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# ***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 Referee2**

**Reviewer’s Comment (RC):** General Comments: The paper is concerning the study of the Ca/nitrate relationship along two coastal-inner transects in Princess Elisabeth Land and Dronning Maud Land, East Antarctica. The topic is surely interesting in order to understand the atmospheric processes involved in the dry deposition on the snow surface of nitrate and mineral dust carried by longrange transport from continental source areas (especially Southern South America). In particular, the formation of nitrate salts is relevant in the persistence of nitrate, since it is not irreversibly fixed in the snowpack, due to post-depositional re-emission into the atmosphere of HNO<sub>3</sub> in low-accumulation

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sites. However, the manuscript contains some weak points that, in my opinion, should be overcome before to be published on The Cryosphere journal.

**Authors' Reply (AR):** We would like to thank the reviewer for the constructive comments that have significantly improved the manuscript. In the revised manuscript, we have incorporated most of the suggestions/modifications recommended by the reviewer.

**RC:** 1. The formation of Ca nitrate and the relevance of  $\text{CaCO}_3$  particles in preserving nitrate record are well known, at least in the ice-core community. I agree that the manuscript reports an interesting data set (41 sites along two transects) in coastal-inner areas of East Antarctica, but Authors say that a complete ion analysis was carried out on the samples. However, just Ca and nitrate were in deep discussed, with a very short discussion on  $\delta^{18}\text{O}$  and Na records. I think that a more comprehensive data discussion on other relevant components of Antarctic snow should be addressed, especially about the coastal-inner profiles of sea spray (here just mentioned) and biogenic compounds (mainly nss-sulfate and MSA). Indeed, ionic balances (in Eq/L) of the snow samples are useful in understanding the changes in the different source contributions (and so, of the snow composition) along the transects. Besides, from the ionic balances, a quantitative evaluation of the relationship between nssCa and nitrate and possible residual acidity can be carried out.

**AR:** A complete major ion analyses was carried out on the snow cores, as mentioned in our original manuscript. The paper mainly focuses on  $\text{Ca}^{2+}$ – $\text{NO}_3^-$  relationship and was therefore discussed in detail in the original manuscript. However, in the revised manuscript, we have included a table comprising the relationships among all major ions as well as a discussion on the ionic balance of all samples from the study region. Further, we have performed a PCA analysis on major ion data in order to strengthen our interpretations on  $\text{HNO}_3$  neutralisation during long-range transport. The statistical results clearly indicate that the relationship between nss $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  remained consistent with our previous interpretation. The ionic balance and results of PCA also gives a brief overview of other ions (sea-spray and biogenic sources) as suggested by

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the reviewer. In the revised manuscript, Tables 1 and 2 are now included and Fig. 3 is modified with the above information.

**RC:** 2. Calcium species in the discussion and in the figures. The reaction between  $\text{CaCO}_3$  and  $\text{HNO}_3$  (including that involving  $\text{N}_2\text{O}_5$ , which give  $\text{HNO}_3$  by hydrolysis) is an acid-base reaction that can involve only basic compounds of Ca (such as  $\text{CaCO}_3$ ) and the acidic species of nitrate (i.e.,  $\text{HNO}_3$ ). In this way, all non-basic Ca compounds, such as sea-spray Ca and crustal  $\text{CaSO}_4$  cannot be considered in the Ca-nitrate relationships. Authors rightly say that just nssCa has to be considered in the reaction with nitrate, but all the discussion and figures report Ca and not nssCa concentrations. At least figure 3 and (necessarily) figure 4 have to be re-plotted by using nssCa and not Ca concentrations. For instance, the evaluation of averaged w/w (or mole/mole) ratios between Ca and nitrate in  $\text{Ca}(\text{NO}_3)_2$  by the slope of the linear regressions of the Ca-nitrate plots (figure 4) can be carried out only if nssCa is used. The Authors just report in Figure 3 the mean percentage of nssCa in coastal and inner areas, but this information is not sufficient because the sea spray contribution (and so, the nssCa fraction) changes very quickly as the distance from the sea and, especially, altitude change. This process can lead to very different nss-Ca contributions sample by sample.

**AR:** We concur with the reviewer. All  $\text{Ca}^{2+}$  calculations in the revised manuscript have been changed into  $\text{nssCa}^{2+}$ . Figures 3 and 4 have been replotted with nssCa concentrations instead of total  $\text{Ca}^{2+}$  as suggested by the reviewer.

**RC:** 3. The third criticism concerns the necessity to carry out a more reliable discussion on the acidic or neutralized species in which nitrate is present in the snow along the transects, and how much nitrate is fixed as calcium salt. Besides, the evaluation of the possible residual acidity of the snow is relevant, in order to understand if the formation of volatile  $\text{HNO}_3$  is possible, even after the formation of  $\text{Ca}(\text{NO}_3)_2$ , by acid-base exchange with  $\text{H}_2\text{SO}_4$  (especially in summer samples, generally characterized by high  $\text{H}_2\text{SO}_4$  content from marine biogenic emissions). Again, such information could be given by the ionic balance carried out on every sample, from which acidity content

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(calculated by anions excess) and nssCa/nitrate ratios can be easily evaluated. For these reasons, I suggest that the manuscript can be accepted for publication in The Cryosphere journal only after major revisions.

**AR:** As recommended, ionic balance calculations were made and a PCA analysis was carried out on the major ion data in the revised manuscript in order to determine the sources/transport pathways of the major ions. The residual acidity of the samples were also determined, which is presented in Fig. 3. A discussion on the ionic balance and the PCA analysis is included in the revised manuscript [Page 8, Lines 266–286].

**RC:** Specific comments.

Abstract.

Line 4, page 2. NssCa, and not Ca, can be used as crustal marker.

**AR:** Non-sea-salt  $\text{Ca}^{2+}$  is used instead of  $\text{Ca}^{2+}$  as suggested by the reviewer. The correlation statistics and data analyses have also been carried out using nss $\text{Ca}^{2+}$  in the revised manuscript (and therefore minor changes in the correlation values have also been made in the necessary sections).

**RC:** Lines 13-14, page 2. The reaction is between  $\text{CaCO}_3$  and  $\text{HNO}_3$  and not with “nitrogen oxides”. A reaction of  $\text{N}_2\text{O}_5$  and  $\text{CaCO}_3$  is also possible, but after hydrolysis (even in heterogeneous phase on  $\text{CaCO}_3$  particles) of  $\text{N}_2\text{O}_5$  to form  $\text{HNO}_3$  ( $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$ ).

**AR:** This correction has been made in the revised manuscript [Page 1, Line 11 and Fig 6].

**RC:** Lines 24-25, page 2. The nitrate fraction bound to nssCa, with respect to the total nitrate content, is not evaluated in the manuscript.

**AR:** We have estimated the nitrate fraction associated with nss $\text{Ca}^{2+}$  and  $\text{HNO}_3$  and discussed in the revised manuscript. [Page 8, Line 269–275]. Hence this line is retained.

**RC:** Introduction.

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Lines 1-2, page 3. This sentence is obvious and should be deleted.

**AR:** Sentence deleted.

**RC:** Line 3, page 3. Please, change “teleconnect” with “teleconnected”.

**AR:** Modified [Page 2, Line 27].

**RC:** Lines 6-7, page 3. There is certain confusion between gas-phase and aerosol components. Besides, nitrate and  $\text{HNO}_3$  cannot be named “oxides” (eventually, N-oxidized species).

**AR:** The sentence is corrected in the revised manuscript. N-oxidised species are separately mentioned to avoid confusion [Page 2, Line 29–30].

**RC:** Sampling and methods.

Lines 15-16, page 5. In order to better evaluate the detection limits, the volume of the IC injection loop should be reported. Besides, the detection limit for Ca does not seem to be “excellent”. Indeed, several DML samples show Ca concentrations lower than 5  $\mu\text{g/L}$ , while the DL is 3  $\mu\text{g/L}$ .

**AR:** The volume of the cation injection loop is 100  $\mu\text{g/L}$  and the volume of the anion loop is 1000  $\mu\text{g/L}$ . This is reported in the revised manuscript [Page 3, Line 84–85]. The cations were analysed using Dionex DX2500 and the detection limit for  $\text{Ca}^{2+}$  was indeed excellent. The detection limit was wrongly mentioned (3  $\mu\text{g/L}$ ), instead of 0.3  $\mu\text{g/L}$ . This is corrected in the revised manuscript [Page 3, Line 86].

**RC:** Authors are requested to report how ssNa (and so, nssCa) was evaluated.

**AR:** We determined the concentrations of  $\text{ssNa}^+$  and  $\text{nssCa}^{2+}$  using methods established in previous studies (e.g. Röthlisberger et al., 2002).

$$\text{ssNa}^+ = (\text{Na}^+)_{\text{snow}} - \text{nssCa}^{2+} / 1.78 \quad (1)$$

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where 1.78 is the crustal average of  $\text{Ca}^{2+}/\text{Na}^+$ .

$$\text{nssCa}^{2+} = (\text{Ca}^{2+})_{\text{snow}} - \text{ssNa}^+ / 0.038 \quad (2)$$

where 0.038 is the marine average of  $\text{Ca}^{2+}/\text{Na}^+$ .

Using the above equations, the  $\text{ssNa}^+$  equation was derived:

$$\text{ssNa}^+ = 1.78(\text{Na}^+)_{\text{snow}} - (\text{Ca}^{2+})_{\text{snow}} / (1.78 - 0.038) \quad (3)$$

The above calculation is included in the revised manuscript [Page 4, Line 99–102].

**RC:** Results.

In all the discussions about the Ca-nitrate relationships, nssCa (and not total Ca) concentrations have to be used. This is especially relevant in the more coastal sites, where the ssCa fraction could be relevant.

**AR:** All discussions are now based on  $\text{nssCa}^{2+}$  in the revised manuscript. A PCA data analysis has been included in order to include the variances due to ss fractions [Page 4, Line 122–132].

**RC:** A discussion on sample ionic balances has to be addressed in order to evaluate the different nssCa/nitrate ratios, the possible excess of nitrate or nssCa, and the sample residual acidity. Ionic balances should contain the ss and nss fractions at least of Ca and sulfate.

**AR:** Ionic balance discussion is included in Page 5, Line 133–140. Figure 3 has also been updated with ionic balance.

**RC:** Discussion.

Lines 18–22, page 7. The atmospheric oxidation of  $\text{NO}_x$ , together with the stratosphere-troposphere transport of  $\text{HNO}_3$ , is the most relevant sources of nitrate

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in the Antarctic PBL.

**AR:** This section about the HNO<sub>3</sub> sources is modified in the revised manuscript [Page 6, Line 169–170].

**RC:** Line 10, page 8. The “small” ss-Ca fraction could be very relevant in the sites nearest the sea and has to be evaluated.

**AR:** We agree. The ssCa<sup>2+</sup> fraction was evaluated and mentioned at P6130L26–P6131L3 of the original manuscript in terms of nssCa<sup>2+</sup>%. According to this calculation, an average of 19 % ssCa<sup>2+</sup> was present in the coastal section of PEL, nearest to the sea. In the revised manuscript, the ssCa<sup>2+</sup> fraction is included [Page 6, Line 187–189].

**RC:** Lines 9-11, page 9. Could this statement to be demonstrated by the high contribution of larger (> 10 μm) dust particles?

**AR:** The particle-size analysis of cores from the mountainous section showed a majority of particles in very fine (1 μm) range. Along with this, a number of particles were also observed in the size range of above 6 μm range along with undissolved visible particles. This is mentioned in the the revised manuscript [Page 6, Line 199–201, 212–214].

**RC:** Mineral dust reactivity.

Lines 21-22, page 9. The first part of this sentence is not necessary true, and the second part is obvious. The sentence should be removed.

**AR:** This sentence is removed in the revised manuscript as suggested.

**RC:** Line 1-17, page 10. The mechanism for the acid-base reaction between carbonate species and HNO<sub>3</sub> is well known. This part should be summarized and reduced. Back and Forward-Trajectory analysis. The percentage of trajectories coming for the different dust potential source areas should be reported for the two seasons.

**AR:** This section has been revised as suggested [Page 8, Line 254–261]. The percentages of forward trajectories from potential dust sources are included in the revised

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manuscript [Page 9, Lines 296–297].

**RC:** Formation of Ca nitrate.

The diagram shown in figure 6 depicts well known and elementary processes. Besides, the figure does not show any relevant news on the atmospheric processes leading to the formation of Ca-nitrate salt. Besides, no experimental evidence was given on the fact that the  $\text{CaCO}_3\text{--HNO}_3$  reaction can be carried out in the atmosphere, during the transport of dust particles, or on the snow surface, after their deposition. I'd suggest deleting the figure.

**AR:** We have now included more information in the figure (estimates of nssCa-associated  $\text{NO}_3^-$  in coastal/inland regions) and have modified it based on this study and suggestions from Reviewer1. This schematic diagram also provides useful information to non-experts and therefore would prefer retaining it.

**RC:** Figure 2. Ca could be replaced by nssCa.

Figures 3 and 4. Ca has to be replaced by nssCa.

**AR:** Figures 3 and 4 have been replaced by nssCa as suggested by the reviewer. Since we used total Ca in determining seasonality, figure 2 is not replaced by nssCa.

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

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