

Interactive comment on “Potential genesis and implications of calcium nitrate in Antarctic snow” **by K. Mahalinganathan and M. Thamban**

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Response to Referee#1

Reviewer’s Comment (RC): The paper presents a new set of surface snow data comparing the nitrate and calcium content of snow across two East Antarctica transects. As many studies before, the authors found a correlation between nitrate and calcium in snow. The data set seems to be of good quality with concentrations found in the range of previous observations for such environment. Interpretations and conclusions given by the authors are in line with past studies. Therefore, while the paper is well written and possesses the rigor to be published in Cryosphere, the conclusions are not

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new and basically repeat conclusions proposed by other authors in the past. In other words, the authors do not offer a substantial advances on this topic. If the authors are in possession of other data such as sodium or sulfate, ionic balance etc as it should be with IC analysis, I will suggest including such data to broaden and increase the impact of the publication (see for instance Iizuka et al. 2008, 2009). As now, I recommend a substantial improvement of the MS before being published in TC.

Author’s Response (AR): We thank the referee for providing valuable comments and suggestions to improve its quality. We have incorporated the ionic balance calculations and have estimated the residual acidity of all the snow samples. Correlation coefficients of NO_3^- and nssCa^{2+} with the rest of the ions (including the sea-salt and biogenic species) is included in the revised manuscript (Table 1). Additionally, Principal Component Analysis (PCA) of major ion data is included (Table 2) and the results show an overall relationship between major ions and also reveal the source/transport pathways of these ions. The PCA results show a strong association between NO_3^- and nssCa^{2+} in all sections (except in the mountainous section in cDML) - which is most likely associated with long-range transport rather than local neutralisation processes, thereby supporting the conclusions made in this manuscript. The articles suggested have been referred to and incorporated in the revised manuscript. We hope our responses to the reviewer’s comments and the modifications/revisions in the manuscript are satisfactory.

RC: Below few remarks to improve the MS:

P6127L12: change Savarino et al, 2006 by Savarino et al. 2007

AR: Corrected [Page 2, Line 34].

RC: P6127L12 to L15: Authors should cite recent publications on the subject. Berhanu, T. A., Savarino, J., Erbland, J., Vicars, W. C., Preunkert, S., Martins, J. F., and Johnson, M. S.: Isotopic effects of nitrate photochemistry in snow: a field study at Dome C, Antarctica, *Atmos. Chem. Phys.*, 15, 11243–11256, 10.5194/acp-15-11243-2015, 2015.

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Erbland, J., Savarino, J., Morin, S., France, J. L., Frey, M. M., and King, M. D.: Air-snow transfer of nitrate on the East Antarctic Plateau – Part 2: An isotopic model for the interpretation of deep ice-core records, *Atmos. Chem. Phys.*, 15, 12079-12113, 10.5194/acp-15-12079-2015, 2015.

Erbland, J., Vicars, W. C., Savarino, J., 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, 10.5194/acp-13-6403-2013, 2013.

AR: The suggested citations are included in the revised manuscript [Page 2, Lines 35–36].

RC: have the authors estimated the insoluble part of the calcium? IC analysis may not represent the full content of calcium in snow. Authors should mention this.

AR: The insoluble part of the Ca^{2+} was not measured during the IC analysis. We did not estimate the insoluble part of the Ca^{2+} for this study. This is clarified in the updated manuscript [Page 3, Line 86].

RC: P6131L19: Replace secondary aerosol by secondary product as nitrate is mainly found in the form of HNO_3 , a gas.

AR: Corrected to “secondary product” [Page 5, Line 167].

RC: P6132L1 to L8: Frey et al. 2009 as well as Erbland et al. 2013 showed a spatial variability of nitrate content in snow scaled with snow accumulation, with top snow concentration higher on the plateau with respect to coastal snow. The present study may have not seen such trend because transects were limited to the edge of the central plateau. The authors should take into consideration the previous studies before writing that nitrate has no spatial variability.

AR: We agree with the reviewer. The discussion on nitrate variability is corrected and references are incorporated in the revised manuscript [Page 6, Line 176–182].

RC: How the authors reconcile the fact that nitrate show poor relation with other anions

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while being associated with the long-range transport as mentioned in their schematic diagram 6? Some correlation would be expected with other species travelling with nitric acid if it was the case.

AR: A correlation table showing correlation of NO_3^- and nssCa^{2+} with other major ions is included in the revised manuscript for a better understanding [Page 23, Table 1]. Nitrate in this study is strongly correlated with nssCa^{2+} in both cDML and PEL. However, in the inland regions, NO_3^- shows a weak association with other species, especially NH_4^+ . Further, the PCA results displayed a strong association of NO_3^- and nssCa^{2+} with the same principal factor – the long range transport/deposition mechanism [Page 5, Lines 141–143 and Lines 153–164; Page 9, Lines 278–286; Page 23, Table 2].

RC: P6132L21: “representative sections”. Can the authors be more specific? What “representative” actually means?

AR: We intended to mention different (coastal, mountainous and inland) regions of the sampling transect using the term ‘representative sections’. This is clarified in the revised manuscript [Page 6, Line 194–195].

RC: P6134L11 to L13: Not very clear what the authors want to say about the two-stage process. If adsorbed HNO_3 reacts to form a surface layer of $\text{Ca}(\text{NO}_3)_2$, I don’t see how it can then further react with bulk carbonate.

AR: We intended to convey that the reaction of HNO_3 with mineral dust is not only limited to the surface of the dust particles, but also can react into the bulk of the particles in the presence of H_2O . This process is clarified along with necessary citation in the revised manuscript [Page 8, Line 240–244].

RC: P6136L19-L27: This proposition is not really new. Nevertheless, based on the available data, it is not possible to conclude on the origin of HNO_3 . The scenario where HNO_3 within the vortex and coming from the stratosphere reacts with dust is also fully compatible with the observations.

AR: As obvious from the text, we did not attempt to conclude on the origin of HNO_3 . Rather, we emphasised that HNO_3 present in the atmosphere reacts with mineral dust

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during the long-range transport of dust. It is also clear from the results of the PCA analysis (Table 2) that this neutralization could mainly take place in the atmosphere (rather than at the local air-snow boundary layer) and this could be responsible for the consistently strong correlation between Ca^{2+} and NO_3^- in different sections - coastal, inland, mountainous - of the geographically distinct sampling transects. Although this dataset covers relatively small regions and may not be robust enough to apply to the whole continent, considering the fact that the transects are separated by >2000 km, the results are highly encouraging. The air mass containing dust particles undergo deposition within the polar vortex and HNO_3 -dust reaction scenario is also possible within this region as mentioned by the reviewer. Some modifications are included in the revised manuscript. [Page 8, Lines 254–285; Page 23, Table 2].

RC: P6137L7: Reference to Legrand and Kirchner, 1990 is outdated. Authors should refer to Davis et al. 2008 for an update of the nitrogen cycle in Antarctica and Erbland 2013-2015 for the latest results. Dry deposition is far from being negligible given the propensity of nitrate to stick on ice crystal and the overwhelming HNO_3 form in the speciation of atmospheric nitrate in Antarctica. The correlation between deposition flux and accumulation is misleading and distorted by the photo-denitrification of the snow pack. Dry deposition is very high as well as photo-denitrification also, giving the false impression that dry deposition is negligible. Any interpretation of nitrate in Antarctic snow must be done in the framework of Davis' interpretation, which has been confirmed by Erbland's work.

AR: We agree with the reviewer. The outdated reference is removed and the views on dry deposition is corrected in the revised manuscript along with the recent citations as suggested [Page 10, Line 324–325].

RC: P6137L27 to L28: the salt form of nitrate doesn't prevent its photolysis as lab experiments shown it when using frozen solution of NaNO_3 (eg Chu and Anastasio, 2003). There is no reason to believe that $\text{Ca}(\text{NO}_3)_2$ will better stabilize nitrate to prevent its photolysis. In fact, even nitrate deposited on soil or surface building show

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some photochemical activity (McCalley and Sparks 2009; Baergen and Donaldson, 2012) demonstrating that the salt form of nitrate has little effect on its photodissociation which make sense as photodissociation brakes the N-O bond and this bond is little influenced by the cation.

AR: We agree with the reviewer that $\text{Ca}(\text{NO}_3)_2$ may not necessary prevent the possible photolysis in Antarctic ice sheet surface. Our study shows that the dust-bound $\text{Ca}(\text{NO}_3)_2$ forms a significant part of the NO_3^- concentration in the Antarctic snow/ice. However, in the absence of sufficient evidence with respect to post-depositional loss of NO_3^- associated with Ca^{2+} in our study, we restrain from inferring the influence of $\text{Ca}(\text{NO}_3)_2$ formation on post depositional loss of NO_3^- in Antarctica. Accordingly we have deleted the lines mentioning post-depositional processes.

RC: "Huge significance" is a little too excessive in my view; "Such reactions are of significance" will be sufficient.

AR: Modified as suggested [Page 10, Line 338].

RC: Figure 1: For PEL, drilling site 19 to 21 are missing on the map.

AR: These cores are located in the coastal section of PEL. We have labelled the locations in the revised manuscript.

RC: Figure 2: Can the author provide the ionic balance of their snow along with the snow concentration profile of Ca^{2+} and NO_3^- ? This will help to put the data in context. Can they also mention the correlation between sulfate and calcium?

AR: The ionic balance is now included in Figure 3. We have included a correlation table as suggested by the reviewer showing the associations of NO_3^- and nssCa^{2+} with other major ions (Table 1). PCA was performed on the ionic data and this gives an insight of the complete dataset, including SO_4^{2-} (Table 2). The PCA results clearly indicate that nssSO_4^{2-} and MSA^- form factor 3, without any significant relation to Ca^{2+} .

RC: Figure 4: Authors should draw the stoichiometry line. This will help to show that the majority of nitrate is in the HNO_3 form and not calcium.

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AR: We have addressed this point by estimating the nssCa^{2+} and HNO_3 associated NO_3^- from the ionic balance and residual acidity. In the coastal sections of both the transects, 70-75% of NO_3^- is in the form of $\text{Ca}(\text{NO}_3)_2$. However, in the inland sections, about 50-55% of NO_3^- was found to be in the form of HNO_3 . This is in line with the previous studies suggesting that post-depositional photochemical loss of NO_3^- occur in the inland regions of Antarctica. This is included on Page 5, Lines 133–140; Page 8, Lines 266–275.

RC: Figure 6: as mentioned before, $\text{HNO}_3/\text{N}_2\text{O}_5$ can be encountered at any stage from emission to deposition. There is no reason to believe that the dust/gas reaction is just happening outside the polar vortex, figure should reflect that. Sulfuric acid is also a major component of the aerosols in the free troposphere. Why is it not associated with Ca too? This could be an indicator that dust/ HNO_3 reaction may well happen in proximity of the snow, if not within the snow.

AR: The Polar vortex zone in this figure is presented as one of the major atmospheric zones and not to denote that HNO_3 -dust reaction happens outside of it. This figure is modified now with more information. Our data shows that the HNO_3 -dust reaction occurs during long-range transport rather than local neutralization processes. Unlike the Ca^{2+} and NO_3^- , there was no significant relation between Ca^{2+} and SO_4^{2-} (Table 2) except in the mountainous section, suggesting that the Ca^{2+} and NO_3^- interaction happen during the long range transport. This is mentioned on Page 8, Line 278–286.

RC: References

lizuka, Y., Horikawa, S., Sakurai, T., Johnson, S., Dahl-Jensen, D., Steffensen, J. P., and Hondoh, T.: A relationship between ion balance and the chemical compounds of salt inclusions found in the Greenland Ice Core Project and Dome Fuji ice cores, *J Geophys Res*, 113, D07303, 10.1029/2007jd009018, 2008.

lizuka, Y., Miyake, T., Hirabayashi, M., Suzuki, T., Matoba, S., Motoyama, H., Fujii, Y., and Hondoh, T.: Constituent elements of insoluble and non-volatile particles during the Last Glacial Maximum exhibited in the Dome Fuji (Antarctica) ice core, *Journal of*

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Glaciology, 55, 552-562, 2009.

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, doi:10.5194/acp-9-8681-2009, 2009.

Erbland, J., Vicars, W. C., Savarino, J., 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, 10.5194/acp-13-6403-2013, 2013.

Erbland, J., Savarino, J., Morin, S., France, J. L., Frey, M. M., and King, M. D.: Air-snow transfer of nitrate on the East Antarctic Plateau – Part 2: An isotopic model for the interpretation of deep ice-core records, *Atmos. Chem. Phys.*, 15, 12079-12113, 10.5194/acp-15-12079-2015, 2015.

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, 9594-9602, 2003.

McCalley, C. K., and Sparks, J. P.: Abiotic Gas Formation Drives Nitrogen Loss from a Desert Ecosystem, *Science*, 326, 837-840, 10.1126/science.1178984, 2009.

Baergen, A. M., and Donaldson, D. J.: Photochemical Renoxification of Nitric Acid on Real Urban Grime, *Environmental Science & Technology*, 47, 815-820, 10.1021/es3037862, 2012.

Davis, D., Seelig, J., Huey, G., Crawford, J., Chen, G., Wang, Y., Buhr, M., Helmig, D., Neff, W., and Blake, D.: A reassessment of Antarctic plateau reactive nitrogen based on ANTCI 2003 airborne and ground based measurements, *Atmos Environ*, 42, 2831-2848, 10.1016/j.atmosenv.2007.07.039, 2008.

Interactive comment on The Cryosphere Discuss., 9, 6125, 2015.

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