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 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.

Authors' 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.
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 87].

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 6, 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 176–183].

RC: 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 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 143–145 and Lines 155–163; Page 9, Lines 277–285; 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 196].

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 $Ca(NO_3)_2$, 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 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].

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 $Ca(NO_3)_2$ will better stabilize nitrate to prevent its photolysis. In fact, even nitrate deposited on soil or surface building show some photochemical activity (McCalley and Spark,s 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 $Ca(NO_3)_2$ may not necessary prevent the possible photolysis in Antarctic ice sheet surface. Our study shows that the dust-bound $Ca(NO_3)_2$ 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 $Ca(NO_3)_2$ 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 337].

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.

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 $Ca(NO_3)_2$. 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 135–142; Page 8, Lines 266–275.

RC: Figure 6: as mentioned before, HNO_3/N_2O_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

3

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 277–285.

RC: References:

Iizuka, 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, 10.1029/2007 jd009018, 2008.

Iizuka, 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 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.

List of all relevant Changes

Page 2, Line 34: Changed reference year from 2006 to 2007
Page 2, Lines 35–36: Included new references - Erbland et al., 2015 and Berhanu et al., 2015
Page 3, Line 87: Clarified sentence for soluble Ca^{2+}
Page 6, Line 167: Corrected to "secondary product"
Page 6, Lines 176–183: Nitrate variability corrected as suggested
Page 6, Line 196: Clarified representative sections
Page 8, Lines 240–244: Clarified the $Ca(NO_3)_2$ formation process
Page 10, Line 324: Removed outdated reference. Modified with new reference
Page 10, Line 337: Sentence corrected as suggested
Page 19, Fig. 1: Labelled locations 19–22
Page 20, Fig. 3: Ionic balance included
Page 23, Table 1: Correlation table included
Page 23, Table 2: PCA factor loading table included
Page 4, Lines 105–110: Methodology of ionic balance and PCA analysis included in section 2
Page 5, Lines 135–142: Results of ionic balance included in section 3
Page 5, Lines 155–163: Results of PCA analysis included in section 3
Page 8, Lines 266–276: Discussion of ionic balance and estimation of nssCa^{2+} associated NO_3^- in section 4.2
Page 9, Lines 277–285: Discussion of PCA analysis results in section 4.2
Page 10: Removed the discussion on post-depositional losses
Page 10: Lines 348–350: Included PCA in conclusions

Response to Referee#2

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 HNO3 in low-accumulation 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 $CaCO_3$ 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 d18O 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 Ca^{2+}–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 HNO_3 neutralisation during long-range transport. The statistical results clearly indicate that the relationship between nssCa^{2+} and 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 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 $CaCO_3$ and HNO_3 (including that involving N_2O_5, which give HNO_3 by hydrolysis) is an acid-base reaction that can involve only basic compounds of Ca (such as $CaCO_3$) and the acidic species of nitrate (i.e., HNO_3). In this way, all non-basic Ca compounds, such as sea-spray Ca and crustal $CaSO_4$ 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 $Ca(NO_3)_2$ 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 Ca^{2+} calculations in the revised manuscript have been changed into nssCa^{2+}. Figures 3 and 4 have been replotted with nssCa concentrations instead of total 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 HNO_3 is possible, even after the formation of $Ca(NO_3)_2$, by acid-base exchange with H_2SO_4 (especially in summer samples, generally characterized by high H_2SO_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 (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 266–285].

RC: Specific comments.

Abstract.

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

AR: Non-sea-salt Ca^{2+} is used instead of Ca^{2+} as suggested by the reviewer. The correlation statistics and data analyses have also been carried out using $nssCa^{2+}$ 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 $CaCO_3$ and HNO3 and not with "nitrogen oxides". A reaction of N_2O_5 and $CaCO_3$ is also possible, but after hydrolysis (even in heterogeneous phase on CaCO3 particles) of N_2O_5 to form HNO_3 ($N_2O_5 + H_2O = 2HNO3$.

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 $nssCa^{2+}$ and HNO_3 and discussed in the revised manuscript. [Page 8, Line 269–275]. Hence this line is retained.

RC: Introduction.

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 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 ug/L, while the DL is 3 ug/L.

AR: The volume of the cation injection loop is $100\mu g/L$ and the volume of the anion loop is $1000\mu g/L$. This is reported in the revised manuscript [Page 3, Line 84–85]. The cations were analysed using Dionex DX2500 and the detection limit for Ca^{2+} was indeed excellent. The detection limit was wrongly mentioned (3 $\mu g/L$), instead of 0.3 $\mu g/L$. This is corrected in the revised manuscript [Page 3, Line 87].

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

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

$$ssNa^+ = (Na^+)_{snow} - \frac{nssCa^{2+}}{1.78} \tag{1}$$

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

$$nssCa^{2+} = (Ca^{2+})_{snow} - \frac{ssNa^+}{0.038} \tag{2}$$

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

Using the above equations, the $ssNa^+$ equation was derived:

$$ssNa^+ = \frac{1.78(Na^+)_{snow} - (Ca^{2+})_{snow}}{(1.78 - 0.038)} \tag{3}$$

The above calculation is included in the revised manuscript [Page 4, Line 101–104].

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 $nssCa^{2+}$ in the revised manuscript. A PCA data analysis has
been included in order to include the variances due to ss fractions [Page 4, Line 124–134; Page 5,
Lines 155–163].

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 135–142. Figure 3 has also been updated
with ionic balance.

RC: Discussion.
Lines 18-22, page 7. The atmospheric oxidation of NOx, together with the stratosphere-troposphere
transport of HNO_3, is the most relevant sources of nitrate in the Antarctic PBL.

AR: This section about the HNO_3 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 $ssCa^{2+}$ fraction was evaluated and mentioned at P6130L26–P6131L3 of the
original manuscript in terms of $nssCa^{2+}\%$. According to this calculation, an average of 19 % $ssCa^{2+}$
was present in the coastal section of PEL, nearest to the sea. In the revised manuscript, the $ssCa^{2+}$
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 um) dust particles?

135   **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 7, Line 201–203, 213–215].

  RC: Mineral dust reactivity.

140 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_3 is well known. This part should by summarized and reduced. Back and Forward-Trajectory

145 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 manuscript [Page 9, Lines 295–296].

150   **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 $CaCO_3$–HNO_3 reaction can be carried out in the atmosphere, during the transport of dust particles, or on the snow surface, after

155 their deposition. I'd suggest deleting the figure.

  AR: We have now included more information in the figure (estimates of nssCa-associated NO_3^- in coastal/inland regions) and have modified it based on this study and suggestions from Reviewer#1. This schematic diagram also provides useful information to non-experts and therefore would prefer retaining it.

160   **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.

List of all relevant changes (Ref #2)

165   Page 1, Line 3: Changed from Ca^{2+} to $nssCa^{2+}$

Page 1, Line 11: Reaction with HNO_3 instead of nitrogen oxides

Page 1, Line 24: Estimated $nssCa^{2+}$ associated NO_3^- at Page 8, Lines 269–275

Page 2: First sentence in Introduction deleted as suggested

Page 2, Line 27: Changed from 'teleconnect' to 'teleconnected'

170   Page 2, Line 29–30: Clarified the sentence on N-oxidised species

Page 3, Lines 84–85: Included sampling loop volume

Page 3, Line 87: Included the correct detection limit

Page 4, Lines 101–104: Included the calculation of $ssNa^+$ and $nssCa^{2+}$

Page 4, Lines 124–134: All results changed to focus on $nssCa^{2+}$ instead of total Ca^{2+} Page 5, Lines

175   135–142: Results of ionic balance included

Page 6, Lines 169–170: Sources of NO_3^- clarified

Page 6, Lines 187–189: Included $ssCa^{2+}$ estimates

Page 7, Lines 201–203, 213–215: Included the dust particle size parameters to support the dust derived from mountains

180   Page 8, Lines 254–261: Summarised and reduced as suggested

Page 9, Lines 295–296: Included trajectory percentages from potential dust sources

Page 20, Fig. 3: Ionic balance included

Page 20, Fig. 4: Total Ca^{2+} replaced by $nssCa^{2+}$

Page 22, Fig. 6: More information and changes included

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Potential genesis and implications of calcium nitrate in Antarctic snow

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Abstract. Among the large variety of particulates in the atmosphere, calcic mineral dust particles have highly reactive surfaces that undergo heterogeneous reactions with ~~nitrogen oxides~~ atmospheric acids contiguously. The association between ~~Ca~~nssCa^{2+}, an important proxy indicator of mineral dust and NO$_3^-$, a dominant anion in the Antarctic snow pack was analysed. A total of 41 snow cores

5 (~ 1 m each) that represent snow deposited during 2008–2009 were studied along coastal–inland transects from two different regions – the Princess Elizabeth Land (PEL) and central Dronning Maud Land (cDML) in East Antarctica. Correlation statistics showed a strong association (at 99 % significance level) between NO$_3^-$ and ~~Ca~~nssCa^{2+} at the near-coastal sections of both PEL ($r = $ ~~0.72~~0.74) and cDML ($r = $ ~~0.76~~0.82) transects. Similarly, a strong association between these ions was also ob-

10 served in snow deposits at the inland sections of PEL ($r = $ ~~0.80~~0.73) and cDML ($r = $ ~~0.85~~0.84). Such systematic associations between ~~Ca~~nssCa^{2+} and NO$_3^-$ is attributed to the interaction between calcic mineral dust and ~~nitrogen oxides~~ nitric acid in the atmosphere, leading to the ~~possible~~ formation of calcium nitrate (Ca(NO$_3$)$_2$) ~~.~~ aerosol. Principal Component Analysis (PCA) revealed a common transport and depositional processes for both nssCa^{2+} and NO$_3^-$ both in PEL and cDML. Forward

15 and back trajectory analyses using HYSPLIT model v. 4 revealed that Southern South America (SSA) was an important dust emitting source to the study region, aided by the westerlies. Particle size distribution showed that over 90 % of the dust was in the range < 4 μm, indicating that these dust particles reached the Antarctic region via long range transport from the SSA region. We propose that the association between ~~Ca~~nssCa^{2+} and NO$_3^-$ occurs during the long range transport due

20 to the formation of Ca(NO$_3$)$_2$ ~~. The Ca(NO$_3$)$_2$ thus formed in the atmosphere undergo deposition over Antarctica under the influence of anticyclonic polar easterlies. However,~~ rather than due to local neutralization processes. However, the influence of local dust sources from the nunataks in cDML and the contribution of high sea-salt in coastal PEL evidently mask such association in the mountainous ~~region.~~ and coastal regions respectively. Ionic balance calculations showed that 70–75 % of

25 NO$_3^-$ in the coastal sections was associated with nssCa^{2+}. However, in the inland sections, 50–55 % of NO$_3^-$ was associated with HNO$_3$. The study indicates that the input of dust-bound NO$_3^-$ ~~may contribute~~ contributes a significant fraction of the total NO$_3^-$ deposited in coastal Antarctic snow.

1 Introduction

~~Geographically, the Antarctic ice sheet may be remote, its atmosphere however, is linked with the rest~~

30 ~~of the planet.~~ Fine aerosols from surrounding continents are transported thousands of kilometers and

~~teleconnect~~ teleconnected with the Antarctic atmosphere. Consequently, the chemistry of the Antarctic atmosphere and its ice sheet is of considerable importance. Apart from sea-salt aerosols, nitrogen

oxides (like $NO_{x, ,}$, NO_2), nitric acid (HNO_3~~and~~) and mineral dust particles make up a significant

component in the Antarctic atmosphere (Weller et al., 2002; Albani et al., 2012; Wolff, 2013). Ni-

35 trate is ubiquitous in the atmosphere and constitutes a large portion of anions in the Antarctic snow.

Several studies have focused on its origin (e.g. Wolff, 1995; Wagenbach et al., 1998; Traversi et al.,

2014), seasonal and spatial variations (e.g. Dahe et al., 1992; Lee et al., 2014; Savarino et al., 2007),

air–snow interactions (e.g. Antony et al., 2010; Erbland et al., 2013, 2015) and its post-depositional

processes (e.g. Wagnon et al., 1999; Weller, 2004; Berhanu et al., 2015). However, there are many

40 uncertainties and speculations over the sources of nitrate, its seasonality and post-depositional losses

(e.g. Traversi et al., 2014; Shi et al., 2015).

Natural mineral dust form an active aerosol component in the atmosphere and model simulations

show that the mineral dust from surrounding continents are directly linked to the Antarctic climate

system (e.g. Li et al., 2008; Gassó et al., 2010). These dust particles are evidently ~~becoming~~ an

45 important factor~~in which~~, considering that they alter the chemical and optical properties of the atmosphere (Nousiainen and Kandler, 2015). The mineralogy of dust particles is of critical importance

since it plays a major role in deciding the manner in which the dust particles alter the chemistry of

the atmosphere (Krueger et al., 2004). Previous field studies and model simulations demonstrate

that throughout the world, mineral dust is frequently associated with NO_3^- (e.g. Jordan et al., 2003;

50 Fairlie et al., 2010). It was reported that almost all of total NO_3^- in high dust regions and $> 40\%$

of the total NO_3^- throughout most of the global atmosphere is coupled with mineral dust (Usher

et al., 2003). This association, depending on the mineralogical composition of the dust, yields various nitrate-salt products (Gibson et al., 2006). Studies also show that dust-associated NO_3^- is a large

component of total atmospheric NO_3^- due to the presence of Ca^{2+} in mineral dust, which has a high

55 buffering capacity to neutralise atmospheric nitric acid (HNO_3) to yield highly hygroscopic calcium

nitrate ($Ca(NO_3)_2$) aerosol (Krueger et al., 2003).

In Antarctica, non-sea-salt Ca^{2+} ($nssCa^{2+} = Ca^{2+} - 0.038\, ssNa^+$) has been used as a proxy for

mineral dust concentration in ice core records (Ruth et al., 2008; Schüpbach et al., 2013). Röthlisberger et al. (2000) have also documented strong associations between NO_3^- and Ca^{2+} throughout

60 the last glacial maximum during which dust concentrations in the Antarctic atmosphere were up to

20 times that of the present day. However, such associations between NO_3^- and Ca^{2+} have not been

widely reported in present day Antarctic snow pack. In this study, we analyse the spatial variability

and association of NO_3^- and nssCa^{2+} from two different regions in East Antarctica – Princess Elizabeth Land (PEL) and central Dronning Maud Land (cDML). We also discuss the possible formation

65 processes of $Ca(NO_3)_2$ during the long range transport of mineral dust and its significance ~~on~~ for Antarctic snow chemistry.

2 Sampling and methods

Forty one snow cores were recovered from the PEL and cDML transects using a KOVACS Mark IV coring system (14 cm diameter) during summer 2008–2009 (Fig. 1). Each snow core was about 1 m

70 deep, enough to cover over a year of snow accumulation. Sampling was carried out in such a way that both transects were perpendicular to the coast and overall slope contours of the region. A total of 21 snow cores were retrieved from coast to inland in PEL covering a distance of 180 km and an elevation of 2100 m a.s.l. Similarly, in cDML, 20 snow cores were retrieved from near-coast to inland region covering a distance of 110–300 km from coast and an elevation up to 2800 m a.s.l.

75 Due to the absence of fresh snow over the Nivlisen ice shelf and the edge of the ice cap, no cores were collected up to 110 km from the coast in cDML (Fig. 1). For the sake of clarity, the actual distance from sea (300 km) is mentioned in cDML throughout this paper. Based on the topography, the cDML transect is spatially divided into near-coastal (110–160 km), mountainous (170–240 km) and plateau (> 240 km) sections (Fig. 1).

80 The snow cores were transferred directly into pre-cleaned high density polyethylene bags and sealed immediately to avoid any contamination during storage and transport. The sample bags were kept in expanded poly propylene (EPP) boxes and were stored at $-20\,°C$ throughout the transit to the ice core laboratory of National Centre for Antarctic and Ocean Research in India. Each core was carefully unpacked and sub-sampled at 5 cm resolution under a laminar flow bench housed at

85 $-15\,°C$ facility. The outer layers of these sub-samples were removed manually by ceramic knives and the innermost portion of the samples were transferred to pre-cleaned vials. These sub-samples were then melted in a Class 100 clean room prior to the analyses. Major ion concentrations were analysed using Dionex DX2500 with IonPac CS17 column for cations (100 μL injection loop) and ICS 2000 with IonPac AS11-HC column for anions (1000 μL injection loop). An excellent low de-

90 tection limit was achieved for both soluble Ca^{2+} (~~3~~0.3 $\mu g\,L^{-1}$) and NO_3^- (5 $\mu g\,L^{-1}$) respectively. Reference standards and duplicate samples were analysed in a routine manner to estimate the analytical precision, which was better than 5 % for both the ions. Dust particle concentration and grain size measurements were carried out using a Multisizer 4 Coulter Counter (Beckman), placed in a Class 100 clean room. Size calibration was made using polystyrene latex beads of 5 μm radius and

95 a precision better than 5 % was obtained.

The seasonality from these snow cores are determined as mentioned in Mahalinganathan et al. (2012). High-resolution $\delta^{18}O$ records of each core were studied to differentiate the summer and winter snow deposition. Annual layers were identified based on the seasonal differences of $\delta^{18}O$. A seasonal $\delta^{18}O$ amplitude of 4‰ was considered large enough to represent the temperature dif-

100 ference between summer and winter precipitation (Stenberg et al., 1998). A minimum seasonal am-
plitude of 6‰ in δ^{18}O values ~~were~~ was observed in all cores (except cores from 110 km in cDML
and from 10, 70 and 100 km in PEL), which was large enough to differentiate between summer and
winter layers.

The concentrations of sea-salt-Na$^+$ (and therefore, nssCa^{2+}) were calculated using the equation
105 ssNa$^+$ = (R$_c$. Na$^+$ − Ca^{2+})/(R$_c$ − R$_m$) derived from Röthlisberger et al. (2002b), where R$_c$ = 1.78
and R$_m$ = 0.038 are the average ratios of Ca^{2+}/Na$^+$ in crust and marine systems, respectively. The
Na$^+$ and Ca^{2+} are respective total concentrations in snow.

Ionic balance and residual acidity (H$^+$) of all snow samples were calculated in terms of μeq L^{-1}
based on the methods specified in Legrand and Mayewski (1997) and Iizuka et al. (2004). In order
110 to identify common sources and/or transport pathways of the species deposited in snow, Principal
Component Analysis (PCA) was carried out separately on snow samples from different sections
of the transects in both cDML and PEL. A varimax rotation procedure was performed in order to
maximize the variances of normalised factor loading across variables for each factor.

3 Results

115 Snow cores from both PEL and cDML clearly showed seasonal variations in δ^{18}O and the major ions
(Fig. 2). ~~The sea-salt~~ Sea-salt (Na$^+$) ions peaked mostly during winter and were in sync with the
δ^{18}O variations. Though Ca^{2+} and NO$_3^-$ peaks were not in sync with the δ^{18}O or sea-salt signatures,
their seasonal variations were well-marked in the snow cores (Fig. 2). The peak values of NO$_3^-$ and
Ca^{2+} were observed during early spring or summer, in agreement with previous studies (Wagenbach
120 et al., 1998; Weller et al., 2011).

Concentrations of NO$_3^-$ and nssCa^{2+} ions showed a significant spatial variability along both PEL
and cDML transects (Fig. 3). Nitrate concentrations in PEL ranged from 40 to 200 μg L^{-1} with few
samples as high as 350 μg L^{-1}. Similarly, NO$_3^-$ in cDML transect ranged from 15 to 350 μg L^{-1}
with outliers as high as 450 μg L^{-1}. ~~Nitrate~~ Even though NO$_3^-$ did not follow any systematic trend
125 either with changes in distance from the sea ~~or with changes in elevation along both transects. In~~
~~general,~~, the inland sites were ~~characterized~~ characterised by relatively higher values along both
transects.

~~Calcium~~ Non-sea-salt calculations revealed that the majority of Ca^{2+} was derived from crustal
sources in both coastal and inland regions of PEL (81 and 94 %, respectively). Similarly, at cDML
130 transect, majority of Ca^{2+} in the mountainous section (96 %), near-coast (92 %) and the plateau
(88 %) regions were also from crustal sources. Non-sea-salt-Ca^{2+} concentrations, on one hand, were
significantly lower than that of NO$_3^-$ and ranged from 10 to 70 μg L^{-1} with few outliers as high as
100 μg L^{-1} in PEL (Fig. 3). On the other hand, nssCa^{2+} concentrations in cDML transect ranged
from 5 to 50 μg L^{-1} except along the mountainous region, where it showed a substantial spread with

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concentrations up to $150\,\mu g\,L^{-1}$ and outliers as high as $230\,\mu g\,L^{-1}$. As a result, the mean Ca^{2+} concentrations were significantly high along the mountainous section in cDML transect. In the plateau region the $nssCa^{2+}$ concentrations were very low with a narrow range (4–$12\,\mu g\,L^{-1}$) irrespective of seasonal variations.

Ionic balance of the samples from PEL and cDML revealed the dominance of sea-salt (Na^+, Mg^{2+}, K^+ and Cl^-) in the near-coastal cores (PEL 75 %, cDML 50 %) followed by NO_3^- (PEL 38 %, cDML 27 %), $nssCa^{2+}$ (PEL 9 %, cDML 19 %) and $nssSO_4^{2-}$ (PEL 9 %, cDML 17 %). The inland samples, however, showed the dominance of NO_3^- (PEL 38 %, cDML 47 %) followed by $nssSO_4^{2-}$ (PEL 14 %, cDML 22 %). Samples from the mountainous section of cDML showed a large fraction of Ca^{2+} and SO_4^{2-} derived from crustal sources. The H^+ calculation revealed that samples from all the regions were acidic except PEL coast, which was basic due to its proximity to the open ocean (Fig. 3).

The correlation analysis of NO_3^- and $nssCa^{2+}$ with other major ions showed a consistent relationship between $nssCa^{2+}$ and NO_3^- from different sections of PEL and cDML transects, except in the mountainous section (Table 1). Further, to verify the consistency, samples representing one complete year (summer–winter pattern) were also evaluated (Fig. 4). Within the near-coastal and the plateau regions of cDML, NO_3^- showed a significant association with $nssCa^{2+}$ ($r = 0.82$ and 0.85 respectively). Near the coast, a stronger association ($r = 0.95$) was observed in winter snow deposits while the samples from plateau section showed a stronger association throughout the year ($r = 0.85$). Compared to these, snow cores from the mountainous region in cDML did not reveal any correlation during winter and showed a comparatively weak correlation only during summer ($r = 0.69$). In PEL transect, NO_3^- and $nssCa^{2+}$ showed a more significant relationship in the inland section during winter ($r = 0.87$). The coastal section of PEL showed a consistent relationship throughout the year ($r = 0.75$). All correlations were significant at 99 % confidence level.

The PCA factor loadings are presented in Table 2 where the loadings greater than 0.5 are mentioned in bold. Based on the factor loadings of the marker ions (such as Na^+, $nssCa^{2+}$ and MSA^-), three principal factors (F1, F2, F3) were identified. Those ions primarily derived from sea-spray sources (Na^+, Cl^-, Mg^{2+} and K^+), and from biogenic sources (MSA^- and $nssSO_4^{2-}$) were grouped together. Interestingly, $nssCa^{2+}$ derived from crustal sources and NO_3^-, derived from upper atmospheric or tropospheric sources were grouped together in all regions indicating long range transport and deposition of these ions in the form of $Ca(NO_3)_2$ aerosol. However, in the mountainous section

of cDML, $nssCa^{2+}$ was associated with $nssSO_4^{2-}$ indicating local sources of $nssCa^{2+}$ from the exposed mountains.

4 Discussion

4.1 Association between $nssCa^{2+}$ and NO_3^- in snowpack from distinct transects

175 Nitrate is one of the major anions with multiple sources in the Antarctic environment. It is predominantly a secondary ~~aerosol~~ product produced via oxidation of NO_x and photo-dissociation of N_2 in the upper atmosphere (Brasseur and Solomon, 1986) and also via sedimentation from polar stratospheric clouds (Legrand and Delmas, 1986; Legrand and Mayewski, 1997). Both stratospheric and ~~lightning sources of NO_x~~ tropospheric transport of HNO_3 are also thought to contribute to NO_3^-

180 deposited in the Antarctic snow (Legrand and Delmas, 1986; Michalski et al., 2005). Furthermore, it is known that post-depositional processes and photochemical mechanisms also lead to NO_3^- loss in low accumulation sites (Röthlisberger et al., 2002; Erbland et al., 2013), resulting in a complex distribution of NO_3^- in the Antarctic snow pack. Due to the variety of its sources, NO_3^- distribution in modern day snow pack is found to be independent of oceanic or topographic influences and is

185 generally expected to have poor relationships with other major ions. ~~Nitrate concentrations in both PEL and cDML did not show any variation with distance from sea or changes in elevation (Fig. 3), indicating a rather mixed input of in the study region.~~ A study of surface snow chemistry across the Antarctic ice sheet by Bertler et al. (2005) also indicated that NO_3^- has no clear associations either with parameters like distance from coast and elevation or with other major ions. However, more

190 recent studies (e.g., Erbland et al., 2013, 2015) have shown that NO_3^- indeed show spatial variation at least on the surface snow with high concentrations in the interior of the continent. Even though NO_3^- concentrations in both PEL and cDML did not show clear variation with distance from sea (Fig. 3), ionic balance clearly revealed an overall increase in NO_3^- concentration towards inland, indicating a rather mixed input of NO_3^- in the study region.

195 Compared to NO_3^-, sources of Ca^{2+} in the Antarctic environment are relatively well known. A small but significant amount of Ca^{2+} derived from sea spray and sea ice surface $(ssCa^{2+})$ is present in the coastal section of Antarctic snow (Sommer et al., 2000). Sea-salt Ca^{2+} may also originate from ikaite crystals ($CaCO_3.6H_2O$) in the Antarctic sea ice during onset of winter (Dieckmann et al., 2008). ~~However, crustal~~ Calculations from the coastal section of PEL showed an input of 33 %

200 $ssCa^{2+}$ (of total Ca^{2+}) due to its proximity to the open ocean. Crustal dust from local sources and remote continents are the major sources of Ca^{2+} (in the form of $nssCa^{2+}$) in the Antarctic atmosphere and ice sheet (Boutron and Martin, 1980). ~~Many ice core studies have demonstrated that dust flux archived in the Antarctic ice sheet was predominantly transported from Southern South America (SSA) and/or Australia .~~ The percentage of estimated $nssCa^{2+}$ component in the total Ca^{2+} in both

205 PEL (> 87 %) and cDML (> 90 %) transects (Fig. 3) support a predominantly crustal origin of Ca^{2+}

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in the study regions. Many ice core studies have demonstrated that dust flux archived in the Antarctic ice sheet was predominantly transported from Southern South America (SSA) and/or Australia (e.g. Basile-Doelsch et al., 1997; Delmonte et al., 2004; Revel-Rolland et al., 2006). Furthermore, particle size analyses of dust from snow cores in ~~representative~~ coastal, mountainous and inland sections of both cDML and PEL transects showed that $> 90\,\%$ of particles were $< 4\,\mu m$ and the majority of them in the $\sim 1\,\mu m$ size range, indicating a distant dust source as demonstrated by model studies (e.g. Li et al., 2008, 2010).

Local sources of dust in Antarctica are usually limited to ice-free coastal areas, nunataks and exposed mountainous regions (Tegen and Lacis, 1996; Mahowald et al., 2013). Snow cores from the mountainous section of the cDML transect revealed significant number of coarser particles ($> 10\,\mu m$) as well as visibly insoluble particles along with a large amount of fine particles. Such coarser particles invariably indicate the influence of locally derived dust, especially from the Wohlthat mountains, in the prevailing wind direction (Fig. 1).

This study revealed a striking relationship between NO_3^- and nssCa^{2+} in snow cores from both PEL and cDML transects in East Antarctica that are $> 2000\,km$ apart (Fig. 4). The Ca^{2+} flux calculations ($F_{Ca^{2+}} = C_{Ca^{2+}} \times A$, where $C_{Ca^{2+}} =$ annual mean concentration of Ca^{2+} and $A =$ annual accumulation) (Burkhart et al., 2004) showed an average of 6.1 and 9.1 $kg\,km^{-2}\,yr^{-1}$ of Ca^{2+} at PEL and cDML transects respectively, indicating a substantial amount of Ca^{2+} reaching the Antarctic environment throughout the year. Calcium concentrations in the mountainous section were nearly three times higher than the rest of the cDML transect, with concentrations up to 150 to 230 $\mu g\,L^{-1}$, strongly implying additional dust input from the Wohlthat mountains in this sector. Also, results from particle size analyses revealed that along with particles under 1 μm range, about 22 % of particles present were >6 μm, implying dust locally derived from the Wohlthat mountains in the vicinity. Such additional input of nssCa^{2+} from local dust sources possibly obscures the nssCa^{2+} / NO_3^- association formed during long-range transport, resulting in poor correlation of NO_3^- and nssCa^{2+} as observed in the mountainous section of the cDML transect. Moreover, the association between NO_3^- and nssCa^{2+} was consistent in snow deposited during both summer and winter throughout the coastal and inland regions of both the PEL and cDML transects (Fig. 4). The excellent correlation between NO_3^- and nssCa^{2+} concentrations at all sites (except the mountainous section) strongly suggest that aerosol interactive processes during long range transport are responsible for influencing their relationship.

4.2 Mineral dust reactivity and possible remote sources

While mineral dust aerosol is often discussed as a single entity aerosol, its chemical characteristics depends on the mineralogy of specific source regions. It is a complex mixture with major minerals like quartz, feldspar, hydrous aluminium silicates and carbonates (Pye, 1987). Mineral dust reactivity with trace gases in the atmosphere depends on the composition of the dust itself (Laskin

et al., 2005). Carbonates such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are found to be the most reactive constituents of mineral dust in the atmosphere in the presence of HNO_3 (Usher et al., 2003; Krueger et al., 2004). Nitrate-salts such as $Ca(NO_3)_2$ and $Mg(NO_3)_2$ are formed when calcic mineral dust undergo heterogeneous reactions with atmospheric HNO_3 according to the following reactions (Gibson et al., 2006):

$$CaCO_3 + 2HNO_3 \xrightarrow{\%RH} Ca(NO_3)_2 + CO_2 + H_2O \tag{R1}$$

$$CaMg(CO_3)_2 + 4HNO_3 \xrightarrow{\%RH} Ca(NO_3)_2 + Mg(NO_3)_2 + 2CO_2 + 2H_2O. \tag{R2}$$

Similarly, there exists a possibility that N_2O_5 present in atmosphere can also react with the calcic mineral dust according to the following reactions:

$$CaCO_3 + N_2O_5 \xrightarrow{\%RH} Ca(NO_3)_2 + CO_2 \tag{R3}$$

$$CaMg(CO_3)_2 + 2N_2O_5 \xrightarrow{\%RH} Ca(NO_3)_2 + Mg(NO_3)_2 + 2CO_2. \tag{R4}$$
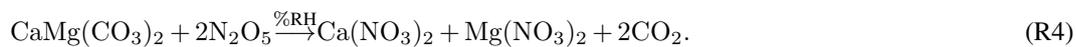
The reaction between mineral dust and atmospheric HNO_3 or N_2O_5 ~~occurs in two-stages~~is enhanced in the presence of H_2O (Goodman et al., 2000). First, HNO_3 is adsorbed on the dust surface to form thin layers of $Ca(NO_3)_2$, even at very low relative humidity (RH) conditions ($\sim 12\,\%$ RH) (Al-Abadleh et al.(2003), Krueger). Then, with increasing RH, the adsorbed HNO_3 reacts with bulk $CaCO_3$ or $CaMg(CO_3)_2$ to form $Ca(NO_3)_2$. However, this reaction in the atmosphere is limited by the availability of HNO_3 (Laskin et al., 2005). Similarly, laboratory studies have shown that N_2O_5 hydrolysis on mineral dust particles is enhanced in the presence of higher relative humidity (Mogili et al., 2006).

Several ice core and model studies have demonstrated that certain regions in SSA like northern Patagonia, Puna Altiplano (PAP) and San Julian's Great Depression are the main dust emitting sources to East Antarctica (Gaiero, 2007; Lambert et al., 2008; Li et al., 2008, 2010). ~~While a few studies have shown that dust from Australia is important in parts of East Antarctica , the SSA region is the single-most important dust source to the Atlantic and Indian Ocean sector .~~ Studies based on large volumes of surface snow samples at Berkner Island by Bory et al. (2010) also showed that the SSA is the dominant dust source in the Atlantic sector of Antarctica. The mineralogical composition of loess and loessoid sediments in SSA reveal the presence of calcic-rich plagioclase and calcite minerals in the dust (Zárate, 2003) that react with HNO_3.

The SSA region is a land mass ~~of significant size~~ extending from 40–56° S ~~, with a typical width varying between 500 and 700. It is located inside the westerly wind belt of the Southern Hemisphere and the~~ and the climate here is controlled mainly by the ~~westerlies~~ Westerlies from the Pacific Ocean ~~which cross the Andes and continue as dry winds towards the east~~ (Iriondo, 2000). The atmospheric circulation in Patagonia is dominated by strong meridional pressure gradients that promote strong ~~westerlies~~ Westerlies and high wind speeds throughout the year (Coronato, 1993). ~~These strong westerly winds have a general tendency to form rising air mass capable of lifting dust and aerosols high into the atmosphere .~~ Owing to extreme dryness of the air (with relative humidity as low as

5 %) in the Patagonian region, the ~~westerlies~~ Westerlies pick up large volumes of dust, which rise ~~to~~ up into the atmosphere (Iriondo, 1989). Furthermore, meridional surface winds and subtropical jet stream intensify, resulting in very strong winds that lead to sizeable dust storms (Gaiero et al., 2013) moving towards the south and east. The Reactions (R1)–(R4) show that ~~,~~ under humid conditions, HNO_3 strongly promotes the hydrolysis process. Though the extremely low RH conditions in the Patagonian region might not be adequate for hydrolysis, partial solvation could initially provide a reactive site to HNO_3 (Usher et al., 2003), followed by further reaction enhanced by the increasing RH over the Southern Ocean.

Results from the ionic balance calculations provided more insight into the associations between $nssCa^{2+}$ and NO_3^- in snow (Fig. 3). The ratio of Cl^-/Na^+ and the correlation coefficients (Table 1) indicated that the sea-salt ions were well-preserved throughout PEL and cDML transects. An estimated 70 % of NO_3^- was associated with the $nssCa^{2+}$ as calculated from the ratio of $nssCa^{2+}$ and NO_3^-. However, in the inland region, only an estimated 10 % of NO_3^- was associated with $nssCa^{2+}$ whereas about 53 % of NO_3^- was associated with HNO_3 and the rest with NH_4^+. The $nssCa^{2+}$ associated NO_3^- was ~ 75 % and 55 % in the coastal and inland regions of PEL transect respectively. An estimated 25 % of NO_3^- was associated with HNO_3 in both the coastal and inland sections of PEL. The estimated values of NO_3^- associated with $nssCa^{2+}$ in PEL transect was relatively higher when compared to the cDML transect. This variation is more likely due to the fact that the PEL transect covers 180 km from the open ocean whereas the cDML covers more interior region (300 km).

The results from PCA analysis displayed $nssCa^{2+}$ and NO_3^- strongly grouped within the same factor suggesting neutralisation of calcium-dust by HNO_3 during long-range transport. Such correlations have also been reported in aerosol studies from the interior Dome C region (Udisti et al., 2004), where $nssCa^{2+}$ and NO_3^- association in aerosol was attributed to the processes during long-range transport of air masses rather than to local neutralisation processes. The mountainous region of cDML showed a completely different association of $nssCa^{2+}$ and NO_3^- with the factors. The association of $nssCa^{2+}$ with $nssSO_4^{2-}$ clearly indicate the influence from the exposed mountains in the vicinity. The coastal section of PEL also showed a weak loading of $nssSO_4^{2-}$ along with a strong loading of $nssCa^{2+}$ and NO_3^- in the same factor.

To further verify the possible dust sources, nine-day forward and back trajectories for everyday at 6 hourly interval for austral winter (JJA) and summer (DJF) during 2008–2009 were reconstructed using the NOAA Hysplit Model v.4 (Draxler and Rolph, 2014) in conjunction with the Global Data Assimilation System datasets (Fig. 5). The forward trajectories were calculated from two prominent dust-emitting hotspots in the SSA region (Li et al., 2010), the North Patagonia (44° S, 67° W, NP in Fig. 5) and San Julian's Great Depression (49° S, 69° W, GD in Fig. 5). The back trajectories were calculated from sampling sites representing coastal, mountainous and inland sections of cDML and PEL. A total of 368 trajectories during winter and 360 trajectories for summer at each location were subjected to a statistical treatment, wherein all trajectories were clustered with lower spatial

315 variance. The forward trajectory clusters revealed that both during summer ~~and winter,~~ (NP: 66 %, GD: 80 %) and winter (NP: 48 %, GD: 42 %), dust-laden air parcels generally circulate towards south and east from dust sources. The back trajectory clusters revealed, in line with previous studies (Li et al., 2008, 2010), that the majority of air parcels at 1500 m level invariably arrived from regions that are influenced by the air parcels from SSA region. These air parcels ultimately get incorporated into

320 the Antarctic Circumpolar Vortex (ACV) before mass compensation by anticyclonic polar easterlies in the East Antarctic region (Dixon et al., 2012). Both forward and back trajectory clusters show that dust reaching the East Antarctic region is a blend of SSA dust sources that feed into the ACV.

4.3 Formation of calcium nitrate and its significance for the Antarctic snow chemistry

During its transport from SSA over the Southern Ocean, calcic mineral dust particles readily un-

325 dergo hydrolysis with atmospheric HNO_3 or N_2O_5 as described in the Reactions (R1)–(R4) above. Higher RH levels over the Southern Ocean more likely aid the effortless conversion of $CaCO_3$ to $Ca(NO_3)_2$. Such progressive reactivity of $CaCO_3$ has been observed in laboratory studies (Krueger et al., 2003; Mogili et al., 2006). A simplified schematic diagram depicting the possible mechanism and processes involved in the formation and deposition of $Ca(NO_3)_2$ aerosol is shown in

330 Fig. 6. The initial process involves hydrolysis of HNO_3 on calcium-rich dust particles ~~supported by comparatively~~ from SSA enhanced by relatively higher RH over the Southern Ocean. The anticyclonic polar easterlies sink the air masses reaching the Antarctic atmosphere from the westerly wind belt (Dixon et al., 2012). The airmass containing dust particles upon reaching the Antarctic region, undergoes mass compensation within the easterlies leading to the deposition of aerosols and dust

335 particles to the Antarctic surface (Iriondo, 2000). It is therefore proposed, that the availability of calcic mineral dust from SSA under the influence of westerlies and its reaction with ~~nitrogen oxides~~ atmospheric HNO_3 over the Southern Ocean has facilitated the formation of $Ca(NO_3)_2$ aerosol and this would explain the strong association between $nssCa^{2+}$ and NO_3^- in Antarctic snow. Such a reasoning is also consistent with the poor relationship between $nssCa^{2+}$ and NO_3^- reported from sites

340 in proximity to mountainous regions that provide additional local dust which has not undergone any atmospheric chemical processes.

Interestingly, the present findings have important implications for Antarctic snow chemistry. It is considered that NO_3^- in Antarctica is usually deposited in the form of gaseous HNO_3, scavenged by or temporarily adsorbed on snow crystals (Wagnon et al., 1999) with ~~negligible dry deposition~~

345 significant dry deposition (Davis et al., 2008). Our study implies that apart from gaseous HNO_3 and NO_3^- from Polar Stratospheric Clouds, dust-bound NO_3^- could also constitute a significant amount of NO_3^- deposited in Antarctic snow. Similar Ca^{2+}/NO_3^- association have been observed in deep ice cores from Vostok (Legrand et al., 1999) and Dome C (Röthlisberger et al., 2002), which was attributed to the high amount of dust in atmosphere during Last Glacial Maximum (LGM). Studies

350 by Lunt and Valdes (2001) have shown that the transport efficiency of dust to East Antarctica is

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greater at the present day suggesting that an overall increase in dust transport is more likely. ~~Yet, it remained inconclusive if such reactions occurred in the atmosphere or in the Antarctic snowpack.~~ Röthlisberger et al. (2002) also speculated that such reactions in the atmosphere would result in a widespread Ca^{2+} / NO_3^- association throughout Antarctica. Yet, it remained inconclusive if such reactions occurred in the atmosphere or in the Antarctic snowpack. Our studies suggest that such association could be widespread, provided the dust-bound nitrate reaches the interior plateau of the continent. However, it is important to consider the possible sources of additional input such as $nssCa^{2+}$ from the exposed mountains or $ssCa^{2+}$ from the oceans along the coast in order to statistically detect the association during data analysis. ~~Further, it is known from several studies that gaseous present in the interstitial snow and adsorbed to snow crystals undergo photolytic loss in the presence of sunlight . Volatile loss of have also been documented as a pathway for loss . However, when is bonded with as in , it could prevent the post-depositional loss of from upper snow layers even in low accumulation regions.~~ Such reactions are of ~~huge~~ significance in the Antarctic atmosphere as they have the ability to modify the properties of original aerosols, resulting in modified climate impact, for instance, by variations in light scattering and photochemical activity (Tegen et al., 1997).

5 Conclusions

This study shows a strong and widespread association between nssCa^{2+} and NO_3^- in snow from two different regions in cDML and PEL, that are $> 2000\,km$ apart in East Antarctica. We hypothesise that such a strong association is due to the interaction between calcium-rich mineral dust and ~~nitrogen oxides~~ nitric acid in the atmosphere, resulting in the formation of $Ca(NO_3)_2$ ~~. The~~ aerosol. The results from ionic balance and residual acidity shows that a majority of NO_3^- in the coastal region is associated with nssCa^{2+}, whereas in the inland region NO_3^- was associated with HNO_3. The forward and back trajectory analyses suggest, that fine calcic mineral dust from the ~~SSA~~ Southern South America (SSA) region has been transported to the East Antarctic region, aided by the ~~westerlies. It is proposed~~ Westerlies. Also, the results from principal component analyses further strengthens our view that $Ca(NO_3)_2$ was formed in the atmosphere ~~over the Southern Ocean~~ during the transport of mineral dust from SSA to the East Antarctic region. The $Ca(NO_3)_2$ aerosol thus formed, is deposited over Antarctica under the influence of anticyclonic polar easterlies. Our study also shows that local input of dust and sea-spray is more likely to mask the association between nssCa^{2+} and NO_3^- . We ~~suggest~~propose, that apart from other significant NO_3^- sources, NO_3^- associated with mineral dust could form a significant portion of total NO_3^- deposited in the East Antarctic snow. We also suggest that such association between Ca^{2+} / NO_3^- could be widespread ~~and the formation may possibly reduce the post-depositional loss in low accumulation regions~~ but may not be observed clearly when study regions are close to the coast or when additional dust is contributed by local crustal sources.

385   *Author contributions.*   Both authors contributed equally to the work presented in this paper. K. Mahalinganathan collected samples, analysed data and wrote the paper. M. Thamban analysed data and wrote the paper.

References

Al-Abadleh, H. A., Krueger, B. J., Ross, J. L., and Grassian, V. H.: Phase transitions in calcium nitrate thin
395   films, Chem. Commun., 22, 2796–2797, doi:10.1039/B308632A, 2003.

Albani, S., Mahowald, N. M., Delmonte, B., Maggi, V., and Winckler, G.: Comparing modeled and observed
changes in mineral dust transport and deposition to Antarctica between the Last Glacial Maximum and
current climates, Clim. Dynam., 38, 1731–1755, doi:10.1007/s00382-011-1139-5, 2012.

Antony, R., Thamban, M., Krishnan, K. P., and Mahalinganathan, K.: Is cloud seeding in coastal Antarc-
400   tica linked to bromine and nitrate variability in snow?, Environ. Res. Lett., 5, 014009, doi:10.1088/1748-
9326/5/1/014009, 2010.

Basile-Doelsch, I., Grousset, F. E., Revel, M., Petit, J. R., Biscaye, P. E., and Barkov, N. I.: Patagonian origin of
glacial dust deposited in East Antarctica (Vostok and Dome C) during glacial stages 2, 4 and 6, Earth Planet.
Sc. Lett., 146, 573–589, doi:10.1016/S0012-821X(96)00255-5, 1997.

405   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,
11243–22256, doi:10.5194/acp-15-11243-2015, 2015.

Bertler, N., Mayewski, P. A., Aristarain, A., Barrett, P., Becagli, S., Bernardo, R., Bo, S., Xiao, C., Curran, M.,
Qin, D., Dixon, D. A., Ferron, F., Fischer, H., Frey, M., Frezzotti, M., Fundel, F., Genthon, C., Gragnani, R.,
410   Hamilton, G. S., Handley, M., Hong, S., Isaksson, E., Kang, J., Ren, J., Kamiyama, K., Kanamori, S.,
Kärkäs, E., Karlöf, L., Kaspari, S., Kreutz, K., Kurbatov, A., Meyerson, E., Ming, Y., Zhang, M., Mo-
toyama, H., Mulvaney, R., Oerter, H., Osterberg, E., Proposito, M., Pyne, A., Ruth, U., Simões, J., Smith, B.,
Sneed, S., Teinilä, K., Traufetter, F., Udisti, R., Virkkula, A., Watanabe, O., Williamson, B., Winther, J.-G.,
Li, Y., Wolff, E. W., Li, Z., and Zielinski, A.: Snow chemistry across Antarctica, Ann. Glaciol., 41, 167–179,
415   doi:10.3189/172756405781813320, 2005.

Bory, A., Wolff, E. W., Mulvaney, R., Jagoutz, E., Wegner, A., Ruth, U., and Elderfield, H.: Multiple sources
supply eolian mineral dust to the Atlantic sector of coastal Antarctica: evidence from recent snow layers at
the top of Berkner Island ice sheet, Earth Planet. Sc. Lett., 291, 138–148, doi:10.1016/j.epsl.2010.01.006,
2010.

420   Boutron, C. and Martin, S.: Sources of twelve trace metals in Antarctic snows determined by principal compo-
nent analysis, J. Geophys. Res.-Oceans, 85, 5631–5638, doi:10.1029/JC085iC10p05631, 1980.

Brasseur, G. and Solomon, S.: Composition and chemistry, in: Aeronomy of the Middle Atmosphere, Atmo-
spheric and Oceanographic Sciences Library, Springer, the Netherlands, 1986.

Burkhart, J. F., Hutterli, M., Bales, R. C., and McConnell, J. R.: Seasonal accumulation timing and preservation
425   of nitrate in firn at Summit, Greenland, J. Geophys. Res.-Atmos., 109, D19302, doi:10.1029/2004JD004658,
2004.

Coronato, F. R.: Wind chill factor applied to Patagonian climatology, Int. J. Biometeorol., 37, 1–6,
doi:10.1007/BF01212759, 1993.

Dahe, Q., Zeller, E. J., and Dreschhoff, G. A. M.: The distribution of nitrate content in the surface snow of the
430   Antarctic Ice Sheet along the route of the 1990 International Trans-Antarctica Expedition, J. Geophys. Res.,
97, 6277–6284, doi:10.1029/92JA00142, 1992.

14

Davis, D. D., Seeling, J., Huey, G., Crawford, J., Chen, G., Wang, Y., Buhr, M., Helmig, D., Neff, W., Blake, D., Arimoto, R., and Eisele, F.: A reassessment of Antarctic plateau reactive nitrogen based on {ANTCI} 2003 airborne and ground based measurements, Atmos. Environ., 42, 2831–2848, doi:10.1016/j.atmosenv.2007.07.039, 2008.

435

Delmonte, B., Basile-Doelsch, I., Petit, J.-R., Maggi, V., Revel-Rolland, M., Michard, A., Jagoutz, E., and Grousset, F.: Comparing the Epica and Vostok dust records during the last 220,000 years: stratigraphical correlation and provenance in glacial periods, Earth-Sci. Rev., 66, 63–87, doi:10.1016/j.earscirev.2003.10.004, 2004.

440 Dieckmann, G. S., Nehrke, G., Papadimitriou, S., Göttlicher, J., Steininger, R., Kennedy, H., Wolf-Gladow, D., and Thomas, D. N.: Calcium carbonate as ikaite crystals in Antarctic sea ice, Geophys. Res. Lett., 35, L08501, doi:10.1029/2008GL033540, 2008.

Dixon, D. A., Mayewski, P. A., Goodwin, I. D., Marshall, G. J., Freeman, R., Maasch, K. A., and Sneed, S. B.: An ice-core proxy for northerly air mass incursions into West Antarctica, Int. J. Climatol., 32, 1455–1465,

445 doi:10.1002/joc.2371, 2012.

Draxler, R. and Rolph, G.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php), NOAA Air Resources Laboratory, College Park, MD, available at: http://ready.arl.noaa.gov/HYSPLIT_ash.php (last access: April 2015), 2014.

450 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, doi: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

455 on the East Antarctic Plateau – Part 2: An isotopic model for the interpretation of deep ice-core records, 15, 12079–12113, doi:10.5194/acp-15-12079-2015, 2015.

Fairlie, T. D., Jacob, D. J., Dibb, J. E., Alexander, B., Avery, M. A., van Donkelaar, A., and Zhang, L.: Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes, Atmos. Chem. Phys., 10, 3999–4012, doi:10.5194/acp-10-3999-2010, 2010.

460 Gaiero, D. M.: Dust provenance in Antarctic ice during glacial periods: from where in southern South America?, Geophys. Res. Lett., 34, L17707, doi:10.1029/2007GL030520, 2007.

Gaiero, D. M., Simonella, L., Gassó, S., Gili, S., Stein, A. F., Sosa, P., Becchio, R., Arce, J., and Marelli, H.: Ground/satellite observations and atmospheric modeling of dust storms originating in the high Puna-Altiplano deserts (South America): implications for the interpretation of paleoclimatic archives, J. Geophys.

465 Res.-Atmos., 118, 3817–3831, doi:10.1002/jgrd.50036, 2013.

Gassó, S., Stein, A., Marino, F., Castellano, E., Udisti, R., and Ceratto, J.: A combined observational and modeling approach to study modern dust transport from the Patagonia desert to East Antarctica, Atmos. Chem. Phys., 10, 8287–8303, doi:10.5194/acp-10-8287-2010, 2010.

Gibson, E. R., Hudson, P. K., and Grassian, V. H.: Physicochemical properties of nitrate aerosols: Implications

470 for the atmosphere, J. Phys. Chem. A, 110, 11785–11799, doi:10.1021/jp063821k, 2006.

Goodman, A. L., Underwood, G. M., Grassian, V. H.: A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles, J. Geophys. Res.-Atmos., 105, 29053–29064, doi:10.1029/2000JD900396, 2000.

Iizuka, Y., Takata, M., Hondoh, T., and Fujii, Y.: High-time-resolution profiles of soluble ions in the last glacial
475   period of a Dome Fuji (Antarctica) deep ice core, 39, 452–456, doi:10.3189/172756404781814302, 2004.

Iriondo, M.: Quaternary lakes of Argentina, Palaeogeogr. Palaeocl., 70, 81–88, doi:10.1016/0031-0182(89)90081-3, 1989.

Iriondo, M.: Patagonian dust in Antarctica, Quatern. Int., 68–71, 83–86, doi:10.1016/S1040-6182(00)00035-5, 2000.

480   Jones, A. E., Weller, R., Wolff, E. W., and Jacobi, H.-W.: Speciation and rate of photochemical NO and NO_2 production in Antarctic snow, Geophys. Res. Lett., 27, 345–348, doi:10.1029/1999GL010885, 2000.

Jordan, C. E., Dibb, J. E., Anderson, B. E., and Fuelberg, H. E.: Uptake of nitrate and sulfate on dust aerosols during TRACE-P, J. Geophys. Res., 108, 8817, doi:10.1029/2002JD003101, 2003.

Krueger, B. J., Grassian, V. H., Laskin, A., and Cowin, J. P.: The transformation of solid atmospheric particles
485   into liquid droplets through heterogeneous chemistry: laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, Geophys. Res. Lett., 30, 1148, doi:10.1029/2002GL016563, 2003.

Krueger, B. J., Grassian, V. H., Cowin, J. P., and Laskin, A.: Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy, Atmos. Environ., 38,
490   6253–6261, doi:10.1016/j.atmosenv.2004.07.010, 2004.

Lambert, F., Delmonte, B., Petit, J. R., Bigler, M., Kaufmann, P. R., Hutterli, M. A., Stocker, T. F., Ruth, U., Steffensen, J. P., and Maggi, V.: Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core, Nature, 452, 616–619, doi:10.1038/nature06763, 2008.

Laskin, A., Wietsma, T. W., Krueger, B. J., and Grassian, V. H.: Heterogeneous chemistry of individual mineral
495   dust particles with nitric acid: a combined CCSEM/EDX, ESEM, and ICP-MS study, J. Geophys. Res., 110, D10208, doi:10.1029/2004JD005206, 2005.

Lee, H.-M., Henze, D. K., Alexander, B., and Murray, L. T.: Investigating the sensitivity of surface-level nitrate seasonality in Antarctica to primary sources using a global model, Atmos. Environ., 89, 757–767, doi:10.1016/j.atmosenv.2014.03.003, 2014.

500   Legrand, M. R. and Delmas, R. J.: Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow, Tellus B, 38, 236–249, doi:10.1111/j.1600-0889.1986.tb00190.x, 1986.

Legrand, M. R. and Kirchner, S.: Origins and variations of nitrate in south polar precipitation, J. Geophys. Res., 95, 3493–3507, doi:, 1990.

Legrand, M. R. and Mayewski, P. A.: Glaciochemistry of polar ice cores: a review, Rev. Geophys., 35, 219–243,
505   doi:10.1029/96RG03527, 1997.

Legrand, M. R., Wolff, E. W., and Wagenbach, D.: Antarctic aerosol and snowfall chemistry: Implications for deep Antarctic ice-core chemistry, Ann. Glaciol., 29, 66–72, doi:10.3189/172756499781821094, 1999.

Li, F., Ginoux, P., and Ramaswamy, V.: Distribution, transport, and deposition of mineral dust in the Southern Ocean and Antarctica: contribution of major sources, J. Geophys. Res., 113, D10207,
510   doi:10.1029/2007JD009190, 2008.

Li, F., Ginoux, P., and Ramaswamy, V.: Transport of Patagonian dust to Antarctica, J. Geophys. Res., 115, D18217, doi:10.1029/2009JD012356, 2010.

Lunt, D. J. and Valdes, P. J.: Dust transport to Dome C, Antarctica, at the Last Glacial Maximum and present day, Geophys. Res. Lett., 28, 295–298, doi:10.1029/2000GL012170, 2001.

515 Mahalinganathan, K., Thamban, M., Laluraj, C. M., and Redkar, B. L.: Relation between surface topography and sea-salt snow chemistry from Princess Elizabeth Land, East Antarctica, The Cryosphere, 6, 505–515, doi:10.5194/tc-6-505-2012, 2012.

Mahowald, N. M., Albani, S., Kok, J. F., Engelstaeder, S., Scanza, R., Ward, D. S., and Flanner, M. G.: The size distribution of desert dust aerosols and its impact on the Earth system, Aeolian Res., 15, 53–71,

520   doi:10.1016/j.aeolia.2013.09.002, 2013.

Michalski, G., Bockheim, J. G., Kendall, C., and Thiemens, M.: Isotopic composition of Antarctic Dry Valley nitrate: implications for NO_y sources and cycling in Antarctica, Geophys. Res. Lett., 32, L13817, doi:10.1029/2004GL022121, 2005.

Mogili, P. K., Kleiber, P. D., Young, M. A., and Grassian, V. H.: Heterogeneous uptake of ozone on reactive

525   components of mineral dust aerosol: an environmental aerosol reaction chamber study, J. Phys. Chem. A, 110, 13799–13807, doi:10.1021/jp063620g, 2006.

Muhs, D. R., and Zárate, M.: Late quaternary eolian records of the Americas and their paleoclimatic significance, in: Interhemispheric Climate Linkages, edited by: Markgraf, V., Academic Press, San Diego, CA, 183–216, doi:10.1016/B978-012472670-3/50015-X, 2001.

530 ~~Mulvaney, R., Wagenbach, D., and Wolff, E. W.: Postdepositional change in snowpack nitrate from observation of year-round near-surface snow in coastal Antarctica, J. Geophys. Res., 103, 11021–11031, doi:, 1998.~~

Nousiainen, T. and Kandler, K.: Light scattering by atmospheric mineral dust particles, in: Light Scattering Reviews 9, edited by: Kokhanovsky, A. A., Springer Praxis Books, Springer, Berlin, Heidelberg, 3–52,

535   doi:10.1007/978-3-642-37985-7_1, 2015.

Pye, K.: Chapter six – Grain size, mineralogy and chemical composition of aeolian dust, in: Aeolian Dust and Dust Deposits, edited by: Pye, K., Academic Press Inc. Ltd, London, 118–141, doi:10.1016/B978-0-12-568690-7.50010-7, 1987.

Revel-Rolland, M., De Deckker, P., Delmonte, B., Hesse, P. P., Magee, J. W., Basile-Doelsch, I., Grousset, F.,

540   and Bosch, D.: Eastern Australia: a possible source of dust in East Antarctica interglacial ice, Earth Planet. Sc. Lett., 249, 1–13, doi:10.1016/j.epsl.2006.06.028, 2006.

Röthlisberger, R., Hutterli, M. A., Sommer, S., Wolff, E. W., and Mulvaney, R.: Factors controlling nitrate in ice cores: evidence from the Dome C deep ice core, J. Geophys. Res., 105, 20565–20572, doi:10.1029/2000JD900264, 2000.

545 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, doi:10.3189/172756402781817220, 2002.

17

Röthlisberger, R., Mulvaney, R., Wolff, E. W., Hutterli, M. A., Bigler, M., Sommer, S., and Jouzel, J.: Dust and

550   sea salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications for southern
       high-latitude climate, Geophys. Res. Lett., 29, doi:10.1029/2002GL015186, 2002.

Ruth, U., Barbante, C., Bigler, M., Delmonte, B., Fischer, H., Gabrielli, P., Gaspari, V., Kaufmann, P., Lam-
       bert, F., Maggi, V., Marino, F., Petit, J.-R., Udisti, R., Wagenbach, D., Wegner, A., and Wolff, E. W.: Proxies
       and measurement techniques for mineral dust in Antarctic ice cores, Environ. Sci. Technol., 42, 5675–5681,

555   doi:10.1021/es703078z, 2008.

Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic con-
       straints on the origin of atmospheric nitrate in coastal Antarctica, Atmos. Chem. Phys., 7, 1925–1945,
       doi:10.5194/acp-7-1925-2007, 2007.

Schüpbach, S., Federer, U., Kaufmann, P. R., Albani, S., Barbante, C., Stocker, T. F., and Fischer, H.: High-

560   resolution mineral dust and sea ice proxy records from the Talos Dome ice core, Clim. Past, 9, 2789–2807,
       doi:10.5194/cp-9-2789-2013, 2013.

Shi, G., Buffen, A. M., Hastings, M. G., Li, C., Ma, H., Li, Y., Sun, B., An, C., and Jiang, S.: Investigation
       of post-depositional processing of nitrate in East Antarctic snow: isotopic constraints on photolytic loss,
       re-oxidation, and source inputs, Atmos. Chem. Phys., 15, 9435–9453, doi:10.5194/acp-15-9435-2015, 2015.

565 Sommer, S., Wagenbach, D., Mulvaney, R., and Fischer, H.: Glacio-chemical study spanning the past 2 kyr on
       three ice cores from Dronning Maud Land, Antarctica: 2. Seasonally resolved chemical records, J. Geophys.
       Res., 105, 29423–29433, doi:10.1029/2000JD900450, 2000.

Stenberg, M., Isaksson, E., Hansson, M., Karlén, W., Mayewski, P. A., Twickler, M. S., Whitlow, S. I., and
       Gundestrup, N.: Spatial variability of snow chemistry in western Dronning Maud Land, Antarctica, Ann.

570   Glaciol., 27, 378–384, 1998.

Tegen, I. and Lacis, A. A.: Modeling of particle size distribution and its influence on the radiative properties of
       mineral dust aerosol, J. Geophys. Res., 101, 19237–19244, doi:10.1029/95JD03610, 1996.

Tegen, I., Hollrig, P., Chin, M., Fung, I., Jacob, D., and Penner, J.: Contribution of different aerosol species to
       the global aerosol extinction optical thickness: estimates from model results, J. Geophys. Res., 102, 23895–

575   23915, doi:10.1029/97JD01864, 1997.

Traversi, R., Udisti, R., Frosini, D., Becagli, S., Ciardini, V., Funke, B., Lanconelli, C., Petkov, B., Scarchilli, C.,
       Severi, M., and Vitale, V.: Insights on nitrate sources at Dome C (East Antarctic Plateau) from multi-year
       aerosol and snow records, Tellus B, 66, 22550, doi:10.3402/tellusb.v66.22550, 2014.

Udisti, R., Becagli, S., Benassai, S., Castellano, E., Fattori, I., Innocenti, M., and Migliori, A., and Traversi, R.:

580   Atmosphere–snow interaction by a comparison between aerosol and uppermost snow-layers composition at
       Dome C, East Antarctica, Ann. Glaciol., 39, 53–61, doi:10.3189/172756404781814474, 2004.

Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, Chem. Rev., 103, 4883–4939,
       doi:10.1021/cr020657y, 2003.

Wagenbach, D., Legrand, M. R., Fischer, H., Pichlmayer, F., and Wolff, E. W.: Atmospheric near-surface nitrate

585   at coastal Antarctic sites, J. Geophys. Res., 103, 11007–11020, doi:10.1029/97JD03364, 1998.

Wagnon, P., Delmas, R. J., and Legrand, M. R.: Loss of volatile acid species from upper firn layers at Vostok,
       Antarctica, J. Geophys. Res., 104, 3423–3431, doi:10.1029/98JD02855, 1999.

Weller, R.: Postdepositional losses of methane sulfonate, nitrate, and chloride at the European Project for Ice Coring in Antarctica deep-drilling site in Dronning Maud Land, Antarctica, J. Geophys. Res., 109, D07301, doi:10.1029/2003JD004189, 2004.

590

Weller, R., Jones, A. E., Wille, A., Jacobi, H.-W., McIntyre, H. P., Sturges, W. T., Huke, M., and Wagenbach, D.: Seasonality of reactive nitrogen oxides (NO_y) at Neumayer Station, Antarctica, J. Geophys. Res., 107, 4673, doi:10.1029/2002JD002495, 2002.

Weller, R., Wagenbach, D., Legrand, M. R., Elsässer, C., Tian-Kunze, X., and König-Langlo, G.: Continuous

595 25-yr aerosol records at coastal Antarctica – I: inter-annual variability of ionic compounds and links to climate indices, Tellus B, 63, 901–919, doi:10.1111/j.1600-0889.2011.00542.x, 2011.

Wolff, E. W.: Nitrate in Polar Ice, in: Ice Core Studies of Global Biogeochemical Cycles, vol. 30 of NATO ASI Series, edited by: Delmas, R., Springer, Berlin, Heidelberg, 195–224, doi:10.1007/978-3-642-51172-1_10, 1995.

600 Wolff, E. W.: Ice sheets and nitrogen, Philos. T. Roy. Soc. B, 368, 20130127, doi:10.1098/rstb.2013.0127, 2013.

Zárate, M. A.: Loess of southern South America, Quaternary Sci. Rev., 22, 1987–2006, doi:10.1016/S0277-3791(03)00165-3, 2003.
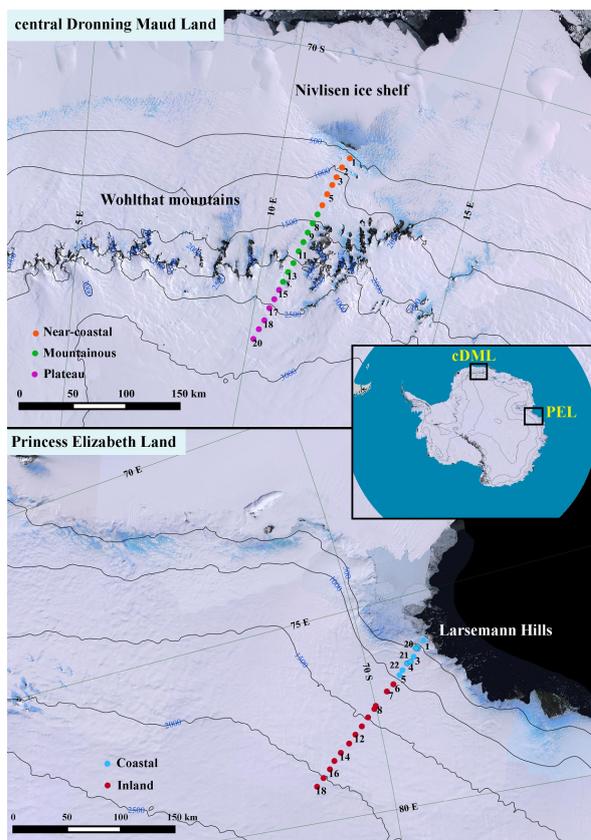
Figure 1. Study region showing sampling locations along transects in central Dronning Maud Land (top panel) and Princess Elizabeth Land (bottom panel), East Antarctica. Colour coded sampling locations indicate different topographic sections. Inset shows the study area highlighted in Antarctica. Maps were created using LANDSAT Mosaic using QGIS Wien (v.2.8) in conjunction with Quantarctica project.
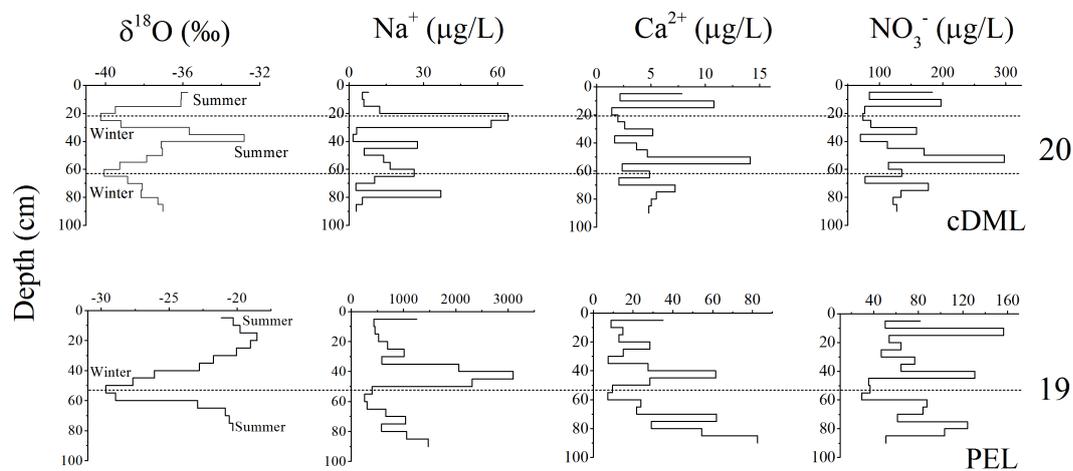
Figure 2. Oxygen isotope ratios and major ions showing seasonality in representative snow cores from inland (cDML, core 20) and coast (PEL, core 19). The dotted lines represent winter maxima in the cores.
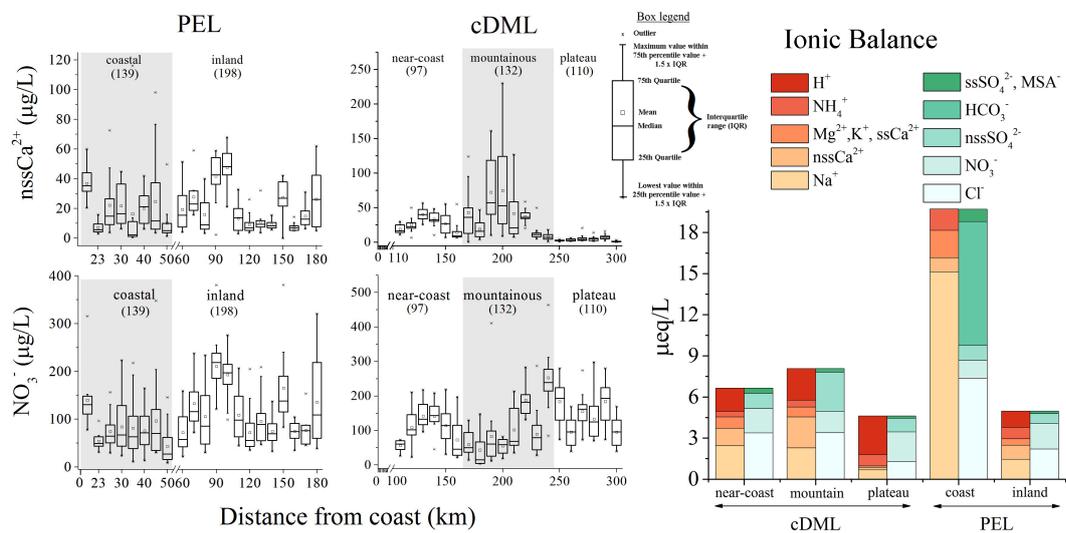
Figure 3. Distribution of nssCa^{2+} and NO$_3^-$ concentrations in snow cores along PEL and cDML transects. The ~~values in circles in plots shows . The~~ numbers inside brackets indicate the total number of samples in respective sections. The balance of ions from all regions are denoted on right panel.
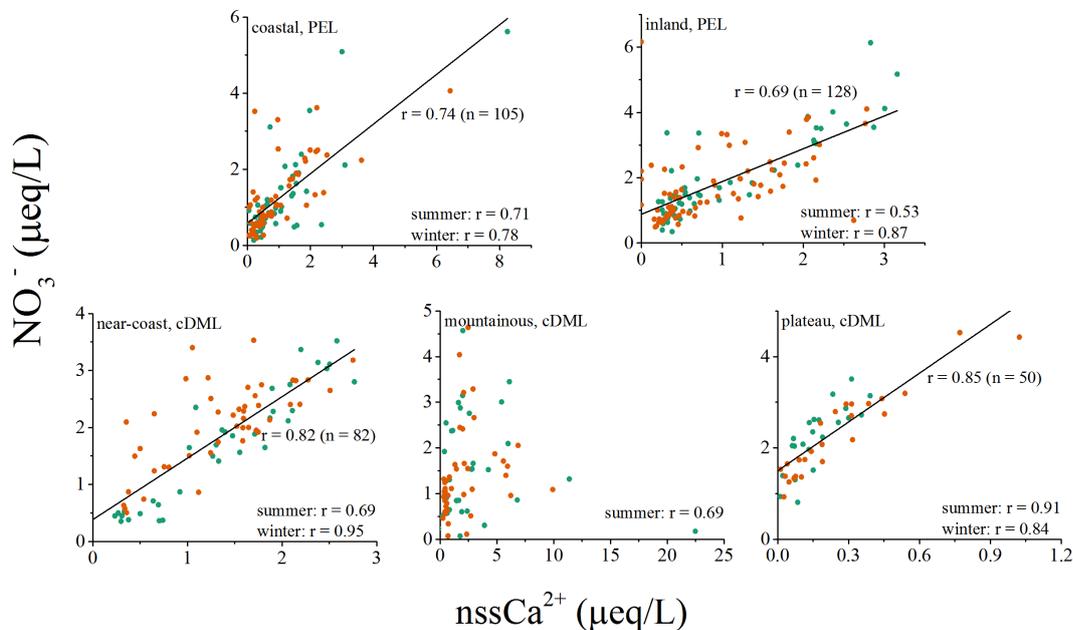
Figure 4. Correlation between nssCa^{2+} and NO$_3^-$ during austral summer (~~green~~brown) and winter (~~pink~~green) in the study regions in cDML and PEL. Samples representing 1 complete year are plotted here to show the seasonal differences. The samples from coastal and inland sections in both cDML and PEL showed a strong association while the mountainous section in cDML transect showed weak association only during summer.

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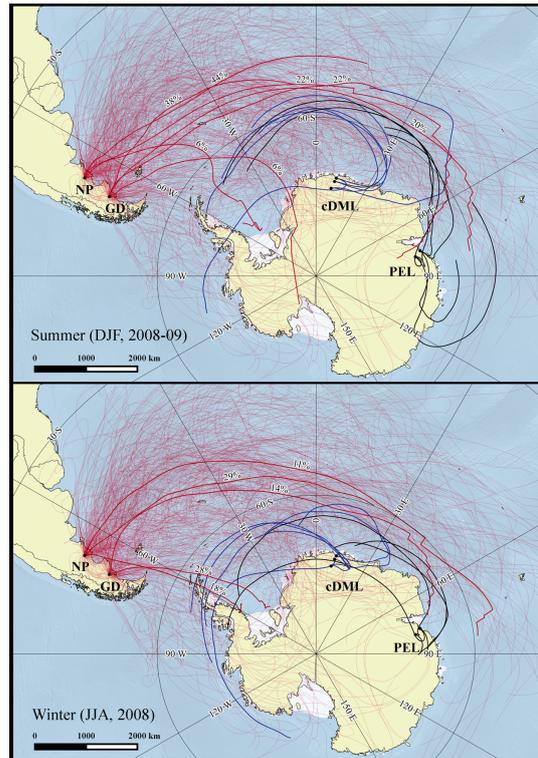
Figure 5. ~~Nine days forward~~ Forward and back trajectory analyses for 9 days using HYSPLIT Model v.4 in conjunction with GDAS dataset. The forward trajectories (red) were calculated from North Patagonia (NP) and San Julian's Great Depression (GD), and the back trajectories (blue, black) were reconstructed from cDML and PEL. The cloud of thin red lines indicate clusters of 6 hourly forward trajectories while the thick red lines show the cluster average. The thick blue and black lines from cDML and PEL region respectively, indicate the cluster average of back trajectories calculated during the same time period.
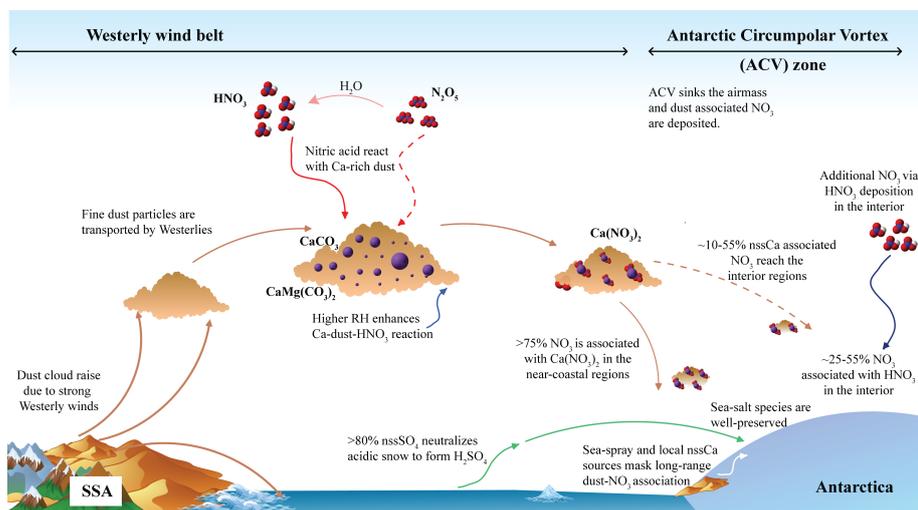
Figure 6. Schematic diagram depicting possible processes and chemical reactions involved during the mineral dust transport from Southern South America (SSA) before depositing over Antarctic ice sheet. The estimates of NO_3^- associated with nssCa^{2+} and HNO_3 are based on data from this study.

Table 1. Correlation coefficients of NO_3^- and $nssCa^{2+}$ with other major ions at 99 % significance.

	cDML			PEL	
	near-coastal	mountainous	plateau	coastal	inland
			NO_3^-		
Na^+	-	-	-0.56**	-	-
K^+	-	0.58*	-0.33	-	0.42**
Mg^{2+}	-	0.41*	-	-	-
$nssCa^{2+}$	0.82	0.69*	0.85	0.74	0.69
NH_4^+	0.57**	0.54**	-	-	-
			$nssCa^{2+}$		
Cl^-	-	0.75**	-	-	-
$nssSO_4^{2-}$	-	0.92	-	0.49	-

Correlations only during *summer and **winter.

Table 2. PCA results for samples from all sampling regions. Factor loadings above 0.5 are highlighted.

	cDML									PEL					
	near-coastal			mountainous			plateau			coastal			inland		
Factors	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3
Na^+	**0.98**	0.05	0.15	**0.96**	0.07	0.11	0.31	-0.20	**0.87**	**0.91**	0.17	0.08	**0.96**	0.04	0.03
Cl^-	**0.95**	-0.05	0.14	**0.94**	0.07	0.16	0.67	-0.25	**0.51**	**0.70**	0.30	0.21	**0.93**	-0.01	0.17
Mg^{2+}	**0.97**	0.01	0.14	**0.82**	-0.09	0.4	0.37	0.09	**0.81**	**0.81**	0.4	0.09	**0.88**	-0.04	0.14
K^+	**0.63**	0.44	0.23	**0.76**	0.26	0.43	0.19	0.1	**0.86**	**0.83**	0.39	0.09	**0.73**	0.23	-0.04
Ca^{2+}	0.11	**0.96**	0.05	0.26	-0.01	**0.91**	0.09	**0.91**	0.16	0.38	**0.87**	-0.02	0.09	**0.96**	-0.02
$nssCa^{2+}$	0.01	**0.97**	0.11	0.28	-0.09	**0.91**	0.03	**0.94**	0.01	0.19	**0.90**	-0.03	0.02	**0.97**	-0.02
NO_3^-	-0.2	**0.83**	0.19	-0.09	**0.77**	0.01	0.01	**0.95**	-0.05	-0.07	**0.80**	0.27	-0.05	**0.90**	0.23
NH_4^+	0.17	**0.75**	0.29	0.21	**0.70**	-0.03	-0.1	0.44	**0.77**	**0.67**	-0.22	0.21	0.21	0.18	-0.03
SO_4^{2-}	0.41	0.1	**0.88**	0.38	**0.64**	**0.54**	**0.94**	0.07	0.24	**0.56**	0.27	**0.67**	0.28	-0.05	**0.90**
$nssSO_4^{2-}$	0.2	0.23	**0.93**	0.26	**0.64**	**0.58**	**0.95**	0.16	0.11	-0.18	0.05	**0.75**	-0.08	0.05	**0.93**
MSA^-	-0.11	0.12	**0.89**	0.11	0.21	**0.55**	**0.76**	-0.08	0.22	0.34	-0.08	**0.73**	0.38	0.01	-0.13
H^+	0.29	0.08	**0.71**	-0.05	**0.76**	-0.3	**0.63**	**0.62**	0.03	-0.36	0.17	0.44	0.14	0.24	**0.79**
HCO_3^-	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	**0.77**	-0.10	-0.20	n.a	n.a	n.a