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

Anonymous Referee #1

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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 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

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for instance Iizuka et al. 2008, 2009). As now, I recommend a substantial improvement of the MS before being published in TC.

Below few remarks to improve the MS:

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

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. 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.

P6129L16: 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.

P6131L19: Replace secondary aerosol by secondary product as nitrate is mainly found in the form of HNO₃, a gas.

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.

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How the authors reconcile the fact that nitrate show poor relation with other anions while being associated with the long-range transport as mentioned in their schematic diagram 6? Some correlation would be expected with other species traveling with nitric acid if it was the case.

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

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.

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.

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.

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 some photo-

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

“Huge significance” is a little too excessive in my view; “Such reactions are of significance” will be sufficient.

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

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?

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.

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.

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