

We thank Dr. Erbland for his careful and thoughtful review of our work. Please see below for point-by-point responses in blue following Dr. Erbland's comments.

Shi et al. report 7 profiles of nitrate mass fraction and isotopic composition (mostly $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. $\Delta^{17}\text{O}$ is measured for P1 only) from 2 to 3 meters depth snow pits dug along the Chinese traverse from Zhongshan station to Dome A in East Antarctica. I congratulate the authors for compiling these amazing datasets both in terms of spatial coverage and depth range.

The datasets are exciting for three reasons. First, because the snow pits were dug in a sector which has never been sampled for this purpose before (to the best of my knowledge) and which includes Dome A, the summit of the East Antarctic ice sheet. Second, because continuous profiles are available below the photic zone. Third, because this study probably reports the highest $\delta^{15}\text{N}(\text{NO}_3^-)$ value (+461 ‰) ever measured in Antarctic snow.

It is disappointing to see that in this study, the Zhongshan – Dome A transect is treated as if it was in a different environment compared to the D10 – Dome C – Vostok transect documented in other recent studies (Frey et al., 2009; Erbland et al., 2013). Both transects are part of the East Antarctic ice sheet and cover similar ranges of elevations, snow accumulation rates, temperatures... I think that these facts are sufficient to encourage a proper comparison of the new datasets obtained to those previously published. To me, the first goal of this paper should be to compare to and confirm other observations on the East Antarctic ice sheet. For instance, Fig. 4 in Erbland et al. (2013) could be reproduced with the new datasets published in the present study.

We agree that the text should include more comparison with the Erbland dataset. We have reproduced the suggested figure (see below) and will include it. The snow samples on the traverse of D10-Dome C-Vostok (referred to as DDV in following) were collected only to the depth of ca. 20cm for most of the snowpits (Frey et al., 2009; Erbland et al., 2013). We thus only compare the apparent fractionation constants (ε_{app}) and asymptotic values (as.) from the depth interval of 0-20cm to make a direct comparison with those in Erbland et al. (2013). It is noted that all of the data from Erbland et al. (2013) were used to make the figure. For the apparent fractionation constants, all of the seven pits in this study were included in the figure, with red squares and green triangles representing $p < 0.05$ and $p > 0.05$, respectively (we do not know the p-values for the data reported in the Erbland et al. study). In terms of the asymptotic values, based on the fact that $w(\text{NO}_3^-)$, $\delta^{15}\text{N}(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ varied significantly along the profiles in the pits P1-P3 (Figure 2 in the manuscript), the calculation of asymptotic values were not performed for P1-P3. The asymptotic values of P4-P7 were included in the figure, with red squares and green triangles representing $p < 0.05$ and $p > 0.05$, respectively.

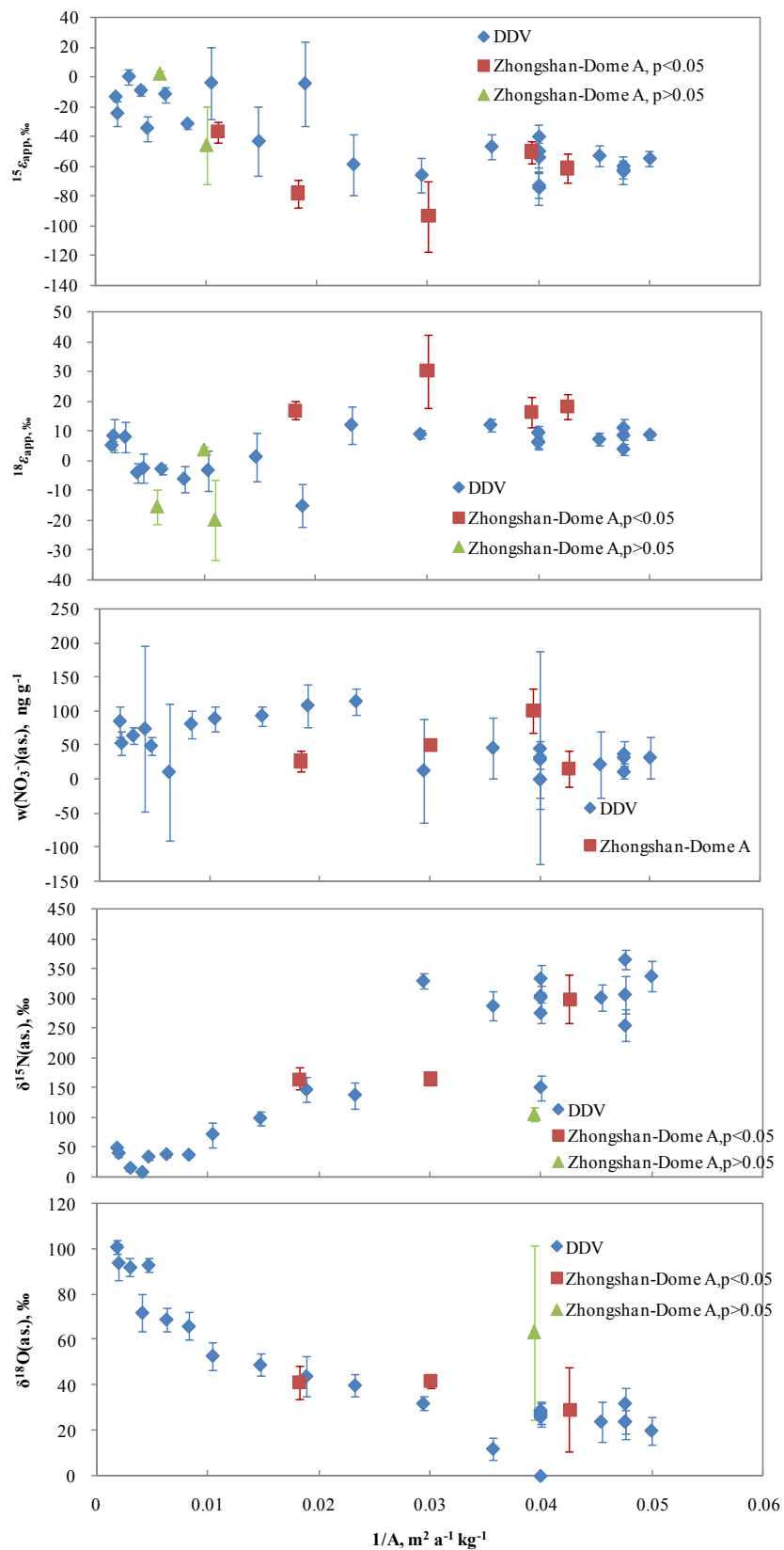


Figure – Comparison of current study data with Erbland et al. (2013) Figure 4.

Unfortunately, the oxygen isotope anomaly ($\Delta^{17}\text{O}$), which is of great interest to track the oxidation of NO_x , has not been measured for 6 of the 7 snow pits. I understand that the measurement of $\Delta^{17}\text{O}(\text{NO}_3^-)$ was not possible because of the small nitrate amounts in most of the snow pits. However, the discussion of this single $\Delta^{17}\text{O}$ profile for one snow pit only has confused me at the end of the manuscript. I wonder if this dataset is at its place in the present manuscript.

We will revisit this in the text, however, because the behavior of nitrate in the coastal snowpits is so different, and we have a complete isotopic dataset for that snowpit specifically, it seems to make the most sense to keep discussion of that data together. However, we can better prepare the reader and distinguish this earlier and again here in the manuscript. For example, anonymous referee #2 suggested including a figure of box and whisker plots to show an overview of all of the data (as opposed to the less effective Table 1 in the original manuscript). This box and whisker plot could also include the $\Delta^{17}\text{O}$ data for P7 to introduce the reader that this data is part of the discussion.

In agreement with Anonymous Reviewer #1, I do not agree with the treatment of the profiles 1 below the photic zone (see my comment below). Also, I wonder if those data could not be placed in a different manuscript or this manuscript could be revisited. Indeed, the profiles below the photic zone speak less than do profiles in the photic about the nature of the loss process at play in the top decimeters but more about the variability of the surface loss process with time. This specific point could a model framework which has recently been submitted to as a companion to Erbland et al. (2013) (Erbland et al., 2015, not available online yet).

While we appreciate this concern, we do not feel it is appropriate to report separately the data above and below the photic zone. Part of the purpose of our study, and indeed the reason it is different than previous work by Dr. Erbland and others, is to test our understanding of what happens to nitrate (isotopically) in the photic zone and how buried nitrate can be interpreted in this context. We have not yet seen the Erbland et al., 2015 manuscript but will keep an eye out for it.

Major comments

In agreement with Anonymous Reviewer #1, my main concern is about the authors' interpretation of the data analysis of the Erbland et al. (2013) study. In this work, an attempt was made to systematically characterize the mass fraction and isotopic composition values attained by nitrate immediately below the photic zone. Below this zone, nitrate can be considered inert with respect to photo-processes. The characterization is achieved by assuming that the post-depositional processing of nitrate is constant throughout the residence of a snow layer in the photic zone. Therefore, the mass fraction and isotopic composition of nitrate in the photic zone were assumed to follow exponential behavior whose decay parameter was fitted in the 1-30 cm range. In Erbland et al. (2013), a few samples were collected below a depth of 60 cm, i.e. 3 times the e-folding attenuation depth (as modelled by Zatko et al., 2013, for remote 19 plateau sites). Those samples share as follows : 8 in DC04 (DC pit) and one in each of the IV, 20 VI, VIII, X, XII, XIV, XVI, XVIII, XX and XXII snow pits (from DC to the coast). Although those samples were not sampled below a depth of

1 m, I acknowledge that it would have been more suitable not to consider them in the calculation of the asymptotic values. However, taking them into account does not lead to significant differences as one can observe from the DC04 snow pit (Fig. 14 in Erbland et al., 2013). Last, I add that if any main deviation from the exponential fit may have appeared, this would have been accounted for in the calculation of the uncertainty in $\omega(\text{as.})$, $\delta^{15}\text{N}(\text{as.})$, $\Delta^{17}\text{O}(\text{as.})$ and $\delta^{18}\text{O}(\text{as.})$.

We appreciate Dr. Erbland sharing additional insight, but it still stands that the published work includes the samples below the photic zone. And while this does not appear to make a significant difference at DC04, this is the pit with the most information (i.e. nitrate sampled well below the photic zone), this can indeed make a significant difference at the rest of the sites as proven in our study. We clearly need to better address the starting assumptions in our work (which are the same assumptions made in Erbland et al. and Frey et al.) and more directly set out what questions we are testing. Over what depth is it appropriate to calibrate the exponential decay (i.e. asymptotic) relationship? We are in fact showing that it is important to understand this and are questioning how to best use this relationship. The uncertainty as measured by standard deviation or standard error alone is incomplete without consideration of the importance of the relationships found, which we are measuring by significance (p-values) and by “fit” (r^2 values).

By no means must the exponential fits be used to predict the mass fraction and isotopic composition of nitrate at depths well below the photic (e.g. below 1 meter). Indeed, nitrate below the active zone of snow photochemistry may vary both in terms of mass fraction and isotopic composition as a result of varying conditions in its post-depositional processing. For example, the residence time of nitrate in the photic zone could vary under the effect of variations in the local snow accumulation rates (which greatly vary at the decimeter scale, Libois et al., 2014). Also the photochemical rates and $^{15}\text{N}/^{14}\text{N}$ fractionation constant could change with time mostly under the effect of changes in the ozone column above site. Similarly to the calculation of the asymptotic values, apparent fractionation constants should be calculated for samples in the photic zone (say the top 60 cm). By the way, I recommend that the author should differentiate the apparent fractionation constants (which could be denoted “ $^{15}\epsilon$ ”) and the fractionation constants associated with a specific process (e. g. “ $^{15}\epsilon_{\text{pho}}$ ” for the $^{15}\text{N}/^{14}\text{N}$ fractionation constant associated with the photolysis of nitrate).

We have recalculated the apparent fractionation factors ($^{15}\epsilon_{\text{app}}$ and $^{18}\epsilon_{\text{app}}$) over the depth intervals of 0-20cm, 0-40cm, and 0-60cm, to better represent our aim. If indeed nothing changes under the photic zone, then the apparent fractionation constant that is derived over an interval below the photic zone, should reflect that for an interval near the surface. In other words, as the nitrate moves out of the photic zone the impact of the photolysis (fractionation constant) should be “locked in.” So if that apparent fractionation constant changes with the depth interval over which it is calculated, why would this be? Our paper aim is to consider this question and test our current understanding of how we explain the changes in the isotopes of nitrate with depth. We have now included a more complete discussion of how the modeled fractionation factors and rate constants change for different ozone boundary conditions. (And see the discussion in our response to reviewer 2 regarding ozone.) We also aim to consider how to effectively use the asymptotic relationships to understand how much the nitrate has varied over time outside of the expectation of the photolytic change alone. Again, the discussion of this in the manuscript (and distinction of the fractionation factors for

different processes) can be clarified and improved upon based upon the concerns raised by Dr. Erbland.

Some additional questions and comments (not comprehensive)

Methods. What is the maximum sample volume that you can inject to the denitrifying bacterial? Line 2 Page 31949, I read that samples with nitrate mass fractions as low as 6.0 ng g⁻¹ can be analyzed. This means that, if you aim for a minimum amount of 5 nmol of nitrate (Line 1 P 15 31949), your injected sample volume is 51.5 ml. Can you explain how you deal with such a high volume? How do you prepare the denitrifying bacteria?

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. As requested by the referee, 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 for correcting the data (i.e. there is a small “volume” effect such that is accounted for by using samples and standards of the same volume), and we apologize for not including detailed information on this originally. Below are 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 $\Delta^{17}\text{O}$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$.

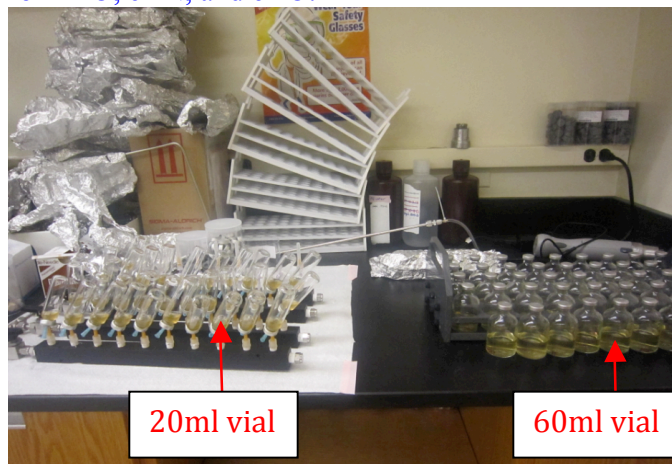


Figure: The two types of injection vials (e.g., 20ml and 60ml) used at Brown University.

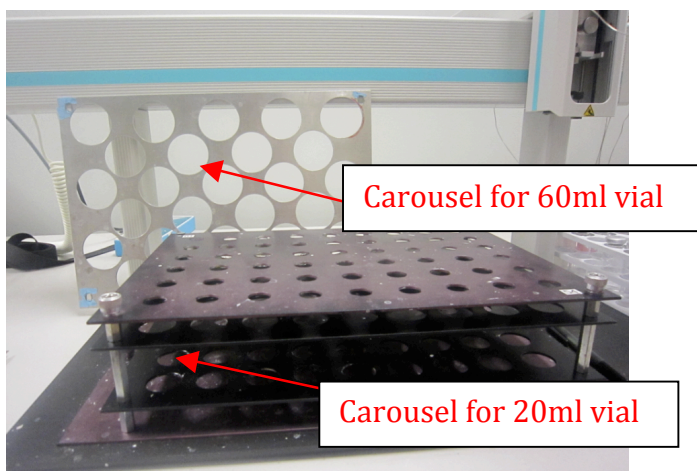


Figure: The autosampler carousel designed to fit either 20 mL vials or 60 mL vials

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 ₂ O		22.1	-0.7	-0.2
flush vial N ₂ O		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 ₂ O		25.5	-1.1	-1.0

KNO3 internal standard.

$\delta^{15}\text{N}$: Mean = 58.37 +/- 0.62‰. Range = 57.52 - 59.59‰.

$\delta^{18}\text{O}$: Mean = 30.65 +/- 0.52‰. Range = 29.55 - 31.50‰.

$\delta^{15}\text{N}$	$\delta^{18}\text{O}$	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

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

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

$\Delta^{17}\text{O}$ (‰)	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

Calculation of $^{15}\epsilon_{\text{pho}}$. I agree with Anonymous Reviewer 2 who questions the calculation of $^{15}\epsilon_{\text{pho}}$. Could you please give more details about your calculation? Which absorption cross section have you used for $\sigma(^{15}\text{NO}_3^-)$ and for $\sigma(\text{N}_2\text{O})$? Also, how have you obtained the actinic flux at the different sites and for solar noon at summer solstice? Have you measured it or have derived it from a radiative transfer model? In the latter case, which ozone column value have you obtained? I also suggest the use of the $\sigma(^{14}\text{NO}_3^-)$ and $\sigma(^{15}\text{NO}_3^-)$ spectrums recommended by Berhanu et al. (2014).

As we noted in the text, the actinic flux was calculated using the TUV (5.0) model for each site, and the fractionation factor calculation used the Chu and Anastasio cross sections and quantum yields. We have now more completely described the inputs, however. We assumed clear sky conditions and no overhead SO_2 or NO_2 . Total overhead ozone was set to 300 DU for both sites. Elevation was that listed in the site descriptions table, which we now note in the text. Albedo was set to 0.97 following Grenfell et al. (1994) (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). We now also provide comparison to using the Berhanu modeled cross sections at 243K to calculate the fractionation factors. In brief, using the C/A data as discussed in the paper, $^{15}\epsilon$ was calculated to be -45.3‰ at P1 and -48.0‰ at P7. Using the Berhanu 243K cross sections, $^{15}\epsilon$ is calculated to be -48.9‰ at P1 and -52.8‰ at P7. Using the Berhanu cross section does not change any of our conclusions.

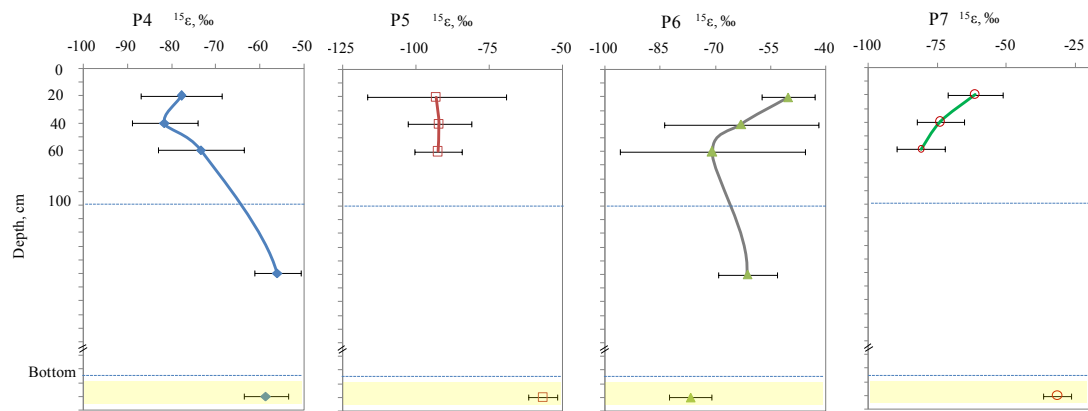
Lines 5 P 31954: Zatko et al. (2013) report a modelled e-folding depth of 18-22 cm which makes the photic zone ca. 60 cm. Why do you then calculate the apparent fractionation constants in the upper 25 cm only?

We have re-calculated the apparent fractionation factors ($^{15}\epsilon_{\text{app}}$ and $^{18}\epsilon_{\text{app}}$) over the depth intervals of 0-20cm, 0-40cm, and 0-60cm, to better represent our aim of understanding changes in the apparent fractionation with depth. Dr. Erbland also points out in comments below the need for calculating uncertainty and that is included here as well (note the ± 1 standard error) in updated tables and figures. The observed fractionation ϵ was obtained from the linear fit of $\ln(\delta_{\text{snow}}+1)$ vs. $\ln(w_{\text{snow}})$. The software package Origin 7.5 was used for the linear fitting and calculation of the standard error.

Table 2. Observed fractionation constants for ^{15}N and ^{18}O of NO_3^- ($^{15}\epsilon_{\text{app}}$ and $^{18}\epsilon_{\text{app}}$) calculated for different snow layer depths from the linear regression of $\ln(\delta_{\text{snow}}+1)$ vs. $\ln(w_{\text{snow}})$ in Eq. (2). Four different depth intervals were selected for calculating ϵ_{app} : 0-20cm, 0-40cm, 0-60cm, 100-bottom and the entire pit. Also given are the standard error (1σ), r^2 values and the significance level, p , where bolded values represent $p < 0.05$.

Snow pit	Depth	^{15}N			^{18}O		
		$^{15}\epsilon_{\text{app}} \pm 1\sigma, \text{‰}$	p	r^2	$^{18}\epsilon_{\text{app}} \pm 1\sigma, \text{‰}$	p	r^2
P1	0-20cm	2.4 ± 2.0	0.379	0.157	-15.3 ± 6.0	0.044	0.588
	0-40cm	-0.4 ± 5.0	0.943	0.000	-8.7 ± 7.0	0.248	0.109
	0-60cm	-3.9 ± 14.0	0.785	0.004	-9.4 ± 10.0	0.368	0.043
	100-Bottom	17.2 ± 14.0	0.248	0.094	-6.5 ± 5.0	0.175	0.127
	Entire	-11.8 ± 7.0	0.098	0.056	-3.7 ± 4.0	0.390	0.015
P2	0-20cm	-45.5 ± 26.0	0.184	0.497	4.0 ± 1.0	0.017	0.887
	0-40cm	0.8 ± 10.0	0.936	0.001	-4.2 ± 4.0	0.274	0.167

	0-60cm	4.1±15.0	0.789	0.007	-2.1±4.0	0.647	0.020
	100-Bottom	21.5±16.0	0.197	0.091	11.2±4.2	0.015	0.287
	Entire	11.9±9.1	0.198	0.043	7.0±3.6	0.060	0.090
P3	0-20cm	-36.8±6.7	0.012	0.909	-19.8±13.5	0.237	0.420
	0-40cm	-27.5±11.0	0.036	0.488	-15.4±11.0	0.188	0.233
	0-60cm	-28.8±9.1	0.009	0.476	-14.0±8.7	0.135	0.192
	100-Bottom	12.3±12.0	0.318	0.059	13.5±18.6	0.478	0.030
	Entire	-1.2±4.9	0.811	0.002	15.4±8.0	0.061	0.092
P4	0-20cm	-77.8±9.2	0.000	0.888	17.1±3.1	0.000	0.778
	0-40cm	-81.6±7.5	0.000	0.868	14.0±2.1	0.000	0.706
	0-60cm	-73.3±9.8	0.000	0.665	11.4±2.5	0.000	0.419
	100-Bottom	-56.0±5.3	0.000	0.703	-3.4±1.3	0.011	0.126
	Entire	-58.7±5.0	0.000	0.584	1.4±1.8	0.433	0.006
P5	0-20cm	-93.1±23.6	0.003	0.633	30.2±12.3	0.036	0.401
	0-40cm	-92.1±10.8	0.000	0.791	24.9±5.5	0.000	0.522
	0-60cm	-92.5±8.1	0.000	0.820	16.0±3.6	0.000	0.412
	100-Bottom	27.3±13.7	0.053	0.083	-9.6±4.0	0.022	0.114
	Entire	-56.9±5.0	0.000	0.577	0.0±1.6	0.985	0.000
P6	0-20cm	-50.2±7.3	0.000	0.889	16.7±5.1	0.017	0.638
	0-40cm	-63.0±21.0	0.010	0.390	16.2±12.1	0.201	0.114
	0-60cm	-70.8±25.1	0.010	0.265	17.9±9.3	0.066	0.145
	100-Bottom	-61.3±8.0	0.000	0.605	-7.8±2.4	0.003	0.216
	Entire	-76.8±5.8	0.000	0.694	11.3±2.1	0.000	0.265
P7	0-20cm	-61.3±9.8	0.000	0.849	18.4±4.1	0.003	0.738
	0-40cm	-73.9±8.5	0.000	0.834	16.4±2.4	0.000	0.753
	0-60cm	-81.0±8.7	0.000	0.789	15.2±1.9	0.000	0.728
	100-Bottom	20.7±14.4	0.154	0.026	10.0±4.5	0.051	0.060
	Entire	-31.5±5.0	0.000	0.251	-0.7±1.7	0.690	0.001



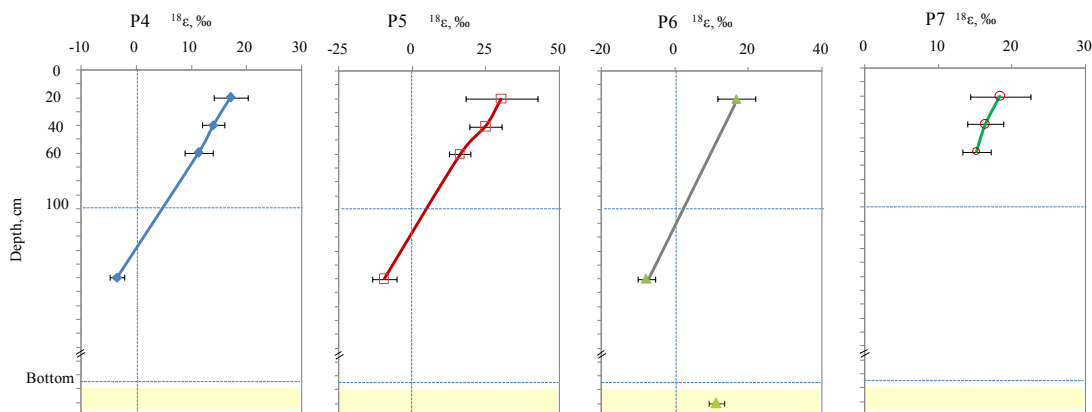


Fig. 4. Observed fractionation constants, $^{15}\epsilon$ (top row) and $^{18}\epsilon$ (bottom row), calculated from the group II snowpits using four different snow depth intervals (0-20cm, 0-40cm, 0-60cm and 100cm-bottom). The ϵ values displayed in the shaded area are those calculated from the entire snowpit (0-bottom). The error bars are the standard errors of observed fractionation constant (1σ). Only statistically significant ϵ values ($p < 0.05$) are shown.

Lines 13-14 P 31957: “This is a substantial exchange of O atoms, indicating that re-oxidation plays a major role in determining the $\delta^{18}\text{O}$ of NO_3^- in the upper snowpack”. I find this statement a little daring. Indeed, what do you mean by “the upper snowpack”? It is the top few centimeters? The top decimeters? If the top few centimeters are considered, $\delta^{18}\text{O}$ of NO_3^- in this part of the snowpack must be close to that in the atmosphere as it is the case when considering, at the extreme, the skin layer (the top 4 mm of the snowpack) (Erbland et al., 2013).

This section needs to be re-named and/or additional text is needed to clarify that we are describing the re-oxidation of nitrate in the condensed phase. The oxygen exchange estimate in the paragraph Dr. Erbland refers to was for the observed changes in the top 25cm, as was noted in the text. This is what “upper snowpack” was meant to refer to. This has been clarified. We agree that as observed by Erbland et al. (2013) the oxygen isotopic composition of nitrate in the skin layer, or that produced locally in the gas phase, should be in equilibrium with local oxidants.

Section 4.2: I don’t understand the author’s goal in this section. Perhaps denoting the quantities with better care will help to understand the point made in this section. Indeed, quantities of interest calculated so far are the apparent fractionation constants (which I suggest to denote with an “app” subscript). The authors decided to calculate those quantities in the 0-25 cm range. As I wrote above, I do not agree with this choice since the loss occurs in the whole photic zone, i.e. ca. 60 cm when considering 95 % of UV radiation extinction (3 times the attenuation depth). Fractionation constants using the data below the photic zone (such as 25-100 cm range or 100 cm to pit base range) could be calculated although I do not see what information are obtained from them. Indeed, the assumption of constant post-depositional conditions is difficult to make depending on the considered depth range. However, if such choice of calculating fractionation constants below the photic zone is made, I recommend to use a different denomination than “apparent” to avoid confusing. The quality of the information obtained from the calculation of apparent fractionation constants depends on the uncertainty linked with each of them. I recommend that the calculated fractionation constants are given with the corresponding uncertainty (e.g. $\pm 1\sigma$) as in Frey et al. (2009) and

Erbland et al. (2013). Indeed, this will test the limitations of the assumed single-step one-way Rayleigh model. I note the authors' effort to report values of statistical interest (e. g. Tab. 2). I observe that those question the approach presented in Fig. 4. Indeed, to me r^2 is a better measure than p to determine the relevance of the calculated fractionation constant. Let's take the example of the $^{15}\epsilon$ and $^{18}\epsilon$ values calculated for the 25-100 cm and 100-bottom ranges as well as for the entire snowpack (Tab. 2). I observe that the ϵ values which significantly differ from those calculated in the 0-25 cm range (i.e. $^{15}\epsilon$ in the 25-100 cm and 100-bottom ranges and the entire snowpack in P7) almost systematically feature low (< 0.5) r^2 values. If uncertainties ($\pm 1\sigma$) were calculated as in the aforementioned studies, I am pretty sure that those would be high when r^2 is low. In other words, I recommend to the author that they use a better measure of the uncertainty in the calculation of fractionation constants in order to conduct their depth dependency analysis (Figure 4).

Thank you for the suggestions, all of these will be incorporated to better distinguish the different quantities and clarify the discussion in the text. We have re-calculated both the apparent fractionation constants and the asymptotic relationships as shown in the response above for 0-20cm, 0-40cm, and 0-60cm, etc. Table 2 has been updated above and now also includes the standard error. The standard errors are not necessarily larger when the relationships are not statistically significant. We therefore feel it is a better measure of "fit" to consider the r^2 and significance values before considering the standard error in evaluating the robustness of this approach for reconstructing the isotopic values of nitrate with depth. For comparison, it would be useful if future work follows the standard practice of reporting the statistical significance of a linear regression in addition to the error for the coefficient of interest.

Section 4.3: The use of exponential fits as in Erbland et al. (2013) is misunderstood (see main 4 comments above).

Please see comments and responses above.

Section 4.4: It seems to me that parts of the discussion in this section rely on the assumption that the $\delta^{15}\text{N}$ signature is conserved at the air-snow interface, in other words, that $\delta^{15}\text{N}$ in skin layer nitrate is the same than $\delta^{15}\text{N}$ in atmospheric nitrate. However, the $\delta^{15}\text{N}$ values measured at the air-snow interface at Dome C show that the annual weighted average in $\delta^{15}\text{N}$ in skin layer nitrate is 24.7 ‰ than that in atmospheric nitrate. A fraction of this observed shift may be linked to a fractionation of the nitrogen isotopes of nitrate during the deposition of this compound from the atmosphere to the snow (Erbland et al., 2013).

Agreed that this is not necessarily a valid assumption and we should indeed include the observation at Dome C in our discussion as it may also help to explain the greater than expected values from stratospheric nitrate as compared to that in Savarino et al. (2007). The observed difference between the skin layer and that in atmospheric nitrate at Dome C, however, is a unique finding. We should indeed consider that this difference may apply in the coastal zone, but note that the partitioning between the atmosphere and skin layer at Dome C might be different in a very different environment.

Line 25 Page 31964: I recommend the authors to consider the $^{15}\epsilon_{\text{phy}}$ value measured at -20 °C (Erbland et al., 2013) with care. Indeed, only little nitrate mass fractions changes were

observed during this two-week experiment.

Thank you for this comment. Our purpose here was to review the state of the science and consider both the theoretical and the experimental results in terms of our observations. The wording in the manuscript needs to be modified to better reflect this.

Tables 2 and 3: See comment above. Can you give an estimate of the uncertainty in the fractionation constants and asymptotic values?

Please see the updated Table 2 and figures in the responses above.

Figure 2: the different scales and broken axis (for nitrate mass fractions in P7) are confusing.

It is important to us to show all of the snowpit data and it is difficult given the significant differences in ranges. We felt this was the best compromise to include a broken axis. We will update the figure to have as many of the axes the same as possible and clearly point out the split axes in the figure caption.

Figure 3: it is confusing here that $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ data are represented against $\omega(\text{NO}_3^-)$ and that slopes are calculated. Indeed, those may confuse the reader who may consider the slopes as fractionation constants (normally derived in the $\ln(\delta + 1)$ versus $\ln(\omega(\text{NO}_3^-))$ space).

We will take care to point out this difference from the fractionation constants calculation in the text and figure caption. The point here was that the simple relationship between concentration and the isotopes were changing with depth and we feel it is illustrative of the point directly without converting to the log scales.

Figure 4: See comment above. A precise estimate of the uncertainty associated with the calculation of $^{15}\epsilon$ and $^{18}\epsilon$ is needed.

Please see the new figure in response above.

Table S1 (Supplementary): I agree with the other reviewers, this table should be placed in the main text. How were the snow accumulation rates computed? From the bamboo sticks you obtain the accumulated snow thickness. Have you made an assumption on the snow density? The accuracy of the mean annual temperatures does not seem sound to me. The sampling date format which is displayed is “YYYYMM” and not “YYMM”. By the way, could you provide the day when the pits were dug? Only the month and year are available.

The table has been updated and will be included in the main text (see below). Please refer to our response to the second reviewer regarding accumulation and temperature.

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

Snowpit	Location	Elevation, m	Distance from coast, km	Mean annual accumulation, $\text{kg m}^{-2} \text{a}^{-1}$ ¹⁾	Mean annual Temperature, $^{\circ}\text{C}$ ²⁾	Depth, cm	Sampling resolution, cm	Sampling date, DD.MM.YYYY
P1	71.13°S, 77.31°E	2037	200	172.0	-29.12	150	3.0	18.12.2012
P2	71.81°S, 77.89°E	2295	283	99.4	-32.87	200	5.0	20.12.2012
P3	73.40°S, 77.00°E	2545	462	90.7	-35.72	200	5.0	22.12.2012
P4	76.29°S, 77.03°E	2843	787	54.8	-41.28	200	2.0	28.12.2012
P5	77.91°S, 77.13°E	3154	968	33.3	-46.37	200	2.0	30.12.2012
P6	79.02°S, 76.98°E	3738	1092	25.4	-53.13	200	2.5	02.01.2013
P7	80.42°S, 77.12°E	4093	1256	23.5	-58.50	300	2.5	06.01.2013

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

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

Minor comments (not comprehensive)

Line 9 P 31953: Wagenbach (not Vagenbach)

Corrected, thanks.