistent with our findings.”

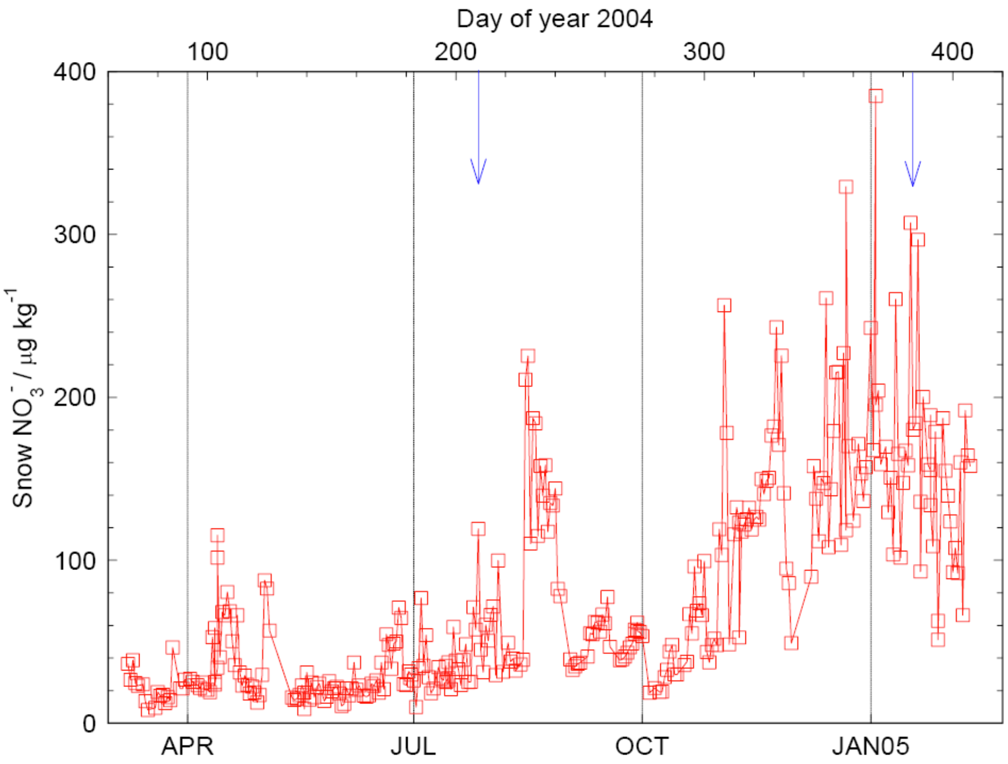


Figure - Nitrate concentrations measured in surface snow samples collected approximately daily at Halley, Antarctica, in 2004 and early 2005. (From Wolff et al., 2008).
(Wolff, E.W., et al., 2008. The interpretation of spikes and trends in concentration of nitrate in polar ice cores, based on evidence from snow and atmospheric measurements. Atmospheric Chemistry and Physics 8, 5627-5634.).

> p31965/l22 ... : Please explain your hypothesis, i.e. why do you expect larger oxygen isotope values in snow nitrate when the ozone hole area is smaller and column ozone minimum larger? e.g. McCabe et al. (2007) found the opposite, a negative correlation between $\Delta^{17}O(NO_3^-)$ and spring time column ozone.

In McCabe et al. (2007), $\Delta^{17}O(NO_3^-)$ in snow anti-correlates with the October-November-December column ozone. Two possibilities were proposed there, 1) the nitrate oxygen isotopes are being primarily affected by increases in tropospheric ozone levels because of increased UV from decreased springtime column ozone levels, or 2) the oxygen isotopes are recording increases in the stratospheric nitrate flux during years of reduced column ozone.
In South Pole, nitrate in ice preserves 25% of the original stratospheric isotopic composition, where 75% possess the tropospheric isotopic composition, due to nitrate produced from the photochemically recycled NO_x on the polar plateau (McCabe et al., 2007).
The situation is really different at our coastal site P1, where the photolysis imprint is rather minor. For the snow nitrate in cold season at P1, the higher $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ were observed, corresponding to the smaller ozone hole (i.e., column ozone is higher). We can clarify this discussion in the text.

> p31966/l12: State R^2 and p values for the correlation.

This will be added to the text: $R^2=0.77$, $p<0.01$.

p31967/l24 - p31968/l10: Cite here again previous work on the East Antarctic Plateau which reached the same conclusions.

These lines discuss the purpose of the study here and summarize the findings in *this study*. Throughout the text we consistently give credit to the previous work done on the EAIS. The latter part of the section noted here also discusses the relationship between w(NO_3^-) and $\delta^{18}O$, which has not been previously pointed out.

Table 1: I recommend to compare profile statistics over a common depth interval (see comment above).

See response above and new figure as suggested by referee.

Figure 6: I suggest plotting as a function of accumulation rate (or its inverse) to compare to other studies (see comment above).

Yes.