

Editor's comments:

Dear Authors,

Thank you for the thoroughly revised version of your paper. Both Reviewers and I appreciate the extra work done to bring your paper up to TC standards. Both Reviewers nevertheless recommend minor changes before publication. Please pay attention to their recommendations and submit a revised version. It is particularly important that you better explain why you think nitric acid neutralization takes place during long range transport and not locally. Apparently, your arguments did not fully convince Reviewer 1. You may want to elaborate on your statement lines 168-170: "Interestingly, nssCa²⁺ derived from crustal sources and NO₃, 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(NO₃)₂ aerosol." I tend to agree with the reviewer that such arguments are not entirely convincing. Perhaps they just need to be better explained.

Likewise, when you write lines 297-300: "the results from PCA analysis displayed nssCa²⁺ and NO₃ strongly grouped within the same factor suggesting neutralisation of calcium-dust by HNO₃ during long-range transport.", I understand that the Reviewer would require more convincing arguments.

In summary, please revise your paper according to the recommendation. I will then evaluate your changes, most likely without further review, and make a decision from there.

One minor change:

Figure 4: please add a caption box explaining colors.

20 Response to the Editor

Dear Editor,

We thank you for reviewing the revised version of the manuscript. We have included an important point to explain why we think that the neutralization takes place during the long range transport and not in the boundary layer. The caption box is included for Figure 4 as you have suggested. We have also included point by point responses to Referee#2 along with a list of relevant changes in the revised manuscript.

Response to Referee#1

Reviewer's Comment: I thank the authors for having incorporated our suggestions. However, I still don't really see where it is demonstrated that the neutralization reaction mainly occurs during the long range transport. Correlation, PCA, ionic balance etc clearly show a Ca/NO₃ association, even across different regions of Antarctica. These are facts and not questionable but I don't see clearly how from these arguments or observations the authors can argue that this association happens mainly during the long range transport of the dust. If the neutralization is happening within the boundary layer or just above the snow, the observations, PCA etc will show exactly the same correlation, so the association of Ca with NO₃ is not a discriminating factor to argue in one or the other directions. However I might have missed something in their argumentation. If the authors can clarify what observations really can discriminate between a local or long range transport neutralization, it will definitely make their conclusion and fig 6 stronger. Therefore I encourage the authors to clearly state why the PCA/ ionic balance or any other observations favor their hypothesis. In absence of such argumentation, they should leave open the scenario where CaCO₃ meet HNO₃ in the BL where large amounts of HNO₃ are formed from NO_x snow emissions.

Authors' Response: We thank you for reviewing our revised manuscript and providing valuable comments. The atmospheric boundary layer above the Antarctic ice sheet lies very low (only up to a few tens of meters above the ground level in coastal Antarctica) and even though it is possible for such neutralization in this layer, there may not be enough time for such reaction before depositing in snow. While we don't completely negate a minor contribution by the processes within the boundary layer, we believe that the dominant process would be during the long range transportation from Southern South America to east Antarctica. Also, the moisture content (which enhances the reaction between Ca dust and HNO₃) in the Antarctic atmosphere varies widely and reduces significantly with decreasing temperatures land inwards. As a result, it is highly unlikely to observe a uniform pattern (of such association between NO₃ and Ca) as demonstrated by this study, had such reactions occurred in the boundary layer. We have modified the manuscript accordingly for clarity.

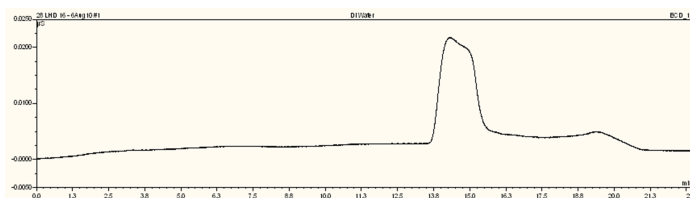
List of all relevant Changes

Page 5, Line 160: deleted "long range transport and"
Page 9, Line 279–287: Inserted new sentences to explain the neutralization processes during long range transport instead of the boundary layer
Page 20, Figure 4: Included a caption box as suggested by the editor

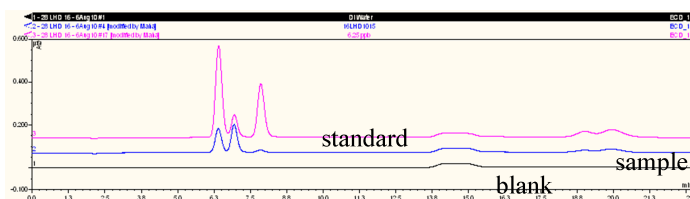
60 **Response to Referee#2**

Reviewer's Comment (RC): I'm not yet convinced about ion chromatography detection limits (DL) for calcium and nitrate. Authors say that a 1000 ul loop was used for anions (i.e., nitrate) and a 100 ul loop for cations (i.e., calcium) determination. It seems to be unusual that the calcium DL (0.3 ug/l) is one order of magnitude lower than the nitrate DL (5 ug/l), although an injection volume ten times lower is used. Authors are requested to check their analytical procedures and the method performance.

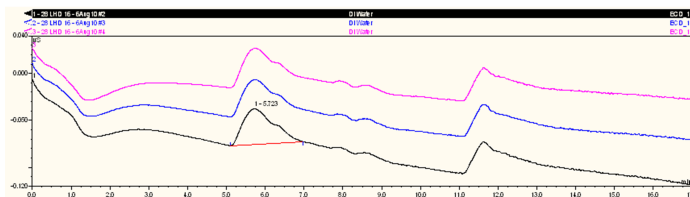
Authors' Response (AR): It is to be noted that two separate instruments were used for cation and anion analyses. The Dionex DX2500 (Cations) system is fitted with Trace Cation concentrator Column (TCC-LP1) while the ICS2000 (Anions) system is fitted with Trace Anion Concentrator column (TAC-2) both of which concentrates the ion components into the analytical columns and lowers the detection limits by an order of 2 - 5 magnitude. The background noise level of the cation system (DX2500) was very low (in the order of 0.00001 μ S) which helped in achieving good results for the cation components. However, due to a relatively higher noise level (in the order of 0.02 μ S) of the anion system (ICS2000) a larger injection loop (1000 μ L) was used in order to safely determine the components. Also, the detection limit of NO_3 (5 $\mu\text{g/L}$) was higher since the background noise level of the instrument was higher. An actual chromatogram from the analyses is given below to show the differences in the background noise levels between these two systems.



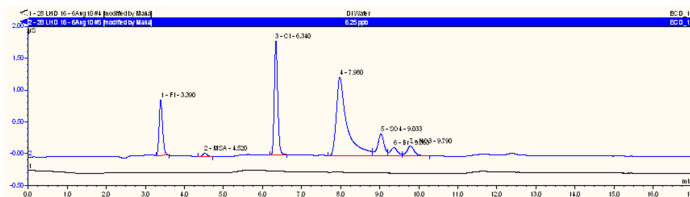
Cation (DX2500) Blank Run



An overlay of blank, standard and sample



An overlay of blank runs in the anion system (ICS2000)

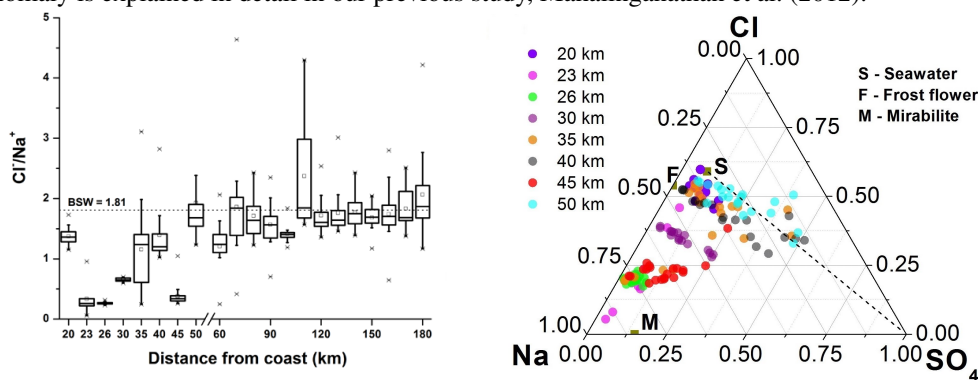


An overlay of blank and standard runs of anions

80

RC: The ionic balance of the coastal part of the PEL transect (Coast PEL) shown in figure 3 is quite surprising. Cations are not balanced by the measured anions and a too large contribution of HCO_3^- (around 50 % of the anion equivalents) is used to balance the ion content. The use of H^+ and HCO_3^- to balance the excess of anion and cation, respectively, is a correct approach. A large anion excess can be justify by the dominance of acidic species, such as H_2SO_4 and HNO_3 (and so, balanced by H^+). On the contrary, a large cations excess is not usual in Antarctica, especially in coastal areas, where aerosol and snow are almost neutralized (at least in winter depositions) or acidic (in summer depositions). The anion lack could be due to problems in evaluating the nss-sulphate or, especially, the chloride contributions. Indeed, the mean nss-sulphate concentration seems to be quite low, while the chloride concentration is surely under-evaluated, with respect to the Na content. In coastal areas, the Na/Cl Eq/Eq ratio is close to 1, because of the proximity of the sea spray source. Instead, in the ionic balance shown in figure 3, the chloride concentration is about one half of the Na concentration. On the other hand, Authors could have over-estimated the Na concentration. Authors are requested to check their calculations or explain this anomaly.

AR: We agree that the Cl/Na ratio in snow is expected to be close to sea-water ratio in the coastal regions. However, our previous study has shown that in coast section of PEL, high Na concentrations in snow occur when the Na is derived from fractionated sea-ice surface (frost flowers / mirabilite) instead of sea-water. We have explained this anomaly from the same cores which showed that the Cl/Na ratios in PEL coast are much lower in comparison with the sea-water as shown in the box plot below (Mahalinganathan et al., 2012). The ternary plot from the above mentioned study is included for easy reference below which also showed that sulphate is depleted due to fractionated sources. This anomaly is explained in detail in our previous study, Mahalinganathan et al. (2012).



RC: A minor question: in several parts of the manuscript (and figure 6), the Authors report: “NO₃- is associated with HNO₃” or “... with Ca(NO₃)₂”. This is not correct and should be changed in “... with H⁺ (to give HNO₃)” or “... with nssCa²⁺ (to give Ca(NO₃)₂)”, or simply: NO₃- is present as HNO₃ or as Ca(NO₃)₂.

AR: We concur. The changes have been included in the revised manuscript.

110 References

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.

List of all relevant Changes

- 115 Page 1, Line 23: Included "associated with Ca^{2+} (to give $\text{Ca}(\text{NO}_3)_2$)"
Page 1, Line 24: Changed "associated with" by "present as HNO_3 "
Page 8, Line 269: Included "(in the form of $\text{Ca}(\text{NO}_3)_2$)"
Page 8, Lines 271–275: Changed "associated with" by "present as" as suggested
Page 11, Line 353: Included "(to give $\text{Ca}(\text{NO}_3)_2$)" and "(to give HNO_3)"
120 Figure 6: Caption modified with " H^+ " instead of " HNO_3 "

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 atmospheric acids contiguously. The association between 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 (~ 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 nssCa^{2+} at the near-coastal sections of both PEL ($r = 0.74$) and cDML ($r = 0.82$) transects. Similarly, a strong association between these ions was also observed in snow deposits at the inland sections of PEL ($r = 0.73$) and cDML ($r = 0.84$). Such systematic associations between nssCa^{2+} and NO_3^- is attributed to the interaction between calcic mineral dust and nitric acid in the atmosphere, leading to the formation of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) 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 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 $< 4 \mu\text{m}$, indicating that these dust particles reached the Antarctic region via long range transport from the SSA region. We propose that the association between nssCa^{2+} and NO_3^- occurs during the long range transport due to the formation of $\text{Ca}(\text{NO}_3)_2$ 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 and coastal regions respectively. Ionic balance calculations showed that 70–75 % of NO_3^- in the coastal sections was associated with nssCa^{2+} (to form $\text{Ca}(\text{NO}_3)_2$). However, in the inland sections, 50–55 % of NO_3^- was associated with present as HNO_3 . The study indicates that the input of dust-bound NO_3^- contributes a significant fraction of the total NO_3^- deposited in coastal Antarctic snow.

1 Introduction

Fine aerosols from surrounding continents are transported thousands of kilometers and 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, NO₂), nitric acid (HNO₃) and mineral dust particles make up a significant component in the Antarctic atmosphere (Weller et al., 2002; Albani et al., 2012; Wolff, 2013). Nitrate 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 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 an important factor, 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 NO₃⁻ (e.g. Jordan et al., 2003; Fairlie et al., 2010). It was reported that almost all of total NO₃⁻ in high dust regions and > 40 % of the total NO₃⁻ 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 NO₃⁻ is a large component of total atmospheric NO₃⁻ due to the presence of Ca²⁺ in mineral dust, which has a high buffering capacity to neutralise atmospheric nitric acid (HNO₃) to yield highly hygroscopic calcium nitrate (Ca(NO₃)₂) aerosol (Krueger et al., 2003).

In Antarctica, non-sea-salt Ca²⁺ ($nssCa^{2+} = Ca^{2+} - 0.038 ssNa^{+}$) 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 NO₃⁻ and Ca²⁺ throughout 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 NO₃⁻ and Ca²⁺ have not been widely reported in present day Antarctic snow pack. In this study, we analyse the spatial variability and association of NO₃⁻ and nssCa²⁺ from two different regions in East Antarctica – Princess Elizabeth Land (PEL) and central Dronning Maud Land (cDML). We also discuss the possible for-

mation processes of $\text{Ca}(\text{NO}_3)_2$ during the long range transport of mineral dust and its significance for Antarctic snow chemistry.

2 Sampling and methods

65 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 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
70 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. 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,
75 the cDML transect is spatially divided into near-coastal (110–160 km), mountainous (170–240 km) and plateau (> 240 km) sections (Fig. 1).

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
80 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 -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
85 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 detection limit was achieved for both soluble Ca^{2+} ($0.3 \mu\text{g L}^{-1}$) and NO_3^- ($5 \mu\text{g L}^{-1}$) 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
90 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 a precision better than 5 % was obtained.

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

ence between summer and winter precipitation (Stenberg et al., 1998). A minimum seasonal amplitude of 6‰ in $\delta^{18}\text{O}$ values 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 $\text{ssNa}^+ = (\text{R}_c \cdot \text{Na}^+ - \text{Ca}^{2+}) / (\text{R}_c - \text{R}_m)$ derived from Röthlisberger et al. (2002b), where $\text{R}_c = 1.78$ and $\text{R}_m = 0.038$ are the average ratios of $\text{Ca}^{2+}/\text{Na}^+$ 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 $\mu\text{eq L}^{-1}$ based on the methods specified in Legrand and Mayewski (1997) and Iizuka et al. (2004). In order 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

Snow cores from both PEL and cDML clearly showed seasonal variations in $\delta^{18}\text{O}$ and the major ions (Fig. 2). Sea-salt (Na^+) ions peaked mostly during winter and were in sync with the $\delta^{18}\text{O}$ variations. Though Ca^{2+} and NO_3^- peaks were not in sync with the $\delta^{18}\text{O}$ 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 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 $200 \mu\text{g L}^{-1}$ with few samples as high as $350 \mu\text{g L}^{-1}$. Similarly, NO_3^- in cDML transect ranged from 15 to $350 \mu\text{g L}^{-1}$ with outliers as high as $450 \mu\text{g L}^{-1}$. Even though NO_3^- did not follow any systematic trend either with changes in distance from the sea, the inland sites were characterised by relatively higher values along both transects.

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 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 $70 \mu\text{g L}^{-1}$ with few outliers as high as $100 \mu\text{g L}^{-1}$ in PEL (Fig. 3). On the other hand, nssCa^{2+} concentrations in cDML transect ranged from 5 to $50 \mu\text{g L}^{-1}$ except along the mountainous region, where it showed a substantial spread with concentrations up to $150 \mu\text{g L}^{-1}$ and outliers as high as $230 \mu\text{g L}^{-1}$. As a result, the mean Ca^{2+} con-

concentrations were significantly high along the mountainous section in cDML transect. In the plateau region the nssCa²⁺ concentrations were very low with a narrow range (4–12 µg L⁻¹) irrespective of seasonal variations.

135 Ionic balance of the samples from PEL and cDML revealed the dominance of sea-salt (Na⁺, Mg²⁺, K⁺ and Cl⁻) in the near-coastal cores (PEL 75 %, cDML 50 %) followed by NO₃⁻ (PEL 38 %, cDML 27 %), nssCa²⁺ (PEL 9 %, cDML 19 %) and nssSO₄²⁻ (PEL 9 %, cDML 17 %). The inland samples, however, showed the dominance of NO₃⁻ (PEL 38 %, cDML 47 %) followed by nssSO₄²⁻ (PEL 14 %, cDML 22 %). Samples from the mountainous section of cDML showed a
140 large fraction of Ca²⁺ and SO₄²⁻ 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 NO₃⁻ and nssCa²⁺ with other major ions showed a consistent relationship between nssCa²⁺ and NO₃⁻ from different sections of PEL and cDML transects, except in
145 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, NO₃⁻ showed a significant association with nssCa²⁺ ($r = 0.82$ 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 ($r = 0.85$).
150 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, NO₃⁻ and nssCa²⁺ 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.

155 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⁺, nssCa²⁺ and MSA⁻), three principal factors (F1, F2, F3) were identified. Those ions primarily derived from sea-spray sources (Na⁺, Cl⁻, Mg²⁺ and K⁺), and from biogenic sources (MSA⁻ and nssSO₄²⁻) were grouped together. Interestingly, nssCa²⁺ derived from crustal sources and NO₃⁻, derived from upper atmospheric or tropospheric sources were grouped together in all regions indicating **long-range-transport**
160 **and the** deposition of these ions in the form of Ca(NO₃)₂ aerosol. However, in the mountainous section of cDML, nssCa²⁺ was associated with nssSO₄²⁻ indicating local sources of nssCa²⁺ from the exposed mountains.

4 Discussion

165 4.1 Association between nssCa^{2+} and NO_3^- in snowpack from distinct transects

Nitrate is one of the major anions with multiple sources in the Antarctic environment. It is predominantly a secondary 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 tropo-
170 spheric transport of HNO_3 are also thought to contribute to NO_3^- 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
175 to be independent of oceanic or topographic influences and is generally expected to have poor relationships with other major ions. 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 recent studies (e.g., Erbland et al., 2013, 2015) have shown that NO_3^- indeed show spatial variation at least on the surface
180 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.

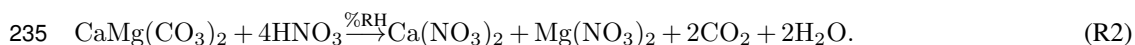
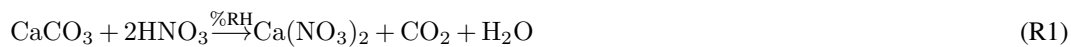
Compared to NO_3^- , sources of Ca^{2+} in the Antarctic environment are relatively well known.
185 A small but significant amount of Ca^{2+} derived from sea spray and sea ice surface (ssCa^{2+}) is present in the coastal section of Antarctic snow (Sommer et al., 2000). Sea-salt Ca^{2+} may also originate from ikaite crystals ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in the Antarctic sea ice during onset of winter (Dieckmann et al., 2008). Calculations from the coastal section of PEL showed an input of 33 % ssCa^{2+} (of total Ca^{2+}) due to its proximity to the open ocean. Crustal dust from local sources and remote continents
190 are the major sources of Ca^{2+} (in the form of nssCa^{2+}) in the Antarctic atmosphere and ice sheet (Boutron and Martin, 1980). The percentage of estimated nssCa^{2+} component in the total Ca^{2+} in both PEL (> 87 %) and cDML (> 90 %) transects (Fig. 3) support a predominantly crustal origin of Ca^{2+} 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
195 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 coastal, mountainous and inland sections of both cDML and PEL transects showed that > 90 % of particles were < 4 μm and the majority of them in the $\sim 1 \mu\text{m}$ size range, indicating a distant dust source as demonstrated by model studies (e.g. Li et al., 2008, 2010).

200 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 μm) 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
 205 mountains, in the prevailing wind direction (Fig. 1).

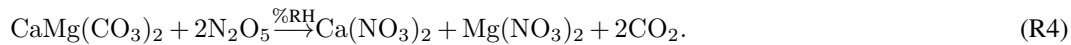
This study revealed a striking relationship between NO_3^- and nssCa^{2+} in snow cores from both
 PEL and cDML transects in East Antarctica that are > 2000 km apart (Fig. 4). The Ca^{2+} flux calcu-
 lations ($F_{\text{Ca}^{2+}} = C_{\text{Ca}^{2+}} \times A$, where $C_{\text{Ca}^{2+}}$ = annual mean concentration of Ca^{2+} and A = annual
 accumulation) (Burkhart et al., 2004) showed an average of 6.1 and 9.1 $\text{kg km}^{-2} \text{yr}^{-1}$ of Ca^{2+} at
 210 PEL and cDML transects respectively, indicating a substantial amount of Ca^{2+} reaching the Antarc-
 tic 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 $\mu\text{g L}^{-1}$,
 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 parti-
 215 cles 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 $\text{nssCa}^{2+} / \text{NO}_3^-$
 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
 220 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

225 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 min-
 erals 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 ($\text{CaMg}(\text{CO}_3)_2$) are found to be the
 230 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 $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ are formed when calcic
 mineral dust undergo heterogeneous reactions with atmospheric HNO_3 according to the following
 reactions (Gibson et al., 2006):



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:



240 The reaction between mineral dust and atmospheric HNO_3 or N_2O_5 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). 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 extending from $40-56^\circ$ S and the climate here is controlled mainly by the Westerlies from the Pacific Ocean (Iriondo, 2000). The atmospheric circulation in Patagonia is dominated by strong meridional pressure gradients that promote strong Westerlies and high wind speeds throughout the year (Coronato, 1993). Owing to extreme dryness of the air (with relative humidity as low as 5 %) in the Patagonian region, the Westerlies pick up large volumes of dust, which rise 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 $nssCa^{2+}$ (in the form of $Ca(NO_3)_2$) 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 nss present as $Ca(NO_3)_2$ whereas about 53 % of NO_3^- was associated with present as HNO_3 and the rest with as NH_4^+ . The $nssCa^{2+}$ associated NO_3^- was $\sim 75\%$ and 55% in the

coastal and inland regions of PEL transect respectively. An estimated 25 % of NO_3^- was associated with present as HNO_3 in both the coastal and inland sections of PEL. The estimated values of NO_3^- associated with nss present as $\text{Ca}(\text{NO}_3)_2$ 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 a more interior region (300 km).

The results from PCA analysis displayed nss Ca^{2+} and NO_3^- strongly grouped within the same factors suggesting, indicating that the nss Ca^{2+} – NO_3^- association occurred either due to the reaction during long range transport or because of similar reaction in the Antarctic boundary layer. Also, the atmospheric moisture content plays an important role in enhancing the reaction between these two components as shown in the reactions (R1-R2) above. It is well-known that the moisture content in the Antarctic atmosphere is very low and varies significantly in coastal and inland regions. Besides, the atmospheric boundary layer above the Antarctic ice sheet is only a few tens of meters above the ground level, thereby limiting the reaction times before deposition. Such conditions suggests that predominantly, the neutralisation of calcium-dust by HNO_3 occurs during long-range transport rather than locally in the boundary layer. Such correlations have also been reported in aerosol studies from the interior Dome C region (Udisti et al., 2004), where nss Ca^{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 nss Ca^{2+} and NO_3^- with the factors. The association of nss Ca^{2+} with nss SO_4^{2-} clearly indicate the influence from the exposed mountains in the vicinity. The coastal section of PEL also showed a weak loading of nss SO_4^{2-} along with a strong loading of nss Ca^{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 variance. The forward trajectory clusters revealed that both during summer (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 the Antarctic Circumpolar Vortex (ACV) before mass compensation by anticyclonic polar easterlies in

310 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 undergo 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 $\text{Ca}(\text{NO}_3)_2$. 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 $\text{Ca}(\text{NO}_3)_2$ aerosol is shown in Fig. 6. The initial process involves hydrolysis of HNO_3 on calcium-rich dust particles 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 air mass containing dust particles upon reaching the Antarctic region, undergoes mass compensation within the easterlies leading to the deposition of aerosols and dust particles to the Antarctic surface (Iriando, 2000). It is therefore proposed, that the availability of calcic mineral dust from SSA under the influence of westerlies and its reaction with atmospheric HNO_3 over the Southern Ocean has facilitated the formation of $\text{Ca}(\text{NO}_3)_2$ 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 in proximity to mountainous regions that provide additional local dust which has not undergone any atmospheric chemical processes.

330 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 (Wagon et al., 1999) with 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 $\text{Ca}^{2+} / \text{NO}_3^-$ 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 by Lunt and Valdes (2001) have shown that the transport efficiency of dust to East Antarctica is greater at the present day suggesting that an overall increase in dust transport is more likely. Röthlisberger et al. (2002) also speculated that such reactions in the atmosphere would result in a widespread $\text{Ca}^{2+} / \text{NO}_3^-$ 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. Such reactions are of 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

350 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 nitric acid in the atmosphere, resulting in the formation of $\text{Ca}(\text{NO}_3)_2$ 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+}
355 (as $\text{Ca}(\text{NO}_3)_2$), whereas in the inland region NO_3^- was associated with H^+ (as HNO_3). The forward and back trajectory analyses suggest, that fine calcic mineral dust from the Southern South America (SSA) region has been transported to the East Antarctic region, aided by the Westerlies. Also, the results from principal component analyses further strengthens our view that $\text{Ca}(\text{NO}_3)_2$ was formed in the atmosphere during the transport of mineral dust from SSA to the East Antarctic region. The
360 $\text{Ca}(\text{NO}_3)_2$ 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 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 $\text{Ca}^{2+} / \text{NO}_3^-$ could be
365 widespread but may not be observed clearly when study regions are close to the coast or when additional dust is contributed by local crustal sources.

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.

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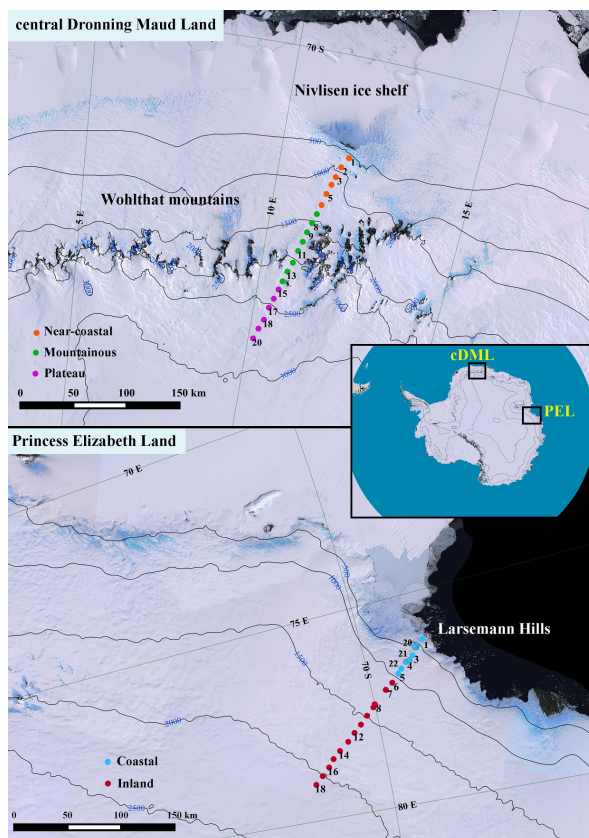


Figure 1. Study region showing sampling locations along transects in central Dronning Maud Land (top panel) and Princess Elizabeth Land (bottom panel), East Antarctica. Colour coded sampling locations indicate different topographic sections. Inset shows the study area highlighted in Antarctica. Maps were created using LANDSAT Mosaic using QGIS Wien (v.2.8) in conjunction with Quantarctica project.

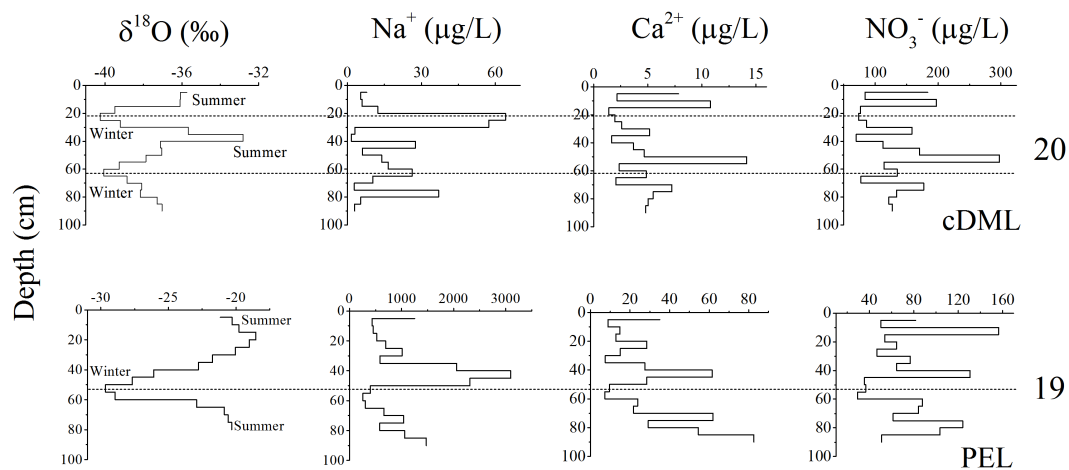


Figure 2. Oxygen isotope ratios and major ions showing seasonality in representative snow cores from inland (cDML, core 20) and coast (PEL, core 19). The dotted lines represent winter maxima in the cores.

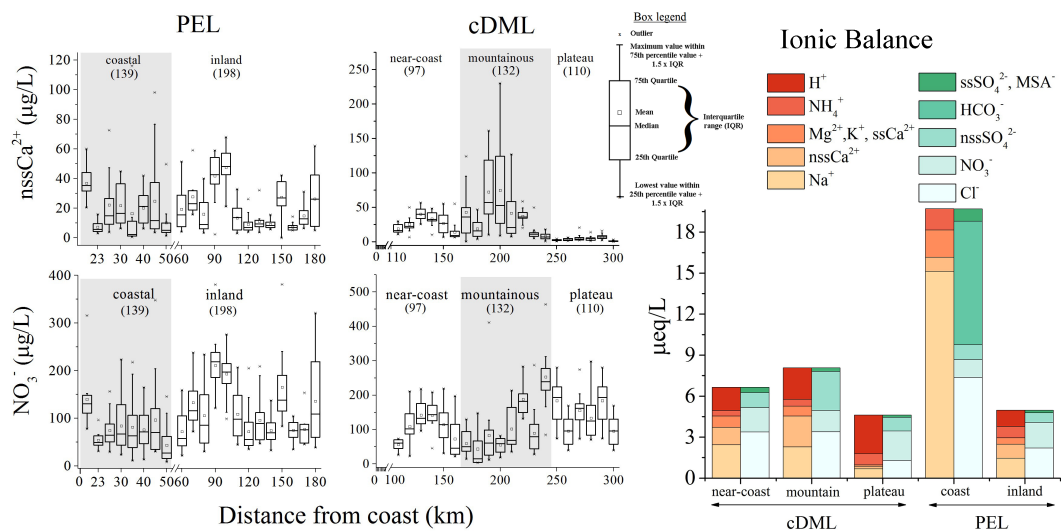


Figure 3. Distribution of nssCa^{2+} and NO_3^- concentrations in snow cores along PEL and cDML transects. The numbers inside brackets indicate the total number of samples in respective sections. The balance of ions from all regions are denoted on right panel.

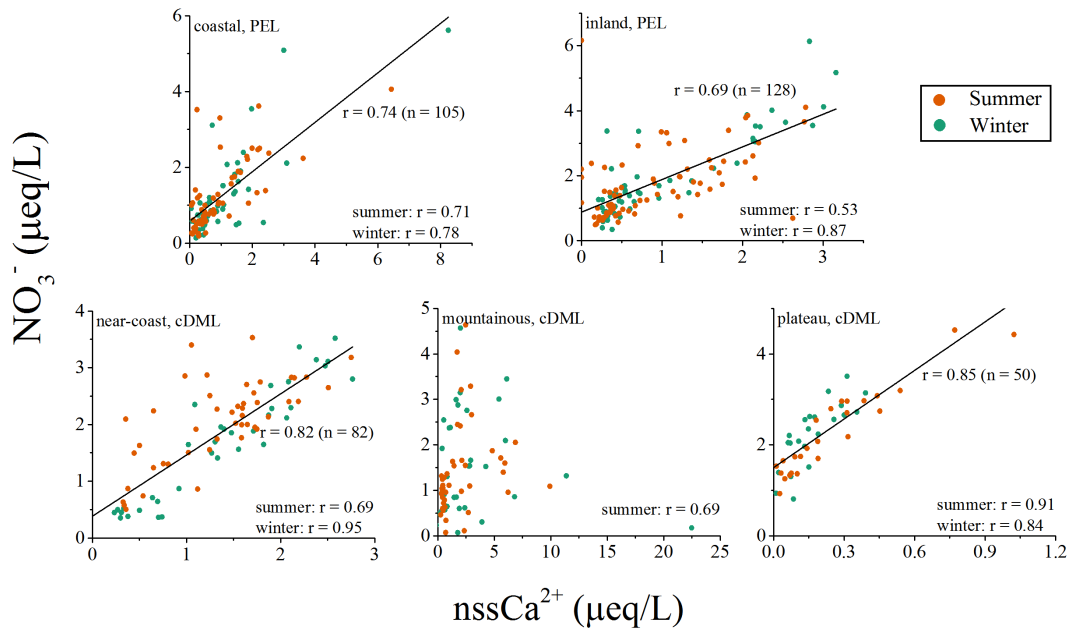


Figure 4. Correlation between nssCa^{2+} and NO_3^- during austral summer (brown) and winter (green) in the study regions in cDML and PEL. Samples representing 1 complete year are plotted here to show the seasonal differences. The samples from coastal and inland sections in both cDML and PEL showed a strong association while the mountainous section in cDML transect showed weak association only during summer.

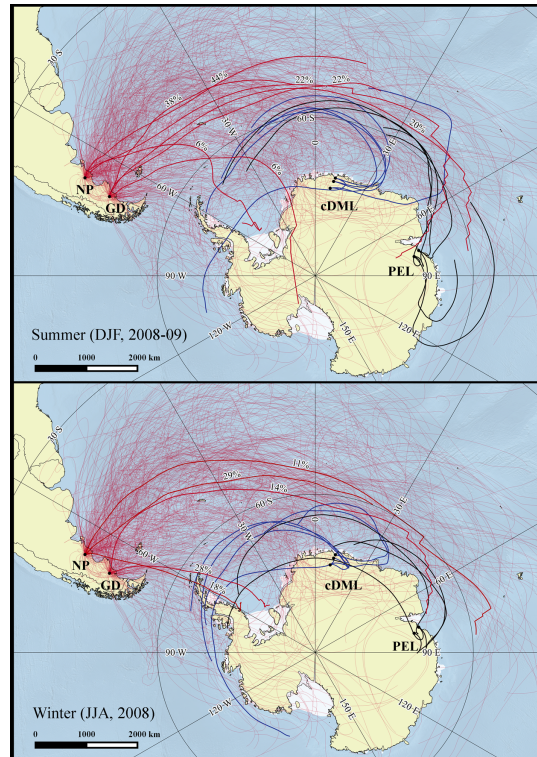


Figure 5. Forward and back trajectory analyses for 9 days using HYSPLIT Model v.4 in conjunction with GDAS dataset. The forward trajectories (red) were calculated from North Patagonia (NP) and San Julian's Great Depression (GD), and the back trajectories (blue, black) were reconstructed from cDML and 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.

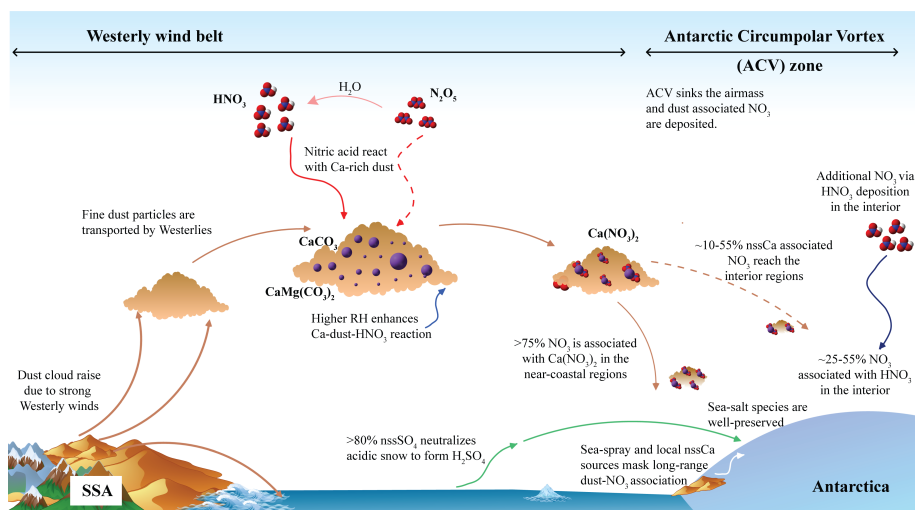


Figure 6. Schematic diagram depicting possible processes and chemical reactions involved during the mineral dust transport from Southern South America (SSA) before depositing over Antarctic ice sheet. The estimates of NO_3^- associated with nssCa^{2+} and H^+ are based on data from this study.

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.

Factors	cDML									PEL					
	near-coastal			mountainous			plateau			coastal			inland		
	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