

1 Reviewer 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.

Shi et al. report in their study snow pit measurements of nitrate and its stable isotopes from an over-land 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 ($<55 \text{ kg m}^{-2}\text{yr}^{-1}$) 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 $\delta^{15}\text{N}(\text{NO}_3^-)$ and depletion in $\delta^{18}\text{O}(\text{NO}_3^-)$. The negative correlation between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- is consistent with the current understanding of post-depositional isotopic fractionation from nitrate photolysis, i.e. enrichment in $\delta^{15}\text{N}(\text{NO}_3^-)$ and depletion in $\delta^{18}\text{O}(\text{NO}_3^-)$. 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 ($91\text{-}172 \text{ kg m}^{-2}\text{yr}^{-1}$) appear to preserve the atmospheric signal, as indicated by generally lower $\delta^{15}\text{N}(\text{NO}_3^-)$ and higher $\delta^{18}\text{O}(\text{NO}_3^-)$ 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 (Erland 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.

2 Detailed Comments

p31945/l9: or halogen radicals (XO)

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

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?

p31948/17: what was the diameter of the vials?

p31951/120: 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.

p31954/111: But Table 2 states for P6 a $^{15}\epsilon$ value of -54.0% . which one is correct?

p31954/112-14: Be specific how fractionation constants compare, i.e. $^{15}\epsilon$ values in pits P4-P7 fall within the range of previous observations on the East Antarctic Plateau of $-59.2\pm 10.4\%$ (mean $\pm 1\sigma$) (Erbland et al., 2013), however $^{18}\epsilon$ values are more positive (range 16-29‰) when compared to $-8.7\pm 2.4\%$ observed by Erbland et al. (2013). Please comment.

p31954/122: disordered

p31954/124-5: For completeness add also reactions of NO_2^- producing NO_x (photolysis and rxn with OH).

p31955/18 ...: 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 $\sigma_{^{14}\text{N}\text{O}_3^-}$ spectrum (measured in lab experiments) to obtain the unknown $\sigma_{^{15}\text{N}\text{O}_3^-}$ spectrum. While model predictions of $^{15}\epsilon$ 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 $\sigma_{^{14}\text{N}\text{O}_3^-}$ 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, $\Delta\text{C}=-32.5\text{ cm}$, 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.

p31955/112: φ ? also it should be $d\lambda$

p31955/113: $\Phi_{\text{NO}_3^-}$; 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.

p31956/110: as first observed in Dome C snow (Frey et al., 2009)

p31957/15: I suggest to introduce the Rayleigh model and equations under methods, i.e. using general equations as developed in Blunier et al. (2005).

p31957/18-15: 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 $\delta^{18}\text{O}(\text{H}_2\text{O})$ measurements, and evaluate how much accumulative exchange of O atoms is needed to explain observations.

p31959/14: If there was only a single process driving isotopic fractionation in snow ...

p31959/I4-22: 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.

p31960/I2: "This can explain ..." is redundant with p31959/I26-7

p31960/I3-9 and below: Your suggestion to explain negative correlations between $w(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ at 100-200cm depth through the dark reaction $\text{NO}_2 + \text{O}_3$ 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 (~ 4 ppbv) and O_3 (~ 16 ppbv) (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 $0.4 \text{ nmol L}_{\text{H}_2\text{O}}^{-1}$ 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.

p31961/I5-8: An important assumption is also that the boundary conditions of deposition (i.e. for photolysis) remain constant.

p31963/I3-5: 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.

p31963/I21: describe dating of the snow pit(s) (along with the accumulation rate measurement) in the method section

p31964/I4: Nitrate profiles in snow and firn show occasionally also winter spikes; for a discussion see Wolff et al. (2008).

p31965/I22 ... : 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 $\Delta^{17}\text{O}(\text{NO}_3^-)$ and spring time column ozone.

p31966/I12: State R^2 and p values for the correlation.

p31967/I24 - p31968/I10: Cite here again previous work on the East Antarctic Plateau which reached the same conclusions.

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

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

studies (see comment above).

References

- Berhanu, T. A., Meusinger, C., Erbland, J., Jost, R., Bhattacharya, S. K., Johnson, M. S., and Savarino, J.: Laboratory study of nitrate photolysis in Antarctic snow. II. Isotopic effects and wavelength dependence, *J. Chem. Phys.*, 140, doi:10.1063/1.4882899, 2014.
- Blunier, T., Floch, G. L., Jacobi, H. W., and Quansah, E.: Isotopic view on nitrate loss in Antarctic surface snow, *Geophys. Res. Lett.*, 32, doi:10.1029/2005GL023011, 2005.
- Chu, L. and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, *J. Phys. Chem. A*, 107(45), 9594–9602, 2003.
- Ding, M., Xiao, C., Li, Y., Ren, J., Hou, S., Jin, B., and Sun, B.: Spatial variability of surface mass balance along a traverse route from Zhongshan station to Dome A, Antarctica, *J. Glaciol.*, 57, 658–666, 2011.
- Erbland, J., Vicars, W. C., J., S., Morin, S., Frey, M. M., Frosini, D., Vince, E., and Martins, J. M. F.: Air–snow transfer of nitrate on the East Antarctic Plateau – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium in summer, *Atmos. Chem. Phys.*, 13, 6403–6419, doi:10.5194/acp-13-6403-2013, 2013.
- Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J. M. F.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, *Atmos. Chem. Phys.*, 9, 8681–8696, 2009.
- Frey, M. M., Roscoe, H. K., Kukui, A., Savarino, J., France, J. L., King, M. D., Legrand, M., and Preunkert, S.: Atmospheric nitrogen oxides (NO and NO₂) at Dome C, East Antarctica, during the OPALE campaign, *Atmos. Chem. Phys. Disc.*, 14, 31 281–31 317, doi:10.5194/acpd-14-31281-2014, 2014.
- Freyer, H. D., Kobel, K., Delmas, R. J., Kley, D., and Legrand, M. R.: First results of ¹⁵N/¹⁴N ratios in nitrate from alpine and polar ice cores, *Tellus B*, 48, 93–105, 1996.
- McCabe, J. R., Thiemens, M. H., and Savarino, J.: A record of ozone variability in South Pole Antarctic snow: Role of nitrate oxygen isotopes, *J. Geophys. Res.*, 112, doi:10.1029/2006JD007822, 2007.
- Meusinger, C., Berhanu, T. A., Erbland, J., Savarino, J., and Johnson, M. S.: Laboratory study of nitrate photolysis in Antarctic snow. I. Observed quantum yield, domain of photolysis, and secondary chemistry, *J. Chem. Phys.*, 140, 244305, doi:10.1063/1.4882898, 2014.
- Miller, C. E. and Yung, Y. L.: Photo-induced isotopic fractionation, *J. Geophys. Res.*, 105(D23), 29 039–29 051, 2000.
- Röthlisberger, R., Hutterli, M. A., Wolff, E. W., Mulvaney, R., Fischer, H., Bigler, M., Goto-Azuma, K., Hansson, M. E., Ruth, U., Siggaard-Andersen, M. L., and Steffensen, J. P.: Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes, *Ann. Glaciol.*, 35, 209–216, 2002.
- Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, *Atmos. Chem. Phys.*, 7, 1925–1945, 2007.
- Wolff, E. W., Jones, A. E., Bauguitte, S. J.-B., and Salmon, R. A.: The interpretation of spikes and trends in concentration of nitrate in polar ice cores, based on evidence from snow and atmospheric measurements, *Atmos. Chem. Phys.*, 8(18), 5627–5634, 2008.