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

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5 Shi et al. report 7 profiles of nitrate mass fraction and isotopic composition (mostly  $\delta^{15}$ N and 6  $\delta^{18}$ O.  $\Delta^{17}$ O is measured for P1 only) from 2 to 3 meters depth snow pits dug along the Chinese 7 traverse from Zhongstan station to Dome A in East Antarctica. I congratulate the authors for 8 compiling these amazing datasets both in terms of spatial coverage and depth range.

9 The datasets are exciting for three reasons. First, because the snow pits were dug in a sector 10 which has never been sampled for this purpose before (to the best of my knowledge) and which 11 includes Dome A, the summit of the East Antarctic ice sheet. Second, because continuous 12 profiles are available below the photic zone. Third, because this study probably reports the 13 highest  $\delta^{15}N(NO_3^{-})$  value (+461 ‰) ever measured in Antarctic snow.

14 It is disappointing to see that in this study, the Zhongstan – Dome A transect is treated as if it was in a different environment compared to the D10 - Dome C - Vostok transect documented 15 16 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, 17 18 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 19 20 be to compare to and confirm other observations on the East Antarctic ice sheet. For instance, 21 Fig. 4 in Erbland et al. (2013) could be reproduced with the new datasets published in the 22 present study.

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Unfortunately, the oxygen isotope anomaly ( $\Delta^{17}$ O), which is of great interest to track the oxidation of NO<sub>x</sub>, has not been measured for 6 of the 7 snow pits. I understand that the measurement of  $\Delta^{17}$ O(NO<sub>3</sub><sup>-</sup>) was not possible because of the small nitrate amounts in most of the snow pits. However, the discussion of this single  $\Delta^{17}$ 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. In agreement with Anonymous Reviewer #1, I do not agree with the treatment of the profiles 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).

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# 9 Major comments

10 In agreement with Anonymous Reviewer #1, my main concern is about the authors' 11 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 12 13 attained by nitrate immediately below the photic zone. Below this zone, nitrate can be 14 considered inert with respect to photo-processes. The characterization is achieved by assuming 15 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 16 17 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 18 19 cm, i.e. 3 times the e-folding attenuation depth (as modelled by Zatko et al., 2013, for remote 20 plateau sites). Those samples share as follows : 8 in DC04 (DC pit) and one in each of the IV, 21 VI, VIII, X, XII, XIV, XVI, XVIII, XX and XXII snow pits (from DC to the coast). Although 22 those samples were not sampled below a depth of 1 m, I acknowledge that it would have been 23 more suitable not to consider them in the calculation of the asymptotic values. However, taking 24 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 25 exponential fit may have appeared, this would have been accounted for in the calculation of the 26 27 uncertainty in  $\omega(as.)$ ,  $\delta^{15}N(as.)$ ,  $\Delta^{17}O(as.)$  and  $\delta^{18}O(as.)$ .

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 1 in the local snow accumulation rates (which greatly vary at the decimeter scale, Libois et al.,

2 2014). Also the photochemical rates and <sup>15</sup>N/<sup>14</sup>N fractionation constant could change with time
3 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 "<sup>15</sup> $\varepsilon$ ") and the fractionation constants associated with a specific process (e. g. "<sup>15</sup> $\varepsilon_{pho}$ " for the <sup>15</sup>N/<sup>14</sup>N fractionation constant associated with the photolysis of nitrate).

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# 11 Some additional questions and comments (not comprehensive)

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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<sup>-1</sup> can be analyzed. This means that, if you aim for a minimum amount of 5 nmol of nitrate (Line 1 P 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?

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19 **Calculation of** <sup>15</sup> $\varepsilon_{pho}$ . I agree with Anonymous Reviewer 2 who questions the calculation of 20 <sup>15</sup> $\varepsilon_{pho}$ . Could you please give more details about your calculation? Which absorption cross 21 section have you used for  $\sigma(^{15}NO_{3})$  and for  $\sigma(N^{18}OO_{2})$ ? Also, how have you obtained the 22 actinic flux at the different sites and for solar noon at summer solstice? Have you measured it 23 or have derived it from a radiative transfer model? In the latter case, which ozone column value 24 have you obtained? I also suggest the use of the  $\sigma(^{14}NO_{3})$  and  $\sigma(^{15}NO_{3})$  spectrums 25 recommended by Berhanu et al. (2014).

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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?

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Lines 13-14 P 31957: "This is a substantial exchange of O atoms, indicating that re-oxidation plays a major role in determining the  $\delta^{18}$ O of NO<sub>3</sub><sup>-</sup> 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,  $\delta^{18}$ O of NO<sub>3</sub><sup>-</sup> 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).

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8 Section 4.2: I don't understand the author's goal in this section. Perhaps denoting the quantities 9 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 10 with an "app" subscript). The authors decided to calculate those quantities in the 0-25 cm range. 11 12 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). 13 14 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 15 16 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 17 18 constants below the photic zone is made, I recommend to use a different denomination than 19 "apparent" to avoid confusing.

20 The quality of the information obtained from the calculation of apparent fractionation constants 21 depends on the uncertainty linked with each of them. I recommend that the calculated 22 fractionation constants are given with the corresponding uncertainty (e.g.  $\pm 1\sigma$ ) as in Frey et al. 23 (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. 24 25 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 26 take the example of the  ${}^{15}\varepsilon$  and  ${}^{18}\varepsilon$  values calculated for the 25-100 cm and 100-bottom ranges 27 as well as for the entire snowpack (Tab. 2). I observe that the  $\varepsilon$  values which significantly differ 28 from those calculated in the 0-25 cm range (i.e.  ${}^{15}\varepsilon$  in the 25-100 cm and 100-bottom ranges 29 and the entire snowpack in P7) almost systematically feature low (< 0.5)  $r^2$  values. If 30 31 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 32

measure of the uncertainty in the calculation of fractionation constants in order to conduct their
 depth dependency analysis (Figure 4).

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

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**Section 4.4**: It seems to me that parts of the discussion in this section rely on the assumption that the  $\delta^{15}$ N signature is conserved at the air-snow interface, in other words, that  $\delta^{15}$ N in skin layer nitrate is the same than  $\delta^{15}$ N in atmospheric nitrate. However, the  $\delta^{15}$ N values measured at the air-snow interface at Dome C show that the annual weighted average in  $\delta^{15}$ 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).

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Line 25 Page 31964: I recommend the authors to consider the  ${}^{15}\varepsilon_{phy}$  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.

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

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

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Figure 3: it is confusing here that  $\delta^{15}N$  and  $\delta^{18}O$  data are represented against  $\omega(NO_3^-)$  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  $\ln(\omega(NO_3^-))$  space).

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

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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.

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# 10 Minor comments (not comprehensive)

11 Line 9 P 31953: Wagenbach (not Vagenbach)

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# 14 **<u>References</u>**

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