



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 snowpack, 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 in East Antarctica – the Princess Elizabeth Land (PEL) and central Dronning Maud Land (cDML). 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^- are 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 revealed common transport and depositional processes for 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 to local neutralisation processes. However, the influence of local dust sources from the nunataks in cDML and the con-

tribution 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 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 kilometres 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 , NO_2), nitric acid (HNO_3), 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 post-depositional processes (e.g. Wagon 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 forms an active aerosol component in the atmosphere, and model simulations show that the min-

eral dust from surrounding continents is 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 NO_3^- (e.g. Jordan et al., 2003; 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 are 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 buffering capacity to neutralise atmospheric nitric acid (HNO_3) to yield highly hygroscopic calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) aerosol (Krueger et al., 2003).

In Antarctica, non-sea-salt Ca^{2+} ($\text{nssCa}^{2+} = \text{Ca}^{2+} - 0.038 \text{ ssNa}^+$) 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 the Last Glacial Maximum (LGM), 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 snowpack. 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 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

Forty-one snow cores were recovered from the PEL and cDML transects using a KOVACS Mark IV coring system (14 cm diameter) during the summer of 2008–2009 (Fig. 1). Each snow core was about 1 m deep, enough to cover over 1 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 the near coast to the inland region, covering a distance of 110–300 km from the coast and an elevation of up to 2800 m a.s.l. Due to the absence of fresh snow over the Nivlisen ice shelf and the

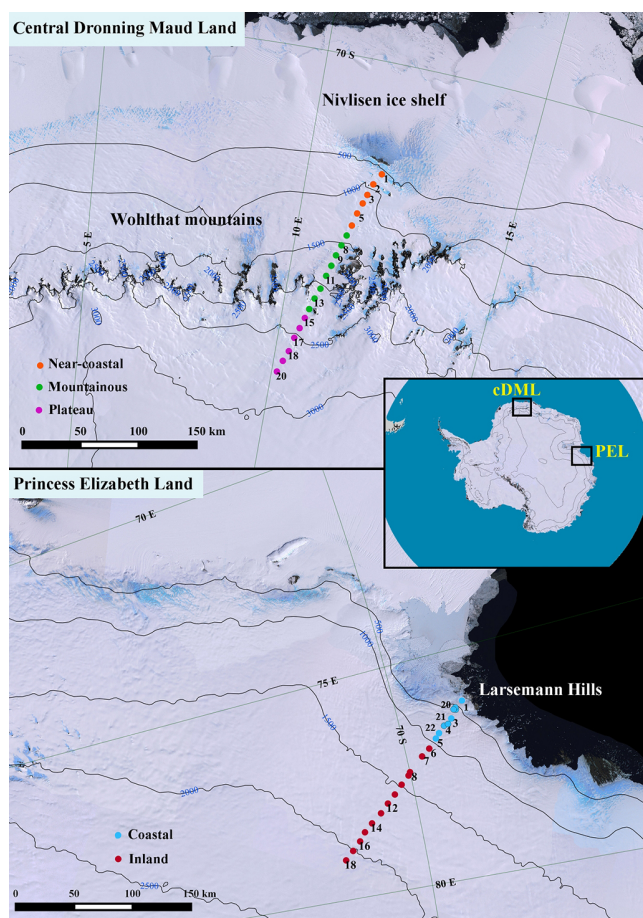


Figure 1. Study region showing sampling locations along transects in central Dronning Maud Land (top panel) and Princess Elizabeth Land (bottom panel), East Antarctica. Colour-coded sampling locations indicate different topographic sections. Inset shows the study area highlighted in Antarctica. Maps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

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).

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 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 subsampled at 5 cm resolution under a laminar flow bench housed at -15°C facility. The outer layers of these subsamples were removed manually by ceramic knives and the

innermost portion of the samples were transferred to pre-cleaned vials. These subsamples 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 detection limit was achieved for both soluble Ca^{2+} ($0.3 \mu\text{g L}^{-1}$) and NO_3^- ($5 \mu\text{g L}^{-1}$). 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 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 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 difference 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 $\text{ssNa}^+ = (R_c \cdot \text{Na}^+ - \text{Ca}^{2+}) / (R_c - R_m)$ derived from Röthlisberger et al. (2002b), where $R_c = 1.78$ and $R_m = 0.038$ are the average ratios of $\text{Ca}^{2+}/\text{Na}^+$ 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 maximise 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 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, the majority of Ca^{2+} in the mountainous (96 %), near-coast (92 %), and plateau (88 %) regions was also from crustal sources. Non-sea-salt Ca^{2+} concentrations, on the 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+} 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 ($4\text{--}12 \mu\text{g L}^{-1}$) 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 1 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

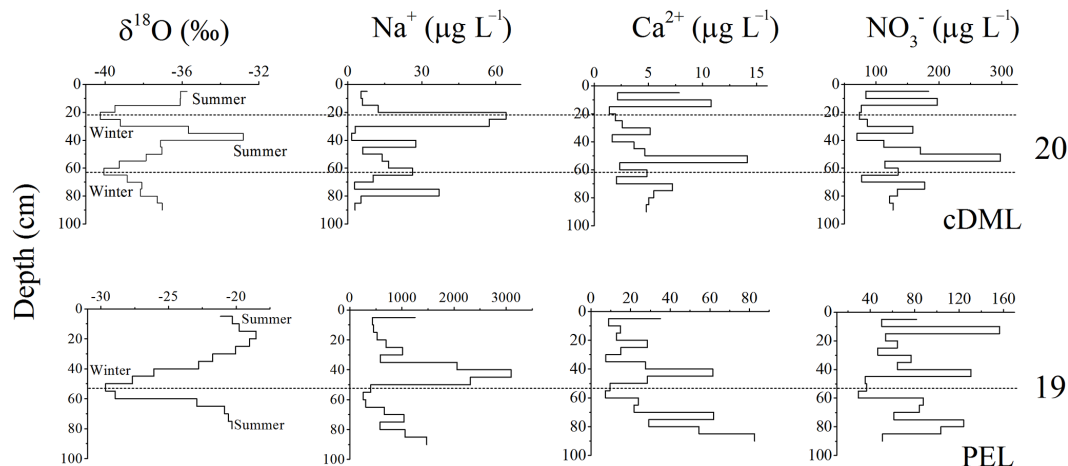


Figure 2. Oxygen isotope ratios and major ions showing seasonality in representative snow cores from inland (cDML, core 20) and coast (PEL, core 19). The dotted lines represent winter maxima in the cores.

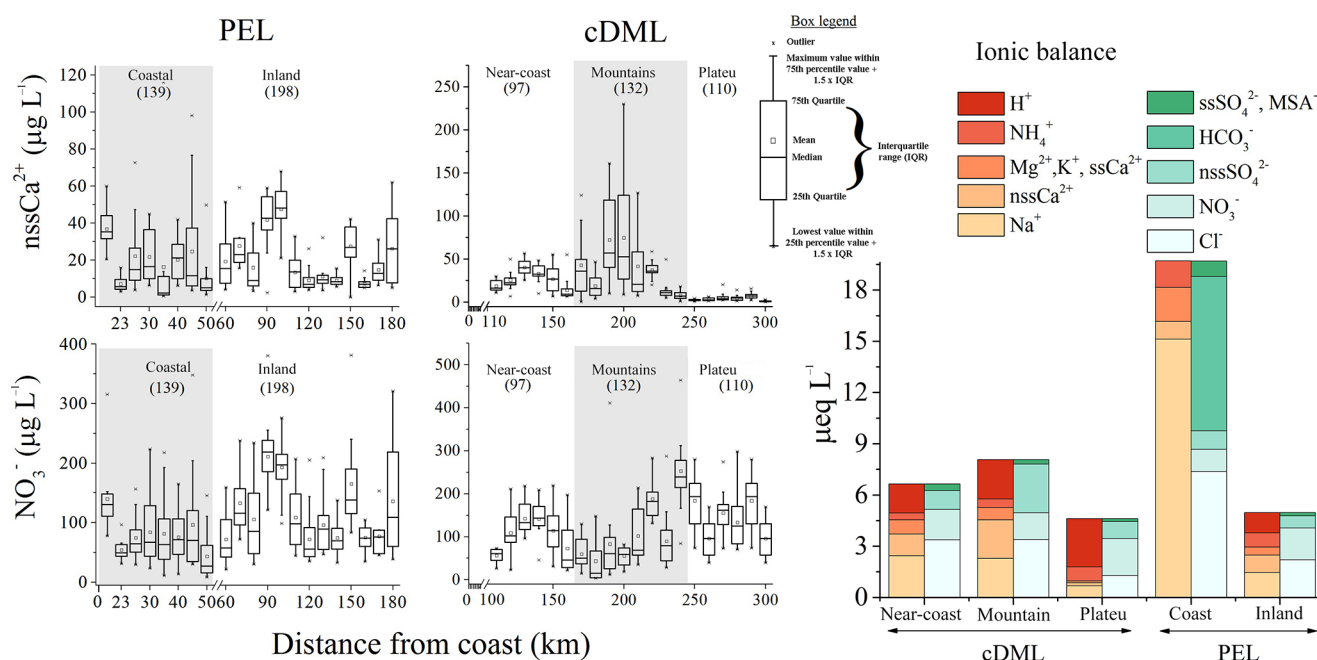


Figure 3. Distribution of nssCa^{2+} and NO_3^- concentrations in snow cores along PEL and cDML transects. The numbers inside brackets indicate the total number of samples in respective sections. The balance of ions from all regions are denoted on right panel.

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 iden-

tified. 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 the deposition of these ions in the form of $\text{Ca}(\text{NO}_3)_2$ 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.

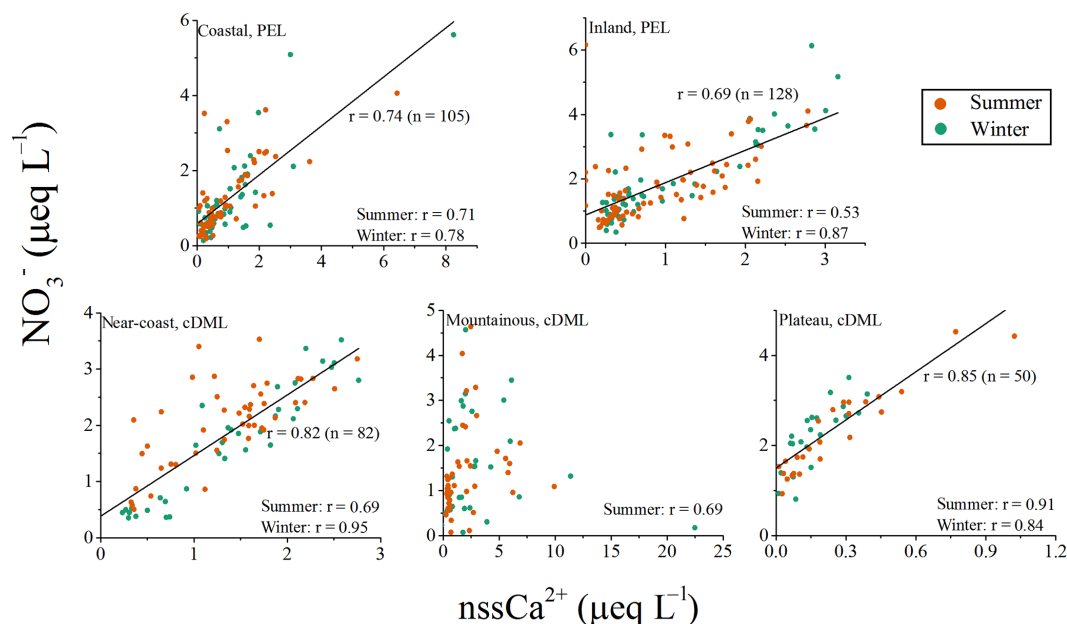


Figure 4. Correlation between nssCa^{2+} and NO_3^- during austral summer (brown) and winter (green) in the study regions in cDML and PEL. Samples representing 1 complete year are plotted here to show the seasonal differences. The samples from coastal and inland sections in both cDML and PEL showed a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

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^b	–	–
K^+	–	0.58^a	-0.33	–	0.42^b
Mg^{2+}	–	0.41^a	–	–	–
nssCa^{2+}	0.82	0.69^a	0.85	0.74	0.69
NH_4^+	0.57^b	0.54^b	–	–	–
nssCa^{2+}					
Cl^-	–	0.75^b	–	–	–
nssSO_4^{2-}	–	0.92	–	0.49	–

Correlations only during ^a summer and ^b winter.

4 Discussion

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 tropospheric transport of HNO_3 is

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., 2002a; Erbland et al., 2013), resulting in a complex distribution of NO_3^- in the Antarctic snowpack. Due to the variety of its sources, NO_3^- distribution in modern-day snowpack is found 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 shows 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.

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 ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in the Antarctic sea ice during onset of winter (Dieckmann et al., 2008). Calculations from

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

Factors	Near-coastal			cDML Mountainous			Plateau			Coastal			PEL		
	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.

the coastal section of PEL showed an input of 33 % ssCa²⁺ (of total Ca²⁺) due to its proximity to the open ocean. Crustal dust from local sources and remote continents are the major sources of Ca²⁺ (in the form of nssCa²⁺) in the Antarctic atmosphere and ice sheet (Boutton and Martin, 1980). The percentage of estimated nssCa²⁺ component in the total Ca²⁺ in both PEL (> 87 %) and cDML (> 90 %) transects (Fig. 3) supports a predominantly crustal origin of Ca²⁺ 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 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 ~ 1 µm 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 a 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 mountains, in the prevailing wind direction (Fig. 1).

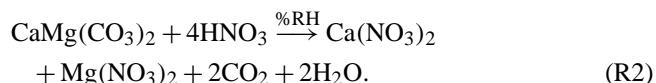
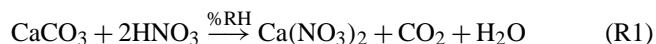
This study revealed a striking relationship between NO₃[−] and nssCa²⁺ in snow cores from both PEL and cDML transects in East Antarctica that are > 2000 km apart (Fig. 4). The Ca²⁺ flux calculations ($F_{\text{Ca}^{2+}} = C_{\text{Ca}^{2+}} \times A$, where $C_{\text{Ca}^{2+}}$ = annual mean concentration of Ca²⁺ and A = annual accumulation) (Burkhart et al., 2004) showed an average of

6.1 and 9.1 kg km^{−2} yr^{−1} of Ca²⁺ at PEL and cDML transects respectively, indicating a substantial amount of Ca²⁺ reaching the Antarctic environment throughout the year. Calcium concentrations in the mountainous section were nearly 3 times higher than the rest of the cDML transect, with concentrations of up to 150 to 230 µg 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 nssCa²⁺ from local dust sources possibly obscures the nssCa²⁺ / NO₃[−] association formed during long-range transport, resulting in poor correlation of NO₃[−] and nssCa²⁺ as observed in the mountainous section of the cDML transect. Moreover, the association between NO₃[−] and nssCa²⁺ 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 NO₃[−] and nssCa²⁺ concentrations at all sites (except the mountainous section) strongly suggest that aerosol interactive processes during long-range transport are responsible for influencing their relationship.

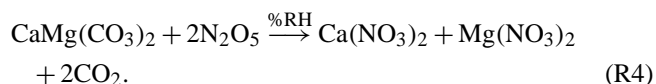
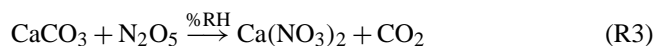
4.2 Mineral dust reactivity and possible remote sources

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 (CaCO₃) and dolomite (CaMg(CO₃)₂) are found to be the most reactive constituents of mineral dust in the atmosphere in the presence of HNO₃ (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 undergoes 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:



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 $\text{Ca}(\text{NO}_3)_2$, even at very low relative humidity (RH) conditions ($\sim 12\%$ RH) (Al-Abadleh et al., 2003). Then, with increasing RH, the adsorbed HNO_3 reacts with bulk CaCO_3 or $\text{CaMg}(\text{CO}_3)_2$ to form $\text{Ca}(\text{NO}_3)_2$. 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, and San Julian's Great Depression (GD) 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 reveals 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 to 56° 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 $\text{Ca}(\text{NO}_3)_2$) as calculated from the ratio of nssCa^{2+} and NO_3^- . However, in the inland region, only an estimated 10% of NO_3^- was present as $\text{Ca}(\text{NO}_3)_2$ whereas about 53% of NO_3^- was present as HNO_3 and the rest as 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 present as HNO_3 in both the coastal and inland sections of PEL. The estimated values of NO_3^- present as $\text{Ca}(\text{NO}_3)_2$ in PEL transect were 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 nssCa^{2+} and NO_3^- strongly grouped within the same factor, indicating that the nssCa^{2+} – NO_3^- association occurred due either to the reaction during long-range transport or to a 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 metres above the ground level, thereby limiting the reaction times before deposition. Such conditions suggest 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 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 indicates 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, 9-day forward and back trajectories for every day 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 data sets (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 GD (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 during 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 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 their 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 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 (Iriondo, 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+}

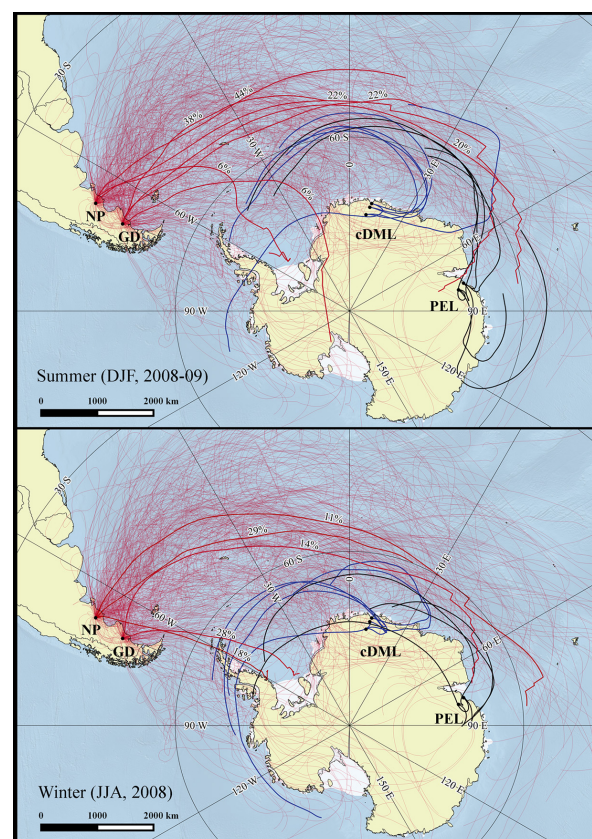


Figure 5. Forward- and back-trajectory analyses for 9 days using HYSPLIT model v.4 in conjunction with Global Data Assimilation System data set. The forward trajectories (red) were calculated from North Patagonia (NP) and San Julian's Great Depression (GD), and the back trajectories (blue, black) were 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.

and NO_3^- reported from sites in proximity to mountainous regions, which provide additional local dust that 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 (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 has been observed in deep ice cores from Vostok (Legrand et al., 1999) and Dome C (Röthlisberger et al., 2002a), which was attributed to the high amount of dust in the atmosphere during LGM. Studies by Lunt and Valdes

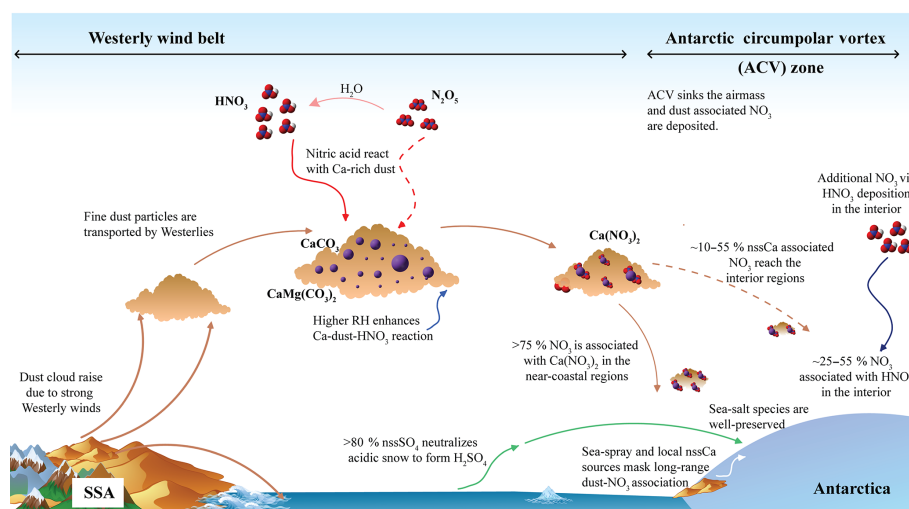


Figure 6. Schematic diagram depicting possible processes and chemical reactions involved during the mineral dust transport from southern South America (SSA) before depositing over Antarctic ice sheet. The estimates of NO_3^- associated with nssCa^{2+} and H^+ are based on data from this study.

(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. (2002a) also speculated that such reactions in the atmosphere would result in a widespread $\text{Ca}^{2+}/\text{NO}_3^-$ association throughout Antarctica. However, it remained inconclusive whether 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

This study shows a strong and widespread association between nssCa^{2+} and NO_3^- in snow from two different regions in cDML and PEL, which 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 show that a majority of NO_3^- in the coastal region is associated with nssCa^{2+} (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 SSA region has been transported to the East Antarctic region, aided by the westerlies. Also, the results from principal component analyses further strengthen 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 $\text{Ca}(\text{NO}_3)_2$ aerosol thus formed and was 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 Ca^{2+} and NO_3^- could be 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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