The Cryosphere

Relation between surface topography and sea-salt snow chemistry from Princess Elizabeth Land, East Antarctica

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Abstract. Previous studies on Antarctic snow have established an unambiguous correlation between variability of sea-salt records and site specific features like elevation and proximity to the sea. On the other hand, variations of Cl^-/Na^+ ratios in snow have been attributed to the reaction mechanisms involving atmospheric acids. In the present study, the annual records of Na^+, Cl^- and SO_4^{2-} were investigated using snow cores along a 180 km coast to inland transect in Princess Elizabeth Land, East Antarctica. Exceptionally high Na^+ concentrations and large variations in Cl^-/Na^+ ratios were observed up to 50 km (~1100 m elevation) of the transect. The steepest slope in the entire transect ($49.3\,\mathrm{m\,km^{-1}}$) was between 20 and 30 km and the sea-salt records in snow from this area revealed extensive modifications, with Cl^-/Na^+ ratios as low as 0.2. Statistical analysis showed a strong association between the slope and variations in Cl^-/Na^+ ratios along the transect ($r = -0.676$, 99 % confidence level). While distance from the coast accounted for some variability, the altitude by itself has no significant control over the sea-salt ion variability. However, the steep slopes influence the deposition of sea-salt aerosols in snow. The wind redistribution of snow due to the steep slopes on the coastal escarpment increases the concentration of Na^+, resulting in a low Cl^-/Na^+ ratios. We propose that the slope variations in the coastal regions of Antarctica could significantly influence the sea-salt chemistry of snow.

1 Introduction

Studies on spatial variability of snow chemistry and accumulation provide a unique opportunity to understand the fundamental factors influencing the ice core records. Spatial variations of snow chemistry in Antarctica are mainly attributed to the site-specific features like elevation, distance from the sea and to an extent, snow accumulation (Bertler et al., 2005). The snow accumulation and sea-salt concentrations decrease with respect to increase in elevation and distance from the coast (Giovinetto et al., 1990). A compilation of previously published data from various Antarctic sites shows that the snow chemistry concentrations varied by up to four orders of magnitude with a distinct geographical pattern across Antarctica (Bertler et al., 2005). Studies have also shown the importance of complex morphology of the snow surface (Goodwin, 1990), including micro-relief features (Frezzotti et al., 2005) and the megadune movement (Frezzotti et al., 2002), which play an important role in the snow accumulation in the Antarctic ice sheets. However, very few studies (Kreutz and Mayewski, 1999; Stenberg et al., 1998; Thamban et al., 2010) have attempted to elucidate the role of surface physical features on snow chemistry in Antarctica. A thorough knowledge of all these parameters is critical, for instance, to understand the past compositional changes in deep ice cores.

The major chemical constituents of the Antarctic snow and ice are the sea-salt ions (Na^+, Cl^-, SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+}), the atmospheric acids (H_2SO_4 and HNO_3) along with minor amounts of biologically derived components (MSA, NH_4^+) and other organic acids (Hall and Wolff, 1998). High concentrations of sea-salt aerosols are common in the coastal margins of Antarctica and have a profound influence on the formation of cloud condensation nuclei. This in turn affects the coastal climate by atmospheric scattering of solar radiation (Murphy et al., 1998). Cl^- and Na^+ constitute the majority of sea-salt aerosols in the coastal Antarctic atmosphere. Sea spray from the ocean surface is considered to

be a major contributor of sea-salt aerosol in the Antarctic atmosphere (Wagenbach, 1996). On the other hand, enhanced biological activity and sporadic volcanic inputs are considered to be the major sources of atmospheric H_2SO_4 (Minikin et al., 1998). During winter, frost flowers on the fresh sea-ice surface and the precipitation of mirabilite are considered to form a dominant source of sea-salt rather than from the open ocean (Rankin and Wolff, 2002). Measurements of the ionic components in snow and ice show that the ratios among Cl^-, Na^+ and SO_4^{2-} are modified with respect to the bulk seawater composition (Benassai et al., 2005). Such modifications in Cl^- and Na^+ involve heterogeneous reactions with atmospheric acids like H_2SO_4 and HNO_3, liberating reactive halogen species (Legrand and Delmas, 1988):

$$NaCl + HNO_3 \rightarrow HCl_{(g)} + NaNO_3 \qquad (R1)$$

$$2NaCl + H_2SO_4 \rightarrow 2HCl_{(g)} + Na_2SO_4 \qquad (R2)$$
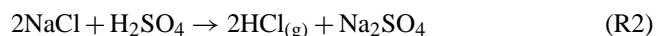
Therefore, a significant variation in the SO_4^{2-} and NO_3^- concentrations observed in snow could partly be explained by the reactions of atmospheric acid with the sea-salt aerosol. Cl^- present in the sea-salt aerosol is continually lost to the gas phase in the form of HCl and changes result in a low average Cl^-/Na^+ ratio, with respect to the bulk seawater composition. The seasonal pattern arising due to the differences in fractionation of sea-salt is phenomenally used in inferring long-term variability of atmospheric conditions (Aristarain and Delmas, 2002). Cl^-/Na^+ ratio in snow or ice is compared with that of seawater ratio to understand the chemical processes that occur during the transport and deposition of snow (Legrand and Delmas, 1988). For instance, Hara et al. (2004) showed that the sea-salt particles are transported over long distances to the coastal (Syowa) and inland (Dome Fuji) sites, resulting in Cl^-/Na^+ ratios closer to the bulk sea water ratio. On the other hand, reduced Cl^-/Na^+ ratios in the snow have been linked to shorter atmospheric residence times of the sea salt aerosols (Legrand and Delmas, 1988) and post-depositional HCl losses in surface snow (Wagnon et al., 1999). Reduced HCl formation in the atmosphere, owing to the higher dust levels, results in a higher Cl^-/Na^+ ratio at certain periods in the past and has also been reported from an ice core study (Röthlisberger et al., 2008).

Hall and Wolff (1998) have demonstrated the importance of coastal topography in regulating the sea-salt concentrations in Antarctic snow. A coast with mountain ranges, for instance, acts as a barrier for sea-salt laden maritime winds or induces the funnelling effect of katabatic winds around the mountains. The present study investigates the possibility of a relationship between the coastal topography with steep slopes and sea-salt snow chemistry, using high resolution data from snow cores along a coast to inland transect in the Princess Elizabeth Land, East Antarctica.

2 Sampling and methodology

Despite having the largest glacier basin in Antarctica, Princess Elizabeth Land is one of the least studied regions in terms of seasonal and spatial variations in snow chemistry. Previous studies in this region indicate that the coastal area is dominated by a steep escarpment zone influenced by katabatic winds (Allison, 1998). On the other hand, the maritime winds in the coastal region constantly blow from the east to northeast direction (Ma et al., 2010). Therefore, prior to the field sampling, adequate planning was made to sample along a transect perpendicular to the elevation contours in order to study the effect of rapid elevation changes and the interacting wind regimes on the chemistry of snow. A RADARSAT Antarctic Mapping Project (RAMP) 5 km digital elevation map was used while planning the transect (Fig. 1).

Beginning at 10 km from the coast, a series of one-meter snow cores was collected approximately at 10 km intervals up to 180 km with the helicopter support. Snow coring was carried out using a KOVACS Mark IV device with a 14 cm diameter barrel. This method allowed a faster way of sampling at higher resolution along the transect. Necessary precautions like sterile, long-hand, powder-free rubber gloves, polyethylene gloves and face masks were used during sampling to reduce the risk of contamination. Further, to avoid contamination due to movement of the transect team, sampling was always carried out ∼50 m upwind from the landing site at each location. Twenty-two snow cores were collected along the transect that covered an elevation up to 2200 m. Within the coastal section between 20 and 50 km, cores were collected at closer intervals to assess the spatial variability due to rapid changes in elevation. The cores were directly transferred from the core barrel in to clean custom made HDPE (high density polyethylene) bags, and sealed immediately. The strong wind action in this region ensured compaction of the snow and prevented the possible disintegration of cores. All samples were transported in EPP (Expanded Poly Propylene) boxes and stored at $-20\,°C$ conditions prior to the laboratory sub-sampling at the National Centre for Antarctic and Ocean Research (Goa, India).

Sub-sampling of snow cores at 5 cm resolution was carried out under clean conditions in a laminar-flow bench, housed in the processing facility in a $-15\,°C$ cold room. All sub-sampling equipment and sample containers were pre-cleaned by rinsing several times with Milli-Q water (18 M Ω), soaking for at least 24 h, followed by rinsing with fresh Milli-Q water and drying in a laminar-flow bench. Samples were melted immediately prior to the analysis in a class 100 clean room facility. Cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analysed using a Dionex DX-2500 with IonPac CS17 column and anions (Cl^-, MSA^-, SO_4^{2-} and NO_3^-) were analysed on a Dionex ICS-2000 with IonPac AS11-HC column. The detection limits were within $2\,\mu g\,l^{-1}$ for Cl^-, SO_4^{2-} and Na^+. Reference standards and random samples were analysed routinely to estimate the analytical precision, which was better
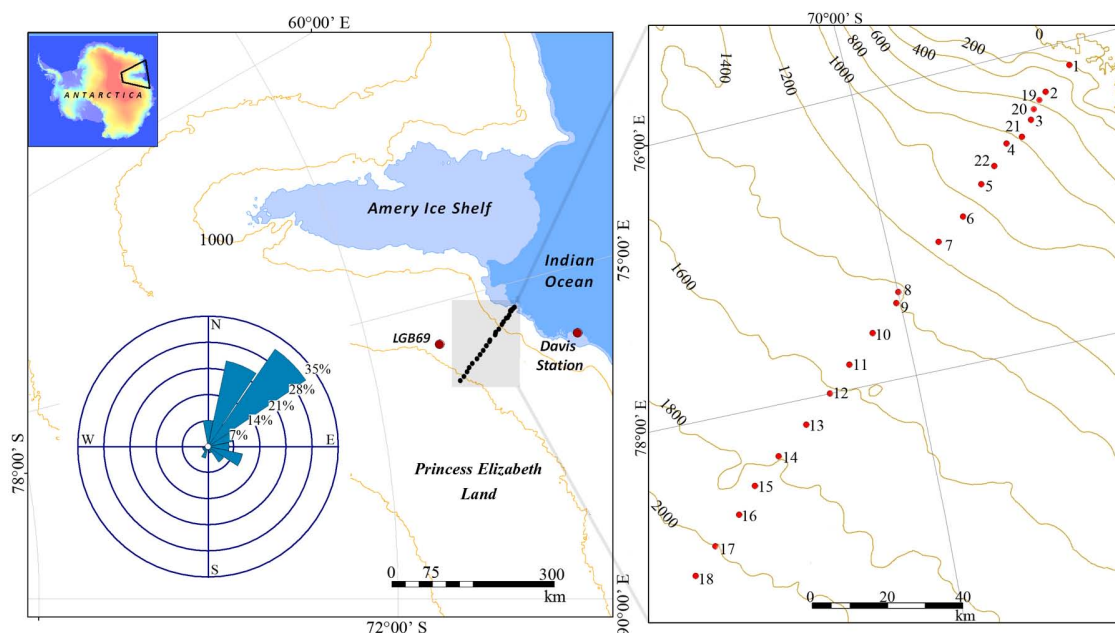
Fig. 1. Map showing the sampling locations in Princess Elizabeth Land transect. Inset on the left corner shows the wind rose chart for 2008, showing prevalent wind direction (NNE–ENE) on the coast.

than 5 % for SO_4^{2-}, NO_3^-, and MSA. For Cl^-, the precision was within 10 %. The cations also had a precision better than 5 %. Stable isotope ratios were measured using a dual inlet, Isoprime Isotope Ratio Mass Spectrometer, following standard analytical procedures (Naik et al., 2010). The external precision obtained using a laboratory standard (CDML 1) on oxygen isotope analysis was ±0.05 ‰.

2.1 Determination of seasonality and annual accumulation from snow cores

$\delta^{18}O$ values were used to delineate individual years as well as to determine the seasonal sea-salt concentrations in the snow cores along the transect. The snow cores were compact enough (density ~0.4 g cm^{-3}) to prevent mixing or crushing during transportation. A seasonal $\delta^{18}O$ amplitude of 4 ‰ was considered large enough to represent the temperature difference between summer and winter precipitation (Stenberg et al., 1998). The seasonal amplitude of $\delta^{18}O$ values for snow cores from Princess Elizabeth Land transect was larger than 6 ‰. $\delta^{18}O$ records were obscured at certain locations, which could be attributed to variations in seasonal amplitude of condensation temperature (Helsen et al., 2005). Annual layers were identified based on the extreme values of $\delta^{18}O$ between summer and winter (Fig. 2).

2.2 Determination of slope

Princess Elizabeth Land showed a marked contrast in elevation changes between the coast and the inland region (Fig. 1). Between 20 km and 50 km (from the coast, unless otherwise

mentioned), the elevation showed a rapid increase from 300 m to 1113 m, indicating a steep escarpment zone. Beyond 50 km, the elevation increased gradually (from 1113 m to 2109 m) up to 180 km. In order to estimate the slope between subsequent sampling points, a combination of elevation data and the distance from the coast along the transect were used. Accordingly, the slope was calculated as elevation change/distance change (between two points). Slope values were subsequently derived in terms of m km^{-1}. The slope variations between the coast and inland region were also prominent. The coastal escarpment zone (between 20 km and 50 km) showed an average slope of 27.1 m km^{-1}. The steepest region was located between 20 km and 30 km, with a slope of 49.3 m km^{-1}. However, the interior region between 50 km and 100 km showed a threefold decrease in slope (9.4 m km^{-1}). Further interior, the slope reduced (7.8 m km^{-1}) between 100 km and 180 km (Fig. 5, inset).

3 Results

The snow accumulation rates showed large variations, ranging between 138 kg m^{-2} yr^{-1} in the inland (120 km) and 389 kg m^{-2} yr^{-1} closer to the coast (30 km) (Table 1). The steepest section (with a slope of 49.3 m km^{-1}) showed largest variability with accumulation rates ranging between 155 and 389 kg m^{-2} yr^{-1} (at 23 and 30 km, respectively). With an exception of this low accumulation rate at 23 km, the escarpment region (with a slope of 27.1 m km^{-1}) up to 50 km showed an average snow accumulation rate of 293 kg m^{-2} yr^{-1}. The section between 50 and 100 km
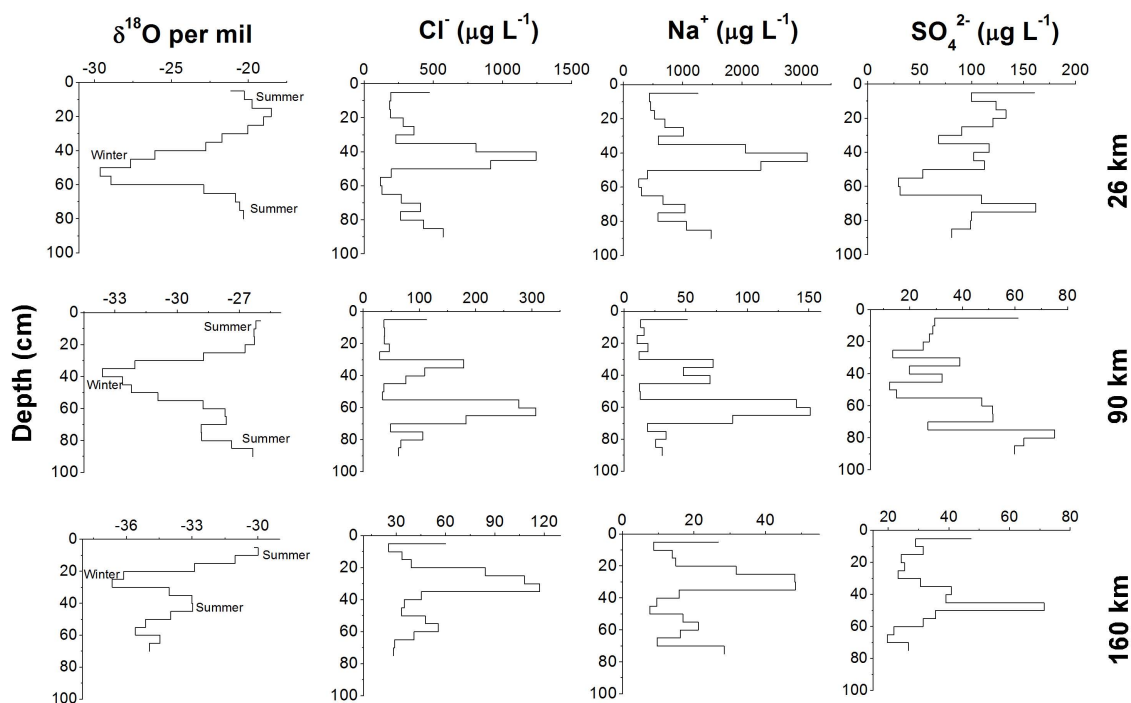
Fig. 2. Temporal records of $\delta^{18}O$, Cl^-, Na^+ and SO_4^{2-} from sites representing coast (26 km), mid-way (90 km) and the interior (160 km) in Princess Elizabeth Land. Seasonality in $\delta^{18}O$ variability was primarily used to determine the annual accumulations within the core, supported by Na^+, Cl^- and SO_4^{2-} records.

(average slope of $9.4\,m\,km^{-1}$) showed an average accumulation rate of $\sim300\,kg\,m^{-2}\,yr^{-1}$. The interior section (average slope of $7.8\,m\,km^{-1}$) beyond showed an average snow accumulation of $\sim270\,kg\,m^{-2}\,yr^{-1}$ (Table 1).

Na^+, Cl^- and SO_4^{2-} showed a wide range in concentration from the coast to inland (Fig. 3a). Concentrations of Na^+ and Cl^- were always higher in the initial 30 km of the transect, exceeding $100\,\mu g\,l^{-1}$ throughout the year (Fig. 3a). Besides, exceptionally high Na^+ concentrations, ranging between 500 and $1500\,\mu g\,l^{-1}$, were measured in snow from the steep coastal sections (Fig. 3a). Cl^- concentrations did not show a similar trend in the steep zone and ranged between 100 and $1000\,\mu g\,l^{-1}$, effectively lesser than that of Na^+. Outliers indicating sporadic events were also present at all the sampling locations, with a maximum Na^+ input of about $3000\,\mu g\,l^{-1}$ between 20 km and 30 km. Concentrations declined logarithmically beyond 50 km, with Na^+ concentration ranging between 10 and $100\,\mu g\,l^{-1}$ and Cl^- between 20 and $200\,\mu g\,l^{-1}$. SO_4^{2-} showed a background concentration of $25\,\mu g\,l^{-1}$ throughout the transect with variations up to $250\,\mu g\,l^{-1}$ within 50 km from the coast. Beyond 50 km, only little variations were observed with concentrations below $75\,\mu g\,l^{-1}$ (Fig. 3a).

Seasonal differences in concentrations of Na^+, Cl^- and SO_4^{2-} showed large variations in the initial 50 km of the transect (Fig. 3b). The annual Cl^- concentrations always exceeded Na^+ during the summer and winter throughout the transect, except in the steep zones, where the annual Na^+ was higher (Fig. 3b). The variations beyond 50 km were minimal for the Na^+ and Cl^- ions, with average annual concentrations ranging well below $150\,\mu g\,l^{-1}$. Seasonal SO_4^{2-} concentrations rarely exceeded $200\,\mu g\,l^{-1}$, with higher concentrations ($\sim150\,\mu g\,l^{-1}$) during summer near the coasts. The winter averages of Cl^- at 23 km, 26 km and 45 km (396, 519 and $193\,\mu g\,l^{-1}$) were lower than that of the Na^+ (502, 1275 and $439\,\mu g\,l^{-1}$). Similarly, the summer averages of Cl^- at these locations (270, 339 and $56\,\mu g\,l^{-1}$) were lower than that of Na^+ (1211, 878 and $102\,\mu g\,l^{-1}$). At 30 km, the summer and winter concentrations of both Na^+ and Cl^- were similar ($\sim152\,\mu g\,l^{-1}$ in summer, $\sim603\,\mu g\,l^{-1}$ in winter).

Annual Cl^-/Na^+ ratios were calculated from all the locations, which averaged slightly lower (1.4) when compared to that of the bulk sea water (1.81 w/w). However, data from the steepest part of the transect (within 50 km from the coast) revealed extremely low average annual Cl^-/Na^+ ratios (Fig. 4a). The lowest average (0.26) was recorded from a site at 26 km, at an elevation of 640 m, followed by 0.33 at 23 km at an elevation of 580 m. The annual Cl^-/Na^+ ratios gradually increased from 0.33 at 23 km to 1.28 at 40 km inland before reducing to 0.38 at 45 km inland. Beyond 60 km the annual Cl^-/Na^+ ranged between 1.05 and 2.5, averaging closer (1.73) to that of the bulk sea water ratio (Fig. 4a).

Table 1. Details of sampling parameters along with slope, accumulation rates and annual Cl$^-$/Na$^+$ values.

Station	Sampling Date	Latitude (S)	Longitude (E)	Elevation (m)	Distance from sea (km)	Slope (m km^{-1})	Accumulation rate (kg m^{-2} yr^{-1})	Annual Cl$^-$/Na$^+$
1	22 Jan 2010	69°29′	76°10′	267	10	26.77	n.a	n.a
2	22 Jan 2010	69°33′	76°18′	300	20	3.33	227	1.39
3	22 Jan 2010	69°36′	76°28′	792	30	49.32	389	0.65
4	22 Jan 2010	69°40′	76°35′	975	40	18.33	329	1.28
5	22 Jan 2010	69°45′	76°49′	1113	50	13.75	347	1.69
6	22 Jan 2010	69°49′	77°00′	1234	60	12.22	270	1.05
7	22 Jan 2010	69°53′	77°08′	1280	70	4.57	n.a	n.a
8	22 Jan 2010	70°00′	77°25′	1494	87	12.59	376	1.71
9	22 Jan 2010	70°01′	77°29′	1509	90	5.09	335	1.54
10	22 Jan 2010	70°05′	77°39′	1585	100	7.64	n.a	n.a
11	27 Jan 2010	70°09′	77°50′	1631	110	4.58	256	2.54
12	27 Jan 2010	70°13′	78°00′	1722	120	9.17	138	1.8
13	27 Jan 2010	70°17′	78°11′	1768	130	4.58	249	1.84
14	27 Jan 2010	70°22′	78°22′	1875	140	10.70	179	1.76
15	27 Jan 2010	70°26′	78°32′	1920	150	4.58	335	1.68
16	27 Jan 2010	70°29′	78°43′	1987	160	6.72	225	1.73
17	27 Jan 2010	70°33′	78°54′	2118	170	13.14	246	1.83
18	27 Jan 2010	70°37′	79°05′	2210	180	9.17	263	2.05
19	02 Feb 2010	69°33′	76°15′	580	23	28.05	155	0.33
20	02 Feb 2010	69°34′	76°17′	640	26	6.02	268	0.26
21	02 Feb 2010	69°38′	76°34′	884	35	9.07	199	1.16
22	02 Feb 2010	69°43′	76°43′	1036	45	6.08	292	0.38

n.a. denotes non availability of annual records due to the shorter cores (<60 cm) due to field constraints.
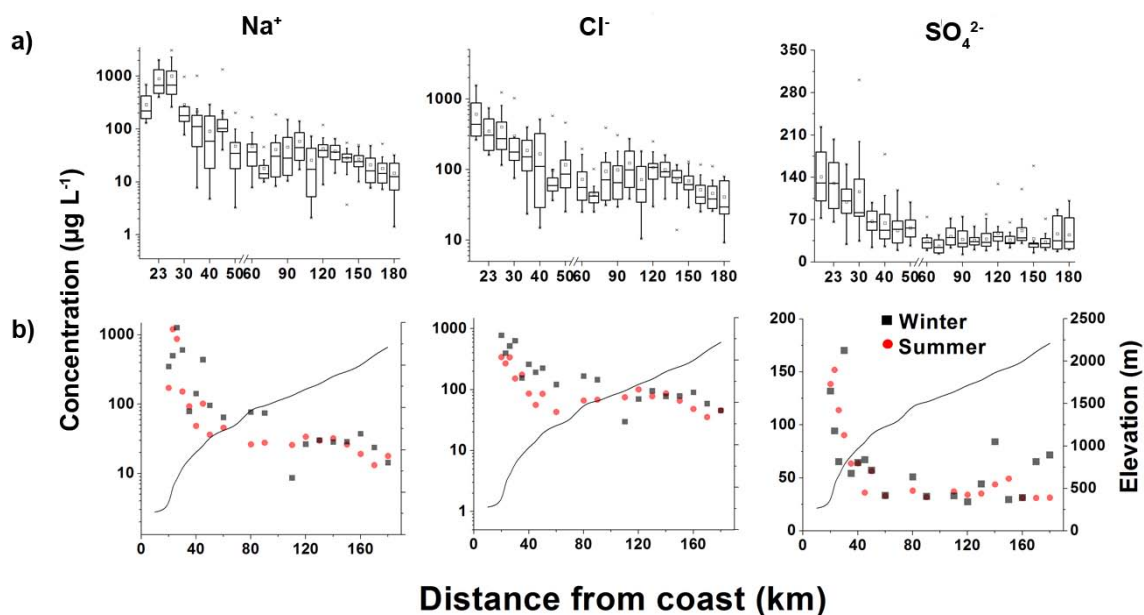

Fig. 3. (a) Spatial distribution and statistical variations in the annual concentrations of Na$^+$, Cl$^-$ and SO$_4^{2-}$ from coast to inland. Note the logarithmic scale for concentrations in Na$^+$ and Cl$^-$ plots. The square and the line inside the box represent mean and median, respectively; the whiskers outside the box represent the upper (99 %) and lower (1 %) quartiles and "x" denotes the outliers. Breaks in the x-axis show difference in sampling interval before and after 50 km. **(b)** The summer and winter concentrations of the respective sea-salt ions along with the elevation profile.

4 Discussion

4.1 Altitudinal influence on snow chemistry

Large changes in the elevation distinguished the coastal section from the rest of the transect with the altitude increasing from mean sea level to $\sim$1100 m within 50 km from the coast (Fig. 1). However, the concentrations were always higher than $100\,\mu g\,l^{-1}$ for both Na^+ and Cl^- up to 50 km, and decreased logarithmically thereafter (i.e. >1100 m altitude). The steepest zone of the escarpment was between 20 km and 30 km. Despite the differences in altitude between these locations (300 m and 795 m), the concentrations of Na^+ exceeded an average of $500\,\mu g\,l^{-1}$ throughout the year (Fig. 3a). Cl^- and SO_4^{2-}, on the other hand, did not show a similar trend in concentrations, resulting in high Na^+ concentration at specific sites within 1000 m altitude (Fig. 3a).

Previous studies have strongly correlated sea-salt chemistry variations with distance from the sea and elevation in Antarctica (Bertler et al., 2005). Correlation statistics from the present study revealed a strong negative correlation (> -0.83, 99 % confidence level) between the sea-salt ions and elevation (Table 3). Elevation showed a strong positive correlation (0.965, 99 % confidence level) with distance from the coast. A strong positive correlation existed between the sea-salt ion concentrations and slope (0.791, 99 % confidence level for Cl^-; 0.951, 99 % confidence level for Na^+). A strong negative correlation also existed between slope and Cl^-/Na^+ ratio (-0.679, 99 % confidence level), a fact that has escaped the attention of previous glaciological studies in Antarctica.

To assess the spatial variations in snow composition from the coastal regions, where the marine influence is greater, it is necessary to determine the individual effects of altitude, distance from the coast as well as the slope variations on snow chemistry. It is clear from Fig. 3 that despite the rapid changes in elevation of $\sim$1100 m, the ion concentrations were always higher than $100\,\mu g\,l^{-1}$ for Na^+ and Cl^-. Previous glaciological studies at higher altitudes of peninsular Antarctica showed that concentrations could reach higher orders because of the influence of the marine air mass (Bertler et al., 2005). For instance, maximum concentrations of 350 and $240\,\mu g\,l^{-1}$ for Na^+ and Cl^- were measured in the ice cores from James Ross Island, at altitudes >1500 m due to the closeness to the sea (Aristarain and Delmas, 2002). To further determine the influence of altitude on sea-salt snow chemistry in the present study, multiple regression was carried out with slope, distance from the sea and elevation as variables affecting the Cl^-/Na^+ ratio (Table 4). Results revealed that only about 41 % of variation in Cl^-/Na^+ ratio attributed to the combining effects of elevation and distance from the coast, whereas 62 % of variation occurred due to combining effect of slope and distance from the coast. Therefore, very high concentrations of Na^+ and Cl^- ($>1000\,\mu g\,l^{-1}$) in the coastal section ($\sim$1100 m altitude)

could be attributed to the influence of sea-salt rich marine air-mass. Altitudinal variations by itself may not have an important role in the sea-salt concentrations in the snow, at least in the coastal sections where the marine influence is strong. However, the spatial variations of sea-salt chemistry in snow from these steep slopes could be attributed to the highly varying slopes in the present study region.

4.2 Cl^- and Na^+ variability in the coastal region

As a result of large variations in sea-salt concentrations up to $\sim$1000 m altitude, the Cl^-/Na^+ ratio in snow reduced significantly with respect to the bulk sea water ratio. Previous studies on East Antarctic snow have shown that post-depositional loss of Cl^- from snow pack in the form of HCl could result in a reduced Cl^-/Na^+ ratio (Wagnon et al., 1999). However, Traversi et al. (2004) suggested that post-depositional loss of HCl by the above means is strongly dependent on snow accumulation rates. Röthlisberger et al. (2003) showed that the post-depositional loss of HCl in snow becomes significant only below a threshold accumulation rate of $40\,kg\,m^{-2}\,yr^{-1}$. Also, Benassai et al. (2005) have reported a threshold of $80\,kg\,m^{-2}\,yr^{-1}$ from another East Antarctic site. The snow accumulation rates in the present study ranged between 135 and $389\,kg\,m^{-2}\,yr^{-1}$, well above these threshold limits, suggesting a negligible post-depositional loss of HCl from the snow pack.

Chloride depletion also occurs by the reaction between atmospheric acids and sea-salt aerosols, leading to the formation of HCl in the gas phase, thereby lowering Cl^-/Na^+ ratios in snow (Legrand and Delmas, 1984). The values of Cl^-/Na^+ ratios thus depend on the availability of atmospheric acids during different seasons. A few studies with year-round measurements of sea-salt aerosols have shown that Cl^- depletion occurs predominantly during the summer months in coastal Antarctica (Kerminen et al., 2000; Jourdain and Legrand, 2002). The chloride depletion is less significant in winter, owing to the reduced atmospheric acidity at this time (Jourdain and Legrand, 2002). The seasonal variations of Cl^-/Na^+ from bulk aerosol studies suggest that Cl^- depletion takes place during the months of November and December (Jourdain and Legrand, 2002), when higher atmospheric H_2SO_4 concentrations scavenge the sea-salt aerosols. In the present study, the lowest Cl^-/Na^+ values occurred specifically within 50 km in the zone of steep coastal escarpment (Fig. 4). The steepest slope ($49.2\,m\,km^{-1}$) was observed between 20 km and 30 km and the snow samples from this section showed the strongest depletion in Cl^-. Seasonal averages revealed a relatively lower Cl^- concentration than Na^+ during summer (Table 2). This pattern continued consistently even in the winter concentrations, resulting in low Cl^-/Na^+ ratios throughout the year. This suggests that the sea-salt modifications in the coastal sections of Antarctic snow are more likely dependent on an invariable physical feature like the coastal escarpment.
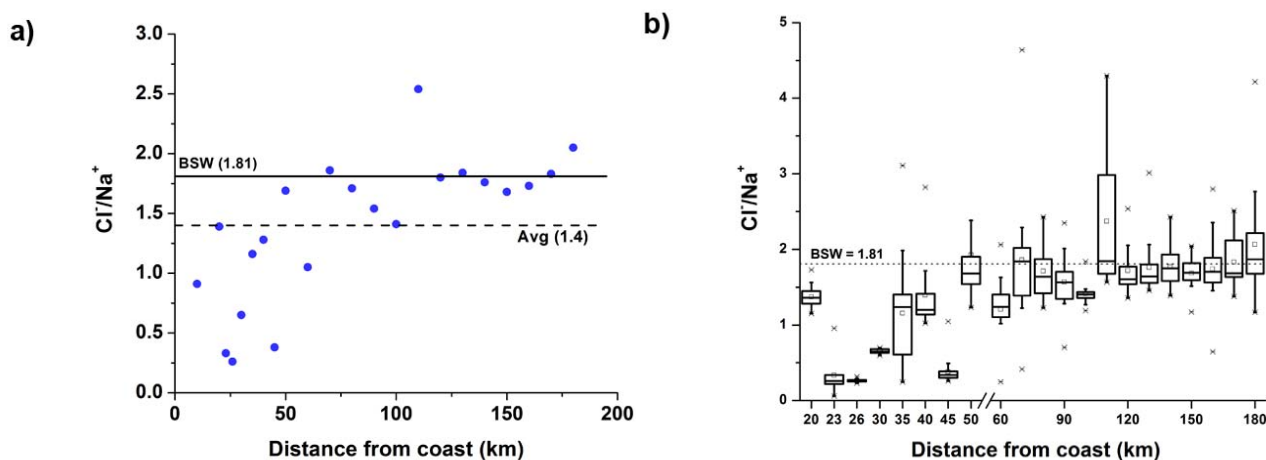
Fig. 4. (a) Average annual Cl^-/Na^+ ratios from coast to inland. The dashed line is the annual average Cl^-/Na^+ ratio along the entire transect and the solid line is bulk sea water (BSW) ratio. **(b)** Seasonal variability in Cl^-/Na^+ ratios from the entire transect. Please note the break in scale along the x-axis.

Table 2. Seasonal and annual average concentrations of Na^+, Cl^- and SO_4^{2-} in snow from the steep escarpment of the transect.

Distance (km)	Na^+ ($\mu g\,l^{-1}$)			Cl^- ($\mu g\,l^{-1}$)			SO_4^{2-} ($\mu g\,l^{-1}$)		
	Summer	Winter	Annual	Summer	Winter	Annual	Summer	Winter	Annual
20	172.45	349.32	285.01	342.28	778.70	620.00	138.67	131.99	134.42
23	1211.37	502.21	899.26	269.80	396.12	350.98	151.99	94.42	130.46
26	877.88	1275.35	1030.75	339.02	519.28	408.35	114.03	65.45	95.34
30	152.82	606.41	304.02	152.37	634.37	313.04	90.43	170.25	117.04
35	93.42	79.25	91.55	176.40	155.40	175.55	63.73	54.36	61.78
40	48.65	142.51	99.28	86.31	260.07	181.49	63.92	64.64	62.48
45	101.93	439.80	228.63	56.34	192.85	107.53	36.26	67.29	47.89
50	36.37	95.96	54.04	85.58	226.18	128.14	56.55	57.28	57.43

In addition to the sea-spray, the main factor influencing the Na^+ in snow is the input of non-sea-salt Na^+ (nssNa^+) fraction from the ice-free coasts, exposed nunataks or crustal dust transported over long ranges from other continents. Na^+ in snow is not known to undergo any post-depositional changes and therefore considered as a conservative species. However, larger input of nssNa^+ tends to increase the total Na^+ content in the snow, thereby lowering the Cl^-/Na^+ ratio with respect to the bulk seawater ratio. Snow samples from the steeper parts of the coasts in the present study showed a relatively higher Na^+ content than Cl^-, indicating a possible Na^+ enrichment. The sea-salt Na^+ content in the snow was obtained by subtracting the crustal contribution from the total Na^+ concentration, calculated on the basis of Ca^{2+} concentration in snow. Results revealed that the majority of the Na+ content (>85 %) in the coastal snow was of marine origin. A per-sample basis statistical evaluation of snow concentration from the steep slopes showed a strong positive correlation (0.86, 99 % confidence level) between Na^+ and Cl^-, indicating the common sea-salt source for these ions. Also, no

sources of crustal sodium (nssNa^+) were present in the vicinity of the transect that could significantly contribute to the Na^+ concentration in snow. A significant positive correlation (0.590, 95 % confidence level) indicates a possible relation between the Na^+ concentration and slope along the transect. It is more likely that the Na^+ in snow is redistributed on the steep coastal slopes, possibly during wind scouring, resulting in a high concentration.

4.3 Influence of slope on snow chemistry

In order to better understand the sea-salt modification processes in the present study, a distance versus elevation plot was sectioned into three distinct zones based on the average slope and the modification of sea-salt composition in snow (Fig. 5). Considering that the dominant Cl^- liberation processes are related to the interaction of sea-salt with the atmospheric H_2SO_4 and Na-Cl-SO_4, ternary plots with composition of snow samples from the transect are presented from the respective zones with reference to the seawater (S), frost flower (F) and mirabilite (M) compositions (Fig. 5).

Table 3. Correlation coefficients (r) between the site specific features and Na^+ and Cl^- ions. Correlations are based on annual ion concentration data. Values marked with [a] and [b] represent correlations that are significant at 95 % and 99 % respectively.

	Distance from sea	Elevation	Slope	Cl^-	Na^+	Cl^-:Na^+
Distance from sea	1	0.963[b]	−0.468[a]	−0.679[b]	−0.721[b]	0.642[b]
Elevation		1	−0.452	−0.841[b]	−0.833[b]	0.629[a]
Slope			1	0.212	0.590[a]	−0.676[b]
Cl^-				1	0.902[b]	−0.468
Na^+					1	−0.686[a]
Cl^-:Na^+						1

Table 4. Multiple regression model summaries explaining the percentage of Cl^-/Na^+ variability attributed to the physical parameters. Model 1 shows the variance due to slope entered in the regression equation followed by distance from sea and elevation while model 2 shows the variation due to elevation, followed by distance from sea and slope.

	Model	Cl^-:Na^+	
		R	Variance (%)
1	Slope	0.685	47.0
	Slope, distance from sea	0.787	62.0
	Slope, distance from sea, elevation	0.796	63.3
2	Elevation	0.629	39.6
	Elevation, distance from sea	0.643	41.3
	Elevation, distance from sea, slope	0.796	63.3

The dotted line joining the "S" and the SO_4^{2-} summit represents the typical tropospheric process of sea-salt aerosol scavenging by the atmospheric H_2SO_4, leading to the liberation of volatile HCl into the atmosphere (Legrand and Delmas, 1984). The area between the "S" and the SO_4 summit also suggests that the composition of sea-salt is modified by the chloride depletion reactions with Cl^- loss or gain, represented below or above the line, respectively. The snow samples beyond 50 km inland showed typical chloride depletion signatures, owing to the H_2SO_4 fluctuations in the atmosphere (Fig. 5b and c) with samples from the summer period closer to the SO_4 summit, indicating predominant H_2SO_4 scavenging. However, the ternary plot representing samples from the steep faces of the escarpment (~1100 m altitude) showed strong fractionation of sea-salt, resulting in compositions enriched with Na^+ at specific segments between 20 km and 50 km (Fig. 5a). This plot also reveals a strong depletion of Cl^- and SO_4^{2-} in samples specifically from 23 km, 26 km and 45 km (pink, green and red circles, Fig. 5a). At 30 km (maroon circles), the snow samples showed a cyclic variation with respect to SO_4^{2-} summit (H_2SO_4 scavenging), along with a constant fractionation of Cl^- with respect to Na^+.

Even though variations in slope of the Antarctic ice sheet surface are known to cause significant impact on the wind processes and the snow accumulation rates, its impact on

snow chemistry variations are the least studied. Frezzotti et al. (2002) have shown that even the smallest changes on the surface slope (~4 m km^{-1}) had a strong impact on the wind speed and direction. Richardson-Näslund (2004) had linked the large spatial variations in snow accumulation rates and the impact of katabatic winds, a unique wind system in the coastal Antarctica. The katabatic winds are remarkably uniform and the strongest of these winds are known to occur in the steep coastal sections of Antarctica (King and Turner, 1997). They are typically under-saturated in sea-salt aerosol as it blows from the higher inland plateau towards the coast (Wendler et al., 1993) and occur in the lowermost tens or few hundreds of meters (Barry, 2008; Argentini et al., 1996) above the surface. However, the influence of the surrounding ocean occurs on a much larger scale, enveloping the coastal region with warm, sea-salt rich and moist air mass.

The convergence of two opposing air masses with distinct temperature and moisture characteristics could result in a localized frontal wedging, especially over the steep coastal escarpments. Depending on the meteorological conditions, the sea-salt aerosols could either be scavenged by the precipitation and wet deposited or directly dry deposited over the snow surface. High annual accumulation rates with an average of 270 kg m^{-2} yr^{-1} between the coast and 50 km suggests that the large amounts of sea-salt aerosols could be washed out of the atmosphere by the precipitating snow. Also, the sea-salt aerosols are known to be hygroscopic and are deliquesced at high relative humidity conditions (60 %–70 %) before depositing on the snow surface. Studies by Ma et al. (2010) showed that high relative humidity conditions (60 %–80 %) existed in the steep escarpment region of Princess Elizabeth Land. Alternatively, when conditions do not favour precipitation, the marine air mass rich in sea-salt aerosols could be intercepted by the steep faces of the escarpment, which would result in turbulence-induced dry deposition of sea-salt particles. Thus, relatively high Na^+ and Cl^- concentrations over the steep faces of the coastal escarpment (Fig. 3) could be due to the preferential wet or dry deposition of sea-salt aerosols by the above deposition mechanisms. However, concentrations of Na^+ exceeded (up to four times) the Cl^- concentrations at specific locations (23, 26 and 45 km) in the steep escarpment throughout the
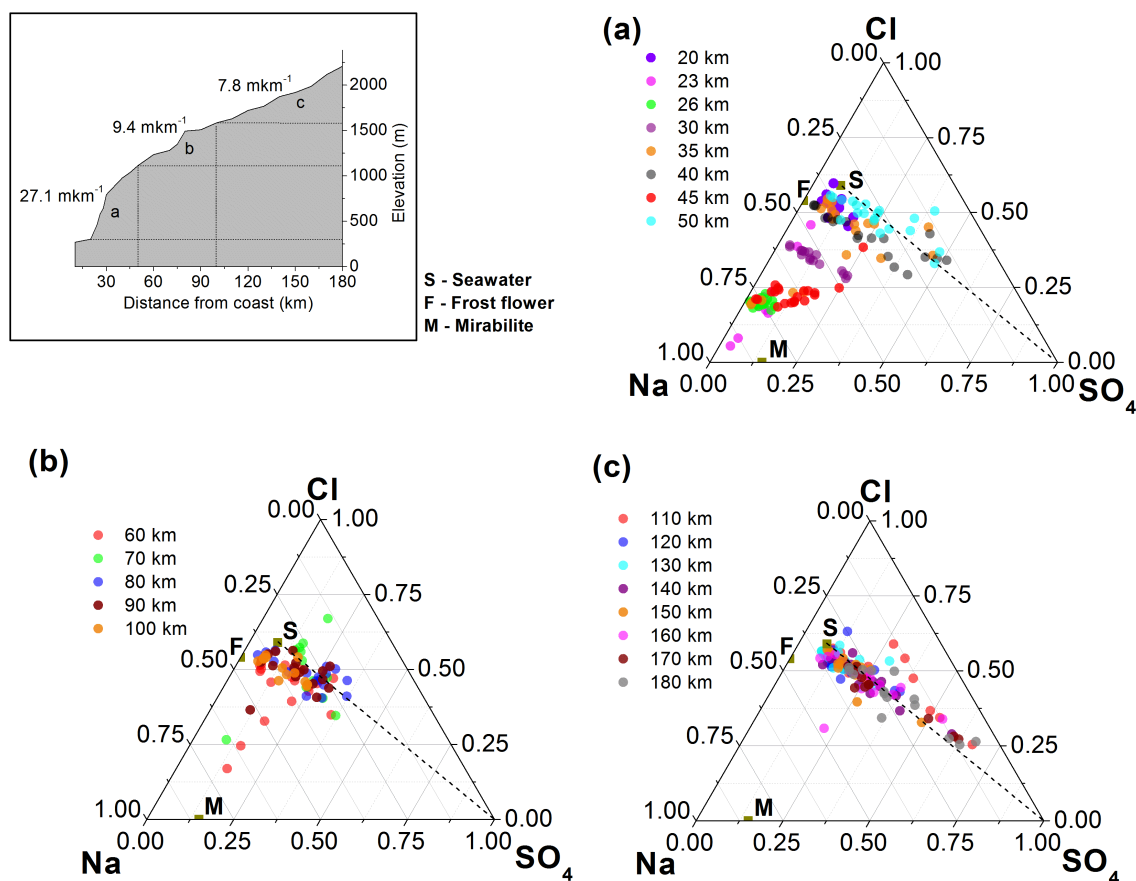
Fig. 5. Plot showing sea-salt modifications with respect to reference seawater (S) in snow samples from coastal **(a)**, midway **(b)** and the interior **(c)** of the transect. Inset on the top left shows changes in the elevation and slope along the transect. See text for details.

year (Table 2). The variability of Na^+ concentration could be attributed to the wind induced redistribution of snow over the steep slopes, during which Cl^- is lost due to its reaction with the atmospheric acids. Unlike Cl^-, Na^+ does not undergo any reaction with the atmospheric acids, thereby getting accumulated (due to continuous sea-salt inputs) and redistributed (due to wind scouring). This fact is evidenced by a positive correlation (0.590, 95 % significance) existing between slope and only Na^+ concentration (since Cl^- is lost during wind redistribution). The varying slope angles and the slope heights are known to affect the katabatic wind strengths (Frezzotti et al., 2002; Vihma et al., 2011) and we propose that the large differences in the slope variations of the coastal escarpment (Table 1) could significantly attribute to the wind redistribution and, in turn, the chemistry of deposited snow.

In the coastal part of Antarctica, most of the sea-salt aerosols are generated from the sea spray due to bubble bursting in the open ocean. However, studies have shown that during winter, a significant amount of sea-salt aerosols are generated from the frost flowers formed on the sea-ice surface (e.g. Wagenbach et al., 1998; Rankin et al., 2000). Sea-salt fractionation is apparent during the sea-ice formation, during

which the highly saline brine or the frost flowers on the ice surface generate fractionated sea-salt aerosols. Multi-year sea ice data (Spreen et al., 2008) showed the presence of dominating sea-ice cover in the adjacent oceans of Princess Elizabeth Land for a major part of the year except summer (December–February). The ternary plot (Fig. 5a) reveals a strong depletion of SO_4^{2-} relative to the sea water, specifically at 23 km, 26 km and 45 km (pink, green and red circles, respectively). The strong depletion of SO_4^{2-} and Na^+ is associated with the aerosols generated from the brine after the precipitation of mirabilite ($Na_2SO_4 \cdot 10\,H_2O$) below $-8\,°C$. The non-sea-salt SO_4^{2-} ($nssSO_4^{2-}$) concentrations, calculated with Na^+ as the sea water reference species using the expression $nssSO_4^{2-} = (SO_4^{2-})_{snow} - 0.121\,(Na^+)_{snow}$, showed negative values on the steep escarpments on the coast. The negative $nssSO_4^{2-}$ generally implies a fractionated sea-salt source originating from the frost flowers during winter conditions (e.g. Wagenbach et al., 1998; Rankin and Wolff, 2002). Negative $nssSO_4^{2-}$ concentrations do not exist when the sea-salt aerosols are generated from the open ocean and when additional $nssSO_4^{2-}$ from biogenic sources is added to the SO_4^{2-} in snow. However, in the present

study, negative $nssSO_4^{2-}$ existed throughout the year, including summer conditions. Wagenbach et al. (1998) associated the most negative $nssSO_4^{2-}$ with high sea-salt concentrations in coastal Antarctica, which tend to give an overestimated fractionation factor. High concentrations of Na^+ affected the $nssSO_4^{2-}$ calculations since the $nssSO_4^{2-}$ value represents a small difference between two large numbers (Maupetit and Delmas, 1992). Therefore, the negative $nssSO_4^{2-}$ values are more likely attributed to the extremely high Na^+ concentrations (ranging between 100 and $1300 \, \mu g \, l^{-1}$) in this region. When $nssSO_4^{2-}$ was calculated using Mg^{2+} (since it precipitates below $-34\,°C$ and occurs at much lower concentrations than Na^+ in sea water) as the sea water reference species, using the expression $nssSO_4^{2-} = (SO_4^{2-})_{snow} - 1.05 \, (Mg^{2+})_{snow}$, the negative $nssSO_4^{2-}$ values were present only in the winter snow.

5 Conclusions

The present study, using annual snow core records from the coast to inland transect in Princess Elizabeth Land, revealed significantly low Cl^-/Na^+ ratios within 50 km from the coast. These sites are also characterized by a steep slope that decreases significantly inland. Strong correlation between slope and Cl^-/Na^+ ratio suggests a predominant influence of slope on sea-salt chemistry of snow. Seasonal patterns revealed that Cl^- concentrations were significantly lower than that of Na^+ on the steep zones throughout the year. The maritime air masses and the katabatic winds strongly interact in the coastal Antarctic regions, with the steep coastal slopes aiding in preferential deposition of sea-salt aerosols in snow. The wind redistribution of snow, influenced by the slope variations increasing the Na^+ concentration, thereby lowers the Cl^-/Na^+ ratios, and a possible overestimation of sea-salt fractionation along the steep slopes. We propose that higher concentrations of Na^+ with Cl^- loss in snow are primarily driven by the steep slopes of coastal Antarctica. A combination of field measurements in snow and the aerosol would reveal more insight into this mechanism on the coastal regions across Antarctica.

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