Brief communication: Spatial and temporal variations in surface snow chemistry along a traverse from coastal East Antarctica to the ice sheet summit (Dome A)

Guitao Shi[1,2], Hongmei Ma[2], Zhengyi Hu[2], Zhenlou Chen[1], Chunlei An[2], Su Jiang[2], Yuansheng Li[2], Tianming Ma[2], Jinhai Yu[2], Danhe Wang[1], Siyu Lu[2], Bo Sun[2], and Meredith G. Hastings[3]

[1] Key Laboratory of Geographic Information Science (Ministry of Education), School of Geographic Sciences and State Key Lab of Estuarine and Coastal Research, East China Normal University, Shanghai 200241, China

[2] Polar Research Institute of China, Shanghai 200062, China,

[3] Department of Earth, Environmental and Planetary Sciences and Institute at Brown for Environment and Society, Brown University, Providence, Rhode Island 02912, USA.

*Correspondence to: G Shi (gtshi@geo.ecnu.edu.cn)

Abstract

To better understand snow chemistry in different environments across the Antarctic ice sheet, we investigated snow ions on a traverse from coast to Dome A. Results show that the non-sea-salt (nss) fractions of K^+, Mg^{2+}, and Ca^{2+} are mainly from terrestrial particle mass, and $nssCl^-$ is associated with HCl. Spatially, the proportions of non-sea-salt fractions of ions to the totals are higher in the interior areas than on the coast, and seasonally, the proportions are higher in summer than in winter. Negative $nssSO_4^{2-}$ on the coast indicates sea salts from the sea ice, and marine biogenic emissions dominate snow SO_4^{2-} in interior areas throughout the year. There is a large variability in environmental conditions across the Antarctic ice sheet, and it is of significance to investigate the snow chemistry at as many locations as possible and over time, given that the ice sheet itself, and precipitation and deposition patterns and trends are changing. The China inland Antarctic traverse from coastal Zhongshan Station to the ice sheet summit (Dome A) covers a variety of environments, allowing for a vast collection of snow chemistry conditions across East Antarctica. Surface snow (the upper ~ 3 cm, mainly representing the summertime snow) and snow pit samples were collected on this traverse during five campaigns, to comprehensively investigate the spatial and temporal variations in chemical ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and the related controlling factors. Results show that spatial patterns of ions in surface snow are consistent among the five campaigns, with Cl^-, Na^+, K^+, and Mg^{2+} decreasing rapidly with distance from the coast and NO_3^- showing an opposite pattern. No clear spatial trends in SO_4^{2-}, NH_4^+, and Ca^{2+} were found. In the interior areas, an enrichment of Cl^- versus Na^+ with respect to seawater composition is ubiquitous as a result of the deposition of HCl, and $nssCl^-$ (nss, non-sea-salt fraction) can account for up to ~ 40 % of the total Cl^- budget, while $nssK^+$ and $nssMg^{2+}$ are mainly associated with terrestrial particle mass. On average, $nssCa^{2+}$ and $nssSO_4^{2-}$ in surface snow account for ~77 and 95 % of total Ca^{2+} and total SO_4^{2-}, respectively. The high proportions of the non-sea-salt fractions of Ca^{2+} and SO_4^{2-} are mainly related to terrestrial dust inputs and marine biogenic emissions, respectively. Snow NH_4^+ is mainly associated with marine biological activities, with slightly higher concentrations in summer than in winter. On the coast, parts of the winter snow are characterized with negative $nssSO_4^{2-}$ values, and a significant negative correlation between $nssSO_4^{2-}$ and Na^+ in wintertime snow was found, suggesting that sea salts originated from the sea ice. In the interior areas, marine biogenic SO_4^{2-} still dominated snow SO_4^{2-} in winter, leading to significant positive $nssSO_4^{2-}$ values. Ion flux assessment suggests an efficient transport of $nssSO_4^{2-}$ to at least as far inland as the ~2800 m contour line.

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1 Introduction

Snow chemistry has been broadly investigated along traverses during the International Trans-Antarctic Scientific Expedition (ITASE), e.g., DDU to Dome C, coast-interior traverse in Terre Adelie, Syowa to Dome F, Terra Nova Bay to Dome C, 1990 ITASE, and US ITASE in West Antarctica (Legrand and Delmas, 1985; Qin et al., 1992; Mulvaney and Wolff, 1994; Proposito et al., 2002; Suzuki et al., 2002; Dixon et al., 2013), and Bertler et al. (2005) has comprehensively summarized the glaciochemical data across the ice sheet, most of which are for surface snow. Among the major ions, sea salt related ions (e.g., Na^+ and Cl^-), in general, are the most abundant species, and typically exhibit a clear spatial trend, with concentrations falling off sharply with distance from the coast. ~~Acidic ions such as nitrate and sulfate (NO_3^- and SO_4^{2-}) are typically also abundant ionic species in snow, both of which can be deposited as salts in aerosols, and as gaseous acids. SO_4^{2-} in the snow is mainly from marine biogenic sulfur species, dimethylsulphide (DMS) (Legrand, 1995; 1997), with a small proportion from sea salt aerosols, while large volcanic eruption emissions can episodically contribute to spikes in SO_4^{2-} concentration (Legrand and Delmas, 1987; Jiang et al., 2012; Cole-Dai et al., 2013). Sources of NO_3^- are sometimes complicated to identify, due to the post-depositional processing after deposition into the snowpack (e.g., photolysis and volatilization) (e.g., Neubauer and Heumann, 1988), and stratospheric input and tropospheric transport from mid-low latitudes have been proposed to be important sources (Legrand and Kirchner, 1990; Savarino et al., 2007; Lee et al., 2014; Shi et al., 2018a). As for calcium (Ca^{2+}) in snow, both long range transport of terrestrial particle mass and sea salt aerosols are important sources, and Ca^{2+} in ice cores recovered from interior areas is more likely associated with terrestrial inputs (e.g., Wolff et al., 2006). Terrestrial sources can also contribute to potassium (K^+) and magnesium (Mg^{2+}) in snow, but the contribution proportion varies significantly among sites (Legrand et al., 1988; Khodzher et al., 2014). In comparison with the other species, ammonium (NH_4^+) in snow has been rarely investigated due to the low concentration, and biogenic emissions in the Southern Ocean and/or mid-latitude biomass burning were proposed to be the major sources, depending on the investigation sites (Legrand et al., 1999; Pasteris et al., 2014). In summary, source identification of ions in Antarctic snow and ice has been conducted intensely, however, the site- and area-specific investigations are needed.~~

Temporally, ~~W~~with varied sources and lifetimes, ions in snow often exhibit different seasonal variations, e.g., sea salt related ions show high concentrations in winter, while elevated concentrations of SO_4^{2-} and NO_3^- are frequently observed in summer (Neubauer and Heumann, 1988; Gragnani et al., 1998; Traversi et al., 2004; Shi et al., 2015). ~~Indeed, these ions are frequently taken as seasonal markers for snow pit and ice core dating.~~ On annual to decadal time scales, ion concentrations in snow and ice tend to be associated with changes in transport from year to year (Severi et al., 2009; Weller et al., 2011), and thus large scale atmospheric and oceanic circulation in the Southern Hemisphere~~, such as the Southern Annular Mode (SAM), Southern Oscillation (SO) and Southern Indian Ocean Dipole (SIOD),~~ could potentially influence variations ~~in ions in ice~~snow and ice chemistry (Russell and McGregor, 2010; Weller et al., 2011; Mayewski et al., 2017). ~~In addition, sea ice coverage around Antarctica plays an important role in variations in ions, and larger sea ice coverage is linked with higher sea salt concentrations, as well as non-sea salt SO_4^{2-} ($nssSO_4^{2-}$) concentrations in ice, particularly over glacial-interglacial time scales (Kaufmann et al., 2010; Wolff et al., 2010; Abram et al., 2013). In addition to sources, lifetime, and transport processes, the preservation of ions are factors influencing concentrations in snow and ice, particularly the volatile species (e.g., NO_3^- and Cl^-). Post-depositional processes can result in significant losses of volatile species in snow, particularly at~~

~~sites with low snow accumulation rate (e.g., East Antarctic plateau) (Wagnon et al., 1999; Sato et al., 2008; Shi et al., 2015).~~

~~In summary, spatial and temporal variations in snow chemistry are influenced by a variety of factors, and further observations of ions in snow are needed to determine the controlling factors for particular times and places.(Shi et al., 2015)~~

Although investigations of snow chemistry have been carried out along several overland traverses, the investigation of snow chemistry under different environmental conditions and over time is needed, given that the Antarctic ice sheet itself, and precipitation and deposition patterns and trends are changing. The China inland Antarctic traverse from coastal Zhongshan Station to the ice sheet summit (Dome A) covers a range of environments (~1250 km), e.g., high snow accumulation rate is present on the coast and in some interior areas, and low accumulation rate is observed on the Dome A plateau~~, and thus provides further opportunity to investigate snow chemistry and its main controlling factors in different environments.~~ . Several investigations have been carried out to determine the concentrations ~~and spatial patterns~~ of a few ionic species and trace elements on the traverse (e.g., Li et al., 2016; Du et al., 2019), but limited snow chemistry data were previously available. ~~Additionally, the interannual variations in snow chemistry and the related controlling factors on the traverse are far from understood.~~ Therefore, we used surface snow and snow pit samples collected during five China inland Antarctic scientific expedition campaigns, to determine the spatial and temporal variations in a comprehensive set of ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) and their controlling factors. ~~This work also presents data on snow chemistry from a less documented area, particularly at Dome A, providing baseline values of snow ions and records of significance for evaluating potential changes in atmospheric chemistry over Antarctica under a warming climate.~~

2 Methods

2.1 Sample collection

Snow samples were collected along the traverse from the coast to the ice sheet summit during five Chinese National Antarctic Research Expedition (CHINARE) campaigns (Fig. S1). ~~In January 1999, 107 surface snow samples were collected on the traverse (from coast to the site ~1100 km from the coast; the Chinese inland traverse coverage did not extend to Dome A then).~~ In January ~~and~~ February in the years 1999, 2011, 2013, 2015, and 2016, 107, 120, 125, 117, and 125 surface snow samples were collected on the traverse, respectively. In total, 594 snow samples were collected during the five seasons. For the snow sampling protocols refer to Shi et al. (2018). It is noted that the surface ~3 cm snow represents different lengths of time at different locations, considering the wide range of snow accumulation rates on the traverse (Fig. ~~2~~1(a)). At locations with high snow accumulation rate on the coast, the upper 3 cm of snow may represent deposition from a few weeks or a single snowfall, while the surface 3 cm of snow could represent deposition over a few months on Dome A plateau. ~~Also, it is possible that the upper 3 cm of snow can be representative of a single snowfall.~~ Still, the information contained in the surface snow generally indicates summertime conditions, as the sampling took place during late January and February in each season. ~~This allows for an investigation of summer snow chemistry patterns on the traverse.~~

In addition to surface snow, snow pits were sampled in three representative areas on the traverse ~~(P1, P2, and P3; Fig. 1).~~ : P1, located on the coast (76.49 °E, 69.79 °S; 46 km from the coast), was sampled in December 2015; P2, located in the interior area (77.03 °E, 76.42 °S; 800 km from the coast), was sampled in January 2016; and P3, located on the Dome A plateau (77.11 °E, 80.42 °S; 1256 km from

the coast), was sampled in January 2010. Sites P1 and P2 are characterized with high snow accumulation rate (>100 kg m^{-2} a^{-1}), while snow accumulation rate at P3 is ~25 kg m^{-2} a^{-1}. The depths of P1, P2, and P3 are 180, 100, and 150 cm, respectively, with the respective sampling resolution of 5, 3, and 1 cm. Details on the snow pit sampling are described in Shi et al. (2015). ~~Snow pit samples were collected using the narrow-mouth HDPE bottles pushed horizontally into the snow wall from the bottom of the pit and moving upwards.~~

~~All of the bottles used for snow sampling were pre-cleaned with Milli-Q water (18.2 MΩ), dried in a class 100 super clean hood and then sealed in clean PE bags that were not opened until the field sampling started. During each sampling campaign, three pre-cleaned bottles filled with Milli-Q water taken to the field and treated to the same conditions as field samples represent field blanks. After collection, the bottles were again sealed in clean PE bags and preserved in clean expanded polypropylene boxes.~~ All snow samples were transported and stored under freezing conditions (~-20 ^{o}C).

2.2 Sample analysis

~~Snow samples were first melted in the closed bottles on a super clean bench (class 100) before chemical measurements.~~ In the class 100 room, about 5 ml of the melted sample was transferred to the pre-cleaned 8-ml ion chromatography (IC) autosampler vials, and then the lid was tightly screwed on to the vials. The samples were analyzed by an ICS-3000 IC system (Dionex, USA)~~IC~~ for the concentrations of ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}). ~~(Note that the IC was installed in a class 1000 clean room). The samples collected in 1999 were analyzed by using the DX-500 IC system (Dionex, USA), while the snow collected in the other campaigns were analyzed using an ICS-3000 IC system (Dionex, USA). The eluents for cations and anions were methanesulfonic acid (MSA) and potassium hydroxide (KOH), respectively.~~ More details on ~~this method~~ion determination are described in Shi et al. (2012). During sample analysis, replicate determinations (n = 5) were performed, and one relative standard deviation (1σ) for all eight ions was generally <5 %. ~~In addition, the pooled standard deviation ($1\sigma_p$) of all replicate samples run in at least two different sets was examined (n = 65) and yielded 0.020, 0.023, 0.038, 0.022, 0.039, 0.005, 0.008, and 0.005 μeq L^{-1} for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, respectively.~~

In Antarctic snow, previous observations suggested that concentrations of H^+ can be reasonably deduced from the ion-balance disequilibrium~~, if the direct measurements of H^+ are unavailable~~ (Legrand and Delmas, 1985; Legrand, 1987)~~: Here, H^+ concentration is calculated as follows.~~

$[H^+] = [SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+] - [NH_4^+] - [K^+] - [Mg^{2+}] - [Ca^{2+}]$ Eq. (1),

where ion concentrations are in μeq L^{-1}. In addition, the non-sea-salt fractions of ions (nssX), including $nssCl^-$, $nssSO_4^{2-}$, $nssK^+$, $nssMg^{2+}$, and $nssCa^{2+}$, can be calculated from the following expression,

$[nssX] = [X]_{snow} - ([X]/[Na^+])_{seawater} \times [Na^+]_{snow}$ Eq. (2),

where [X] is the concentration of ion X, and $[X]/[Na^+]$ ratios in seawater are 1.17 (Cl^-), 0.12 (SO_4^{2-}), 0.022 (K^+), 0.23 (Mg^{2+}) and 0.044 (Ca^{2+}) (in μeq L^{-1}). ~~The values of nssX are identical to the concentrations in excess with respect to the seawater composition in previous observations (e.g., Legrand and Delmas, 1985).~~

~~2.3 Principal component analysis (PCA) of ions~~

~~The essence of PCA is converting the observed variables into factors or principal components, so that a minimized set of underlying variables can be identified. Bartlett sphericity test and~~

~~Kaiser-Meyer-Olkin test indicated that the raw data (i.e., ion concentrations in surface snow) were suitable for PCA ($p<0.001$). Varimax with Kaiser normalization rotation was applied to maximize the variances of the factor loadings across variances for each factor. The regression method was selected for calculating the factor score coefficient. Three components with eigenvalue >1.0 were extracted. The loadings were obtained from the eigenvalues of the three components and their corresponding eigenvectors.~~

~~Because the samples collected in 1999 did not cover the whole traverse and the ion concentrations were determined using a different IC system, the ion data of 1999 were excluded in the PCA analysis in the following.~~

~~**(Bertler et al., 2005; Shi et al., 2015)**~~

3 Results

3.1 ~~Chemical i~~Ion variations in snow pits

Clear seasonal cycles of Na^+ and $nssSO_4^{2-}$ are present in P1 and P2, and thus the two pits can be well dated, spanning ~3 years (~~Figs. 3 (a) and (b)~~Fig. S2). ~~Based on the snow pit dating, it is estimated that snow accumulation rate is ~50 (P1) and ~33 cm snow per year (P2), agreeing well with the field measurements (P1: ~150 kg m^{-2} a^{-1}; P2: ~100 kg m^{-2} a^{-1}; Fig. 2(a)), assuming a snow density of ~0.33 g cm^{-3}. At P1, negative $nssSO_4^{2-}$ values are observed in winter snow, i.e., SO_4^{2-}/Na^+ ratio below that of bulk seawater, while all of the $nssSO_4^{2-}$ data in P2 pit are positive. It is difficult to assign the samples in the snow pits to the four distinct seasons based on the measured parameters, and thus, in the following discussion, we choose a conservative assignment method, i.e., a summer season featured with higher $nssSO_4^{2-}$ and SO_4^{2-}/Na^+ ratio (and lower Na^+) and a winter season characterized with the opposite patterns.~~ In addition to SO_4^{2-} and Na^+, the other species also show seasonal variations, especially ~~in pit~~in P1, where elevated levels of NO_3^- and NH_4^+ are generally present in summer ~~snow~~, and the ~~values~~ concentrations of Cl^-, K^+, Mg^{2+}, and Ca^{2+} are high in winter. ~~It is noted that even in the same season, ion concentrations could vary among samples at a single site (e.g., shaded areas in Figs. 3(a) and (b)).~~ As for $nssSO_4^{2-}$ at P3, the very large signal at the depth of ~120 cm is most likely the fallout from the massive eruption of Pinatubo in 1991 (Fig. S2~~Fig. 3(c)~~), based upon previous observations at Dome A (e.g., Hou et al., 2007). ~~Based on $nssSO_4^{2-}$ signals and the method proposed by Cole-Dai et al. (1997), 19 continuous samples have been identified as influenced by Pinatubo eruption, covering ~2.5 years, possibly suggesting that the effects of Pinatubo eruption on atmospheric chemistry lasted at least for 2.5 years over Dome A. Interestingly,~~It is noted that only elevated SO_4^{2-} concentrations are present during this period~~, and anomalous high or low concentrations of other ions are absent. Additionally, no correlation was found between $nssSO_4^{2-}$ and other species during the 2.5 years~~, possibly suggesting that Pinatubo volcanic emissions contribute less to the ion budgets other than SO_4^{2-} at Dome A. ~~Previous investigations proposed that Na^+ and $nssSO_4^{2-}$ in surface snow (top ~1 cm) collected during a full year at central Antarctica show clear seasonal cycles, with high (low) Na^+ in winter (summer) snow (Udisti et al., 2012). At P3, Na^+, $nssSO_4^{2-}$ and the ratios of SO_4^{2-}/Na^+ fluctuate significantly (Fig. 3(c)), and these contrasts are unlikely indicative of the seasonal cycles as that for P1 and P2. In a full year of snow accumulation at P3, on average, about 7-8 samples were collected, allowing for examining the seasonal variability of ions. Following the field measurements of snow accumulation rate at Dome A during 2008-2011 (~20 kg m^{-2} a^{-1}; Ding et al., 2015), the snow samples covering the years 2008 and 2009 can be roughly identified, assuming an even distribution of snow accumulation throughout the~~

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~~year. In total, there are 7 and 8 samples identified in the years 2008 and 2009, respectively (Fig. S1), and no seasonal cycles in Na^+, $nssSO_4^{2-}$, and SO_4^{2-}/Na^+ ratio were found due to the low snow accumulation rate at P3. In addition, the post depositional processes (e.g., migration, diffusion, and ventilation processes) and/or wind scouring can obscure the original signal, resulting in the absence of seasonal cycles of ions at P3.~~

In terms of the non-sea-salt fractions ~~in snow pits~~, $nssCl^-$ is lower at P1 (0.25±0.28 μeq L^{-1}) than at the inland sites P2 and P3 (0.42±0.18 and 0.58±0.34 μeq L^{-1}, respectively), while the concentrations of $nssK^+$, $nssMg^{2+}$, and $nssCa^{2+}$ generally show a similar spatial pattern~~s, possibly due to the low snow accumulation rate in interior areas~~. ~~Different from the sea salt ions and $nssSO_4^{2-}$~~ In general, $nssCl^-$, $nssK^+$, $nssMg^{2+}$, and $nssCa^{2+}$ in ~~pits. P1 and P2~~snow pits~~,~~ do not show ~~significant~~ clear seasonal ~~patterns~~cycles. ~~In the coastal pit P1, the non sea salt fractions account for less (<~30%) of the total ions, and the contribution percentages of non-sea-salt fractions increased at inland sites P2 and P3, about 30-70 %.~~

3.2 Ion concentrations in surface snow

Concentrations of ions in surface snow ~~collected during the five seasons~~ are shown in Fig. ~~2~~1, and the ~~ranges (mean) of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} are 0.15-14.6 (1.29), 0.48-12.6 (3.37), 0.37-5.63 (1.52), 0.09-12.74 (0.68), 0.04-0.77 (0.16), 0.01-0.27 (0.04), 0.11-2.76 (0.22), and 0.01-0.50 (0.13) μeq L^{-1}, respectively. These~~ values generally fall within the reported ranges of the ITASE program sampling (Bertler et al., 2005). ~~Ion concentrations are both spatially and temporally variable, with the coefficient of variation (ratio of one standard deviation over mean) of >0.48, suggesting a large variability across the traverse. In general, ion concentrations do not follow a normal distribution (p>0.05, One-Sample Kolmogorov-Smirnov Test), with the values of skewness and kurtosis above 1.0, but they correspond to a logarithmic normal distribution.~~ Spatially, Cl^-, Na^+, K^+, and Mg^{2+} show very high concentrations within the narrow coastal region, and decrease sharply further inland, with minimum values on the Dome A plateau (>~1000 km from the coast). It is noted that some samples on the coast also show elevated Ca^{2+} concentrations. The high ion concentrations near the coast may be associated with the strong marine air mass intrusions (Hara et al., 2014). NO_3^- shows an opposite spatial trend, with increasing values towards inland. As for SO_4^{2-} (and $nssSO_4^{2-}$), NH_4^+, and Ca^{2+}, no clear spatial trend was found.

Among the chemical ions in surface snow, the most abundant species is H^+, accounting for 30-40 % of the total ions, followed by NO_3^-, SO_4^{2-}, and Cl^-. In general, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} are the smallest component of the ionic composition, with the four cation summing to (6.0±3.4) % of the total (Fig. S3).

~~pH values of surface snow sampled in 2013 were measured with a glass pH electrode in a class 100 room at room temperature (~20°C), and H^+ concentrations deduced from pH are correlated well with the values calculated from the ion-balance method (Fig. 4(a)). On average, H^+ concentrations obtained from the ion balance approach are ~25 % lower than those deduced from pH. It is noted that pH measurements in this study remain uncertain considering that snow samples are highly undersaturated with respect to carbon dioxide (CO_2) immediately after melting in the lab. On the other hand, organic acids, e.g., monocarboxylic and methanesulfonic acids (MSA), were excluded in H^+ calculation (Eq. 1), although their concentrations in Antarctic snow tend to be very low. If the contribution of organic acids to H^+ in snow is negligible, the x-intercept of ~2.4 μeq L^{-1} in the linear regression (Fig. 3(a)) can be regarded as the contribution from dissolved CO_2 in snow during pH measurements. This value is close to that of pure water in equilibrium with CO_2 in the atmosphere, with pH=5.6 corresponding to H^+~~

concentration of ~2.5 μeq L^{-1}. Here, the calculated H^+ concentrations vary in the range of 0.51-10.01 μeq L^{-1}, with a mean of 3.53±1.61 μeq L^{-1}. In general, the calculated H^+ values of the coastal surface snow are generally comparable to previous direct measurements in Terre Adelie.

3.3 Spatial patterns of ions in surface snow

The spatial distribution patterns of ions on the traverse are consistent among the five campaigns (Fig. 2). In general, Cl^-, Na^+, K^+, and Mg^{2+} show very high concentrations within the narrow coastal region, and decrease sharply further inland, with low values on Dome A plateau (~1000-1250 km from the coast). It is noted that some samples on the coast also show elevated Ca^{2+} concentrations. The spatial patterns are consistent with previous observations, and the high ion concentrations near the coast have been explained by the strong marine air mass intrusions.

Different from other species, NO_3^- concentrations near the coast are low, and increase towards inland, with the highest values on the Dome A plateau. A significant correlation is found between NO_3^- and distance from the coast, with $r = 0.56$ and $p < 0.001$. The spatial trend of NO_3^- is generally opposite to that of snow accumulation rate on the traverse (Figs. 2(a) and (c)), possibly associated with post-depositional cycling of NO_3^- in surface snow. Similarly, there is a close relationship between H^+ and distance from the coast ($r = 0.48$, $p < 0.001$), suggesting a higher acidity of inland snow. As for SO_4^{2-} (and $nssSO_4^{2-}$), NH_4^+, and Ca^{2+}, no clear spatial trend was found on the traverse.

It is noted that the surface snow mainly represents the summertime deposition (section 2.1), and therefore the spatial patterns of ions here can only indicate summertime conditions. In addition, the spatial variations of ions in surface snow may arise from the temporal changes in chemical ions, considering that the upper ~3cm corresponds to deposition over different time at varied locations.

Previous investigations of ions in surface snow covered various depths among different traverses or campaigns, e.g., 1.0 m deep layer for the traverse from Terra Nova Bay to Dome C and top 25 cm snow for the 1990 ITASE. It is noted that different sampling depths can result in varied ion concentrations in snow. For instance, in inland Antarctica, NO_3^- is often concentrated on the top few-centimeter snow, and decreases significantly with increasing depth. Thus, any comparison of ion concentrations in surface snowpack collected from different campaigns should be made with caution.

The percentages of each constituent to the total ions in surface snow on the traverse are shown in Figs. 4(b)-(d). The most abundant species is H^+, accounting for about 30-40 % of the total ions, followed by NO_3^-, SO_4^{2-}, and Cl^-. In general, ions NH_4^+, K^+, Mg^{2+}, and Ca^{2+} are the smallest component of the ionic composition, with the four cation summing to ~5 % of the total. Spatially, the contribution percentages of H^+ and NO_3^- increase with increasing distance from the coast, with the highest values on Dome plateau (42.3 and 34.5 %, respectively), while Cl^-, Na^+, Mg^{2+}, and NH_4^+ show an opposite pattern and no clear trend was observed for SO_4^{2-}. The high contribution percentage of H^+ is consistent with previous investigations, and suggests acidic characteristics of summertime surface snow.

(Bertler et al., 2005; Erbland et al., 2013)

4 Discussions

4.1 Non-sea-salt fractions of ions in surface snow

The positive (negative) nssX values indicate the enrichment (depletion) of an ion with respect to the seawater composition. In surface snow, the non-sea-salt fractions of Cl^-, SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+} are 0.51±0.44, 1.44±0.84, 0.03±0.02, 0.08±0.06, and 0.09±0.08, respectively. In the following, we will discuss the non-sea-salt fractions of ions in surface snow by plotting the ions versus Na^+.

Correlation plots of ions versus Na^+ in surface snow are shown in Fig. ~~5~~2~~, and the plots above (below) the seawater dilution line represent the enrichment (depletion) of the ions. The further the plots deviate away from the line, the higher degree of enrichment or depletion of the ions~~. On the coast, most of the Cl^-/Na^+ data are distributed close to the seawater dilution line (Fig. 22(a))~~, indicating a quantitative sea salt tracer of snow Cl^-, while most of the plots in the interior areas are above the seawater line, suggesting an enrichment of ~~snow~~ Cl^-. ~~On this traverse,~~ $nssCl^-$ accounted for ~~an average of 38~~ (39±24) % of ~~total~~ Cl^- on the traverse, with ~~lower (~~higher~~) percentages~~ values ~~on the coast (plateau~~in the interior areas~~), generally in line with previous reports (e.g., Suzuki et al., 2002)~~. The elevated fractions of $nssCl^-$ are likely associated with the 'secondary' HCl which is produced by the reactions between sea salts and acids (e.g., HNO_3 and H_2SO_4)~~The modifications in Cl^- with respect to bulk seawater can occur via the heterogeneous reactions, as follows~~ (Finlayson-Pitts, 2003).

~~$NaCl + H_2SO_4 = HCl + Na_2SO_4$ (R1)~~

~~$NaCl + HNO_3 = HCl + NaNO_3$ (R2)~~

~~In the atmosphere, the production of HCl will result in depletion of Cl^- in sea salt aerosol. The 'secondary' HCl, in the gas phase and/or fine aerosol mode, can be transported further inland due to the longer lifetime (versus the coarse sea salt aerosols removed preferentially from the atmosphere). In this case, an enrichment of Cl^- would be expected in the inland snowpack. On the other hand, Cl^- is not irreversibly deposited to the snow, and it can be released back into the atmosphere through the formation of HCl, resulting in an enrichment of Cl^- in surface snow via re-deposition. Post depositional losses of HCl are thought to be associated with snow accumulation rate, with larger losses occurring at sites with snow accumulation generally <40 kg m^{-2} a^{-1}. Indeed, a negative correlation was found between snow accumulation and $nssCl^-$ (Fig. 6(a)) for most interior areas that featured low snow accumulation and consequently an enhanced cycling of Cl^-.~~

~~Different from Cl^-,~~ Mg^{2+} is irreversibly deposited into the snow~~. Most of the Mg^{2+}/Na^+ data points are above or close to the seawater dilution line, similar to that of Cl^-/Na^+ (Fig. 2(d)). On the coast, Mg^{2+}/Na^+ data points are in general close to the seawater dilution line, suggesting the main source is sea salt aerosols, while most of the inland samples are slightly enriched with Mg^{2+}, agreeing with previous observations (e.g., Dome F; Hara et al., 2014).~~ , and the~~The~~ fraction of $nssMg^{2+}$, on average, represents (44±19) % of Mg^{2+} in snow, with lower (higher) values on the coast (plateau) (Fig. 2(d)). The enrichment of Mg^{2+} has not been observed in sea salt particles produced by bubble bursting (Keene et al., 2007), and thus enriched Mg^{2+} in the snow is unlikely associated with sea salt spray. In the atmosphere, sea salt aerosols ~~would~~ can ~~also~~ be modified at low temperatures via the formation of mirabilite, thus leading to an elevated ratio of Mg^{2+}/Na^+ if mirabilite precipitates from the aerosols. However, the solid-liquid separation of mirabilite in the aerosol droplet was not observed in the experiments (Wagenbach et al., 1998). Thus, the enrichment of Mg^{2+} in surface snow is unlikely associated with sea salt fractionation. Although it is proposed that Mg^{2+} separation in sea salts can occur in surface snow due to the re-freezing process on surface snow (i.e., the quasi-liquid layers on the crystal surface can act like seawater freezing; Hara et al., 2014), our measurement of Mg^{2+} in bulk snow is unlikely to support this process responsible for Mg^{2+} enrichment. A previous observation conducted near this traverse showed a moderate correlation of Mg^{2+} with element Al in the surface snowpack (r=0.53, p<0.05), indicating a contribution of continental dust (Khodzher et al., 2014). Thus, the most plausible interpretation of ~~enriched~~ $nssMg^{2+}$ ~~in surface snow~~ is the contribution of terrestrial aerosols.

Similar to Mg^{2+}, most of K^+/Na^+ data points are close to the seawater dilution line on the coast,

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suggesting a primary contribution of sea salt spray (Fig. ~~5~~2(c)). ~~Slightly e~~Enriched K^+ ~~was present~~is ubiquitous in ~~inland snow~~interior areas, possibly ~~indicating other sources such as~~associated with ~~biological activity on the coast,~~ mineral transport, and combustion emissions in the Southern Hemisphere (Virkkula et al., 2006; Hara et al., 2013). Note that ~~the~~ all sampling sites are at least several tens of kilometers away from the coast, the contribution of biological activity to snow K^+ would be rather minor (Rankin and Wolff, 2000). A lack of correlation between K^+ (or $nssK^+$) and refractory black carbon (rBC, unpublished data; Fig. S4), which mainly represent the biomass burning emissions in the Southern Hemisphere (Sigl et al., 2016), suggests that K^+ in surface snow is unlikely dominated by biomass burning emissions. ~~A previous investigation of the atmospheric particles~~

~~Positive $nssCa^{2+}$ is generally present on the traverse, with most of the Ca^{2+}/Na^+ data points above the seawater dilution line, especially at inland sites (Fig. 5(e)).~~ The fraction of $nssCa^{2+}$, on average, accounts for (73±26) % of total Ca^{2+} in surface snow, with high percentages in the interior areas~~, indicating other dominant sources~~. In Antarctica, snow $nssCa^{2+}$ ~~has been~~was thought to be mainly associated with terrestrial inputs, possibly from both South America and Australia ~~(Bertler et al., 2005; Wolff et al., 2010).~~ (Bertler et al., 2005; Wolff et al., 2010; Du et al., 2018). ~~Previous modeling studies suggest that the dust mass reaching East Antarctica mainly originates from South America, specifically Patagonia (Basile et al., 1997; Wolff et al., 2006; Mahalinganathan and Thamban, 2016). Metal isotopes in snow collected on this traverse suggested that Australian mineral dust also can contribute to snow particles (Du et al., 2018). In addition, Antarctic ice free areas were thought to be a contribution to snow dust (Delmonte et al., 2013; Du et al., 2018). If the dust mass originated from ice free area near the coast and dominated $nssCa^{2+}$, then $nssCa^{2+}$ concentrations near the coast would be expected to be higher, while the data shows the opposite. Thus, terrestrial dust mass, possibly from both South America and Australia likely dominates snow $nssCa^{2+}$. It is noted that some Ca^{2+} concentrations in surface snow (e.g., coastal and some inland sites) are above 0.2 μeq L^{-1} (Fig. 2(i)), slightly higher than most reports of snow and ice under present day climate. On the coast, the high concentrations could be related to marine inputs, while the elevated values in the inland regions (about 500-900 km from the coast, where the glaze/dune are distributed) are possibly associated with the low and fluctuating snow accumulation rate due to the strong wind scouring. Similarly, in the glaze/dune regions on the US ITASE traverses across East and West Antarctica, concentrations of Ca^{2+} in snow and ice are also often above ~0.2μeq L^{-1}.~~

~~Positive $nssSO_4^{2-}$ is present in all surface snow (Fig. 5(b)), together with the minimum sea ice coverage around East Antarctica in late summer (Holland et al., 2014), suggesting that sea salts in surface snow are from open seawater rather than from the sea ice. On the traverse,~~ $nssSO_4^{2-}$ represents (94±5) % of total SO_4^{2-} in surface snow, with lower (higher) proportions on the coast (plateau~~).~~) (Fig. 2(b)), suggesting a dominant role of marine bioactivities. ~~In Antarctica, $nssSO_4^{2-}$ essentially originates from marine biogenic production of DMS and occasionally from explosive volcanism. In this study, the significant enrichment of SO_4^{2-} suggests a dominant role of ocean bioactivities.~~ Different from the coarse sea salt aerosols, $nssSO_4^{2-}$ originating from marine biogenic production of DMS can form fine aerosol particles in the atmosphere (Legrand et al., 2017a), resulting in long atmospheric residence time (>10 days to weeks) and consequently efficient transport (Bondietti and Papastefanou, 1993; Hara et al., 2014). This can help explain the elevated deposition flux of $nssSO_4^{2-}$ frequently found at inland Antarctic sites, e.g., site P2 (discussed below). ~~On this transect, a negative relationship was found between snow accumulation rate and SO_4^{2-} (or $nssSO_4^{2-}$) (Figs. 6(c) and (d)), suggesting that snow accumulation rate can influence snow SO_4^{2-} concentration, possibly via dilution effects, but overall~~

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~~< 10 % of the variation in SO_4^{2-} concentrations can be explained by the relationship.~~

~~(Guo et al., 2020)The ternary diagram of Cl^-, Na^+, and SO_4^{2-} can well characterize the modification processes to sea salt aerosols, and the ternary plot of the three ions in surface snow is shown in Fig. 7. The values of the ions were normalized via the following equation,~~

~~$X=[X]/([Na^+]+[Cl^-]+[SO_4^{2-}])$ Eq. (3),~~

~~where [X] is the concentration of ion X in the snow (in $\mu eq\ L^{-1}$). The dashed line between the seawater reference value and the SO_4^{2-} vertex represents the sea salt aerosol composition with additional SO_4^{2-}; i.e., the ratio of Cl^-/Na^+ keeps constant (1.17) with additional SO_4^{2-} along the dashed line. The presence of acids (HNO_3 and H_2SO_4) would result in the liberation of HCl into the atmosphere via reactions R1 and R2, resulting in the changes in Cl/Na ratios, i.e., either Cl^- loss or gain are located right or left of the line, respectively. It is shown that all of the data points are above the seawater plot, suggesting an enrichment of SO_4^{2-} in surface snow. Most of the data points are located left of the line, indicating the general enrichment of Cl^- due to reactions R1 and R2 occurring in the atmosphere and/or in the snowpack. But the coastal data points are generally close to the line, suggesting that the degree of sea salt modification is generally low in the snow.~~

~~4.2 Groups of ions in surface snow~~

~~PCA is a powerful tool for identifying the common sources and/or transport process of chemicals in different environments. The PCA results (i.e., loadings in each PC), communalities, initial eigenvalues, and explained cumulative percent of the ions in surface snow are listed in Table 1. The first three PCs accounted for 76 % of the variation of the eight original variables. PC1 accounts for 46 % of the variance and is highly loaded by Cl^-, Na^+, K^+, and Mg^{2+}, with the factor loadings higher than 0.7. In addition, the four species are correlated well with each other (Table 2), suggesting the variation of the four species is dominated by sea salt aerosols. PC2 accounts for 17 % of the total variance, and the loading values of NH_4^+ and Ca^{2+} in PC2 are high, ~0.8. Ca^{2+} is mainly from terrestrial particle mass, while NH_4^+ is thought to be mainly associated with biological decomposition of organic matter in the Southern Ocean. In addition, biomass burning from mid-latitudes can contribute to snow NH_4^+ at some sites, and the penguin colony emissions can be important inputs to NH_4^+ in snow several km from the colony. On this traverse, no correlation was found between NH_4^+ and biomass burning tracers (e.g., black carbon and phenolic compounds) in surface snow, suggesting a minor role of biomass burning emissions. Thus, the high NH_4^+ concentrations on the coast are likely associated with marine biogenic emissions. In this case, it is possible that a similar transport pathway can explain, at least in part, the positive loadings of both NH_4^+ and Ca^{2+} in PC2.~~

~~NO_3^- is highly loaded in PC3, which accounts for 13 % of the system variance. On this traverse, NO_3^- in the snow has been extensively investigated, and it is proposed that NO_3^- concentrations were influenced by post-depositional processing which is largely dependent on snow accumulation rate(Freyer et al., 1996; Shi et al., 2015). A negative relationship was found between NO_3^- and snow accumulation rate (Fig. 6(b)), suggesting a high degree of NO_3^- cycling driven by photolysis at low snow accumulation sites.~~

~~SO_4^{2-} did not show high loadings in any of the three extracted components. Its positive loading in PC1 (0.55) and weak relationships between SO_4^{2-} and sea salts (Cl^- and Na^+) likely supports the contribution of sea salt aerosols, although a minor one. A positive loading of SO_4^{2-} is also present in PC3 (0.42), and a weak correlation was found between SO_4^{2-} and NO_3^-. Both SO_4^{2-} (or $nssSO_4^{2-}$) and~~

~~NO_3^- are negatively correlated with snow accumulation rate (Fig. 6), but with distinct mechanisms. $nssSO_4^{2-}$ can be concentrated due to dry deposition at sites with low snow accumulation rate, while elevated NO_3^- concentrations are linked to the photochemical cycling and re-deposition (discussed above). In addition, $nssSO_4^{2-}$ and NO_3^- are mainly associated with the secondary aerosols, and the production of both species in summer is closely related to the oxidants HO_x, RO_x, etc, which may also contribute to the correlation between SO_4^{2-} and NO_3^-.~~

4.~~3~~ 2 Non-sea-salt fractions and fluxes of Iions in snow pits~~: the non-sea-salt fractions and ion fluxes~~

~~In this section, we discuss the fluxes and the non-sea-salt fractions of ions at different depths (i.e., summer and winter snow) in the three snow pits. The bottom ~30 cm layer of P3 will be excluded in the discussion, since it represents a snow layer clearly impacted by volcanic (Pinatubo) eruption emissions.~~

~~Ion fluxes in snow can be determined by multiplying the concentrations by snow accumulation rate, and the results in the 3 snow pits are shown in Fig. 8. The highest fluxes of ions except for NO_3^- were present at P1, followed by P2 and P3. The flux of NO_3^- shows a different pattern, with the highest value at P2, possibly due to the redistribution of NO_3^- across the Antarctic ice sheet driven by photolysis (Shi et al., 2018b). It is noted that $nssSO_4^{2-}$ fluxes at P1 (99.4±46.7 μeq m^{-2} a^{-1}) and P2 (109.2±21.6 μeq m^{-2} a^{-1}) are comparable, although P1 is located on the coast and P2 located further inland (~800 km from the coast). In addition, the ratio of $nssSO_4^{2-}$ flux at P1 over that at P3 is 2.2, the lowest value among the ratios for the observed ions (17.2, 7.5, 26.7, 8.5, 17.4, 17.0, and 10.0 for Cl^-, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, respectively), suggesting more efficient transport of $nssSO_4^{2-}$. In other words, atmospheric $nssSO_4^{2-}$ from the open ocean can be efficiently transported to at least as far inland as ~800 km from the coast (~2800 m above sea level; site P2).~~

At P1, ~~the plots of Cl^-, K^+, Mg^{2+}, and Ca^{2+} versus Na^+ are all close to the bulk seawater dilution line (Fig. 9), with~~ the slope values of the linear regression between Na^+ and the four ions are close to those of seawater (Fig. 3), suggesting a dominant source of sea salt aerosols. The proportions of the non-sea-salt fractions of K^+, Mg^{2+}, and Ca^{2+} to the ions in snow are much lower in winter than in summer, as a result of the high sea salt inputs in winter. Negative $nssCl^-$ is present in summer snow, indicating the modification to sea salts (i.e., formation of mirabilite in the atmosphere) in summer when the acid levels (e.g., HNO_3) are relatively high (Savarino et al., 2007). ~~In addition, the non-sea-salt fractions of Cl^-, K^+, Mg^{2+}, and Ca^{2+} are 0.25±0.27, 0.02±0.01, 0.04±0.07, and 0.09±0.06 μeq L^{-1}, respectively, contributing less to the total ion budgets. As for SO_4^{2-} in the snow, the proportion of $nssSO_4^{2-}$ to SO_4^{2-} is much higher in summer (~86 %) than in winter . All $nssSO_4^{2-}$ in summer snow is positive, while s~~Some winter snow samples featured negative $nssSO_4^{2-}$, i.e., SO_4^{2-}/Na^+ ratio below the value of seawater (Fig. 3S2~~(a)~~), suggesting sea salt aerosols ~~in winter~~ originating from the sea ice (Marion et al., 1999). In the winter snow, if all ~~of the~~ SO_4^{2-} is from sea salt aerosols, $nssSO_4^{2-}$ is expected to be lower than or close to zero. However, 13 out of the 17 samples classified as winter snow at P1 were characterized with positive $nssSO_4^{2-}$, suggesting a significant contribution from marine biogenic emissions. It is interesting that $nssSO_4^{2-}$ has a strong negative correlation with Na^+ in winter ~~snow~~ ($r=0.82$, $p<0.001$), raising two potential cases: 1) stronger winds transport more sea salt aerosols to P1 featured with depleted SO_4^{2-} from sea ice, thereby resulting in low concentrations of $nssSO_4^{2-}$ and assuming a stable SO_4^{2-} input flux from marine biogenic emissions; and/or 2) with a larger extent of sea ice and strong transport, a large sea salt flux would still result but carry less $nssSO_4^{2-}$ from marine

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biogenic emissions due to the longer transport distance (Wolff et al., 2006 and references therein). If case 2) dominated $nssSO_4^{2-}$ variations in the winter snow, lower $nssSO_4^{2-}$ would be expected in the end than at the beginning of winter when a sea ice coverage minimum is present. The observation at P1, however, does not support this expected seasonal trend (Fig. ~~3a~~S2). It is most likely, then, that sea salt aerosol inputs dominate $nssSO_4^{2-}$ variations in the winter snow instead of the marine biogenic emissions. ~~In addition, NH_4^+ concentration at P1 (0.16±0.05 μeq L^{-1}) is slightly higher than the previous reports of ice cores but comparable to some coastal observations (e.g., coastal sites in Terre Adelie) (Legrand and Delmas, 1985; Legrand et al., 1998), possibly associated with marine biogenic emissions (i.e., close to the coast) (discussed above).~~

The patterns of relationships between ions and Na^+ at P2 are similar to those of P1 except for Ca^{2+} (Fig. ~~9~~3). ~~The non-sea-salt fractions of Cl^-, K^+, and Mg^{2+} at P2 are 0.42±0.18, 0.005±0.008, and 0.06±0.02 μeq L^{-1}, respectively, accounting for less of the total ion concentrations. $nssCa^{2+}$, 0.13±0.01 μeq L^{-1},~~Non-sea-salt fractions of Ca^{2+} account~~s~~ for (79±9) % of the total ~~Ca^{2+} in snow pit P2~~, suggesting a dominant role of the terrestrial source. ~~Different from the other species,~~It is noted that Ca^{2+}~~,~~ remains relatively constant with increasing Na^+ (Fig. ~~9~~3), possibly suggesting insignificant seasonal variations in terrestrial dust inputs. ~~As for SO_4^{2-}, it is significantly enriched, and t~~The fractions of $nssSO_4^{2-}$ to SO_4^{2-} in summer and winter snow are (94±4) and (88±4) %, respectively~~. The very high SO_4^{2-} to Na^+ ratio in winter (~1.6, versus 0.12 of bulk seawater),~~ suggesting~~s~~ ~~that~~ a dominant role of marine biogenic emissions ~~dominate SO_4^{2-} other than the sea salt aerosols~~, different from that at P1. ~~It is suggested that the sea salt aerosol flux from the sea ice in winter is much lower in the inland Antarctica than on the coast.~~ Previous investigations proposed that sea salt aerosols emitted from sea ice are an important contribution to the sea salt budget in central Antarctica in winter (Legrand et al., 2016; Legrand et al., 2017b). Here, ~~our data~~the high $nssSO_4^{2-}$ concentrations indicate that~~–~~ marine emissions could also be an important source of ions in winter.

At P3, Cl^-, K^+, and Mg^{2+} are also correlated well with Na^+ (Fig. ~~9~~3)~~, and the non-sea-salt fractions of the 3 ions are 0.58±0.34, 0.02±0.01, and 0.12±0.04 μeq L^{-1}, respectively, higher than those of P2~~. The non-sea-salt fractions of Cl^- make up (38±24) % of the total, similar to that at P2, indicating ~~Although the sea salt fractions of Cl^-, K^+, and Mg^{2+} account for most of their total budgets in the snow, the other sources can occasionally be important. On average, $nssCl^-$ accounts for ~40 % of the total Cl^-, suggesting that, Cl^- at Dome A is mainly from the sea salt aerosols, but~~ the importance of HCl deposition, and consequently results in Cl^- not being a quantitative indicator of sea salts in the interior areas. ~~of HCl is also an important contribution. This percentage is higher than that at P2 (~30 %), suggesting a more important role of HCl on Cl^- budget in further inland snow. At P3, $nssCa^{2+}$ accounts for % of total Ca^{2+}, close to that of P2, suggesting the terrestrial particle mass as the primary source. In terms of~~ $nssSO_4^{2-}$~~,~~ at P3~~the non-sea-salt fraction~~ accounts for ~~–~~(95±2) % of ~~total~~ SO_4^{2-}~~,~~. ~~comparable to that of~~Together with the observations at P2~~. At P2 and P3,~~, it can be inferred that SO_4^{2-} ~~in both summer and winter snow~~in the interior areas ~~–~~is dominated by marine biogenic emissions throughout the year ~~(i.e., no negative $nssSO_4^{2-}$ observed)~~, generally in line with the observation at Dome C (Udisti et al., 2012).

Ion fluxes in the 3 snow pits can be determined by multiplying the concentrations by snow accumulation rate, and the highest fluxes of ions except for NO_3^- were generally present at P1, followed by P2 and P3 (Fig. S5). It is noted that $nssSO_4^{2-}$ fluxes at P1 (99.4±46.7 μeq m^{-2} a^{-1}) and P2 (109.2±21.6 μeq m^{-2} a^{-1}) are comparable, although P1 is located on the coast and P2 located further inland (~800 km from the coast). In addition, the ratio of $nssSO_4^{2-}$ flux at P1 over that at P3 is 2.2, the

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lowest among the ratios for the observed ions (17.2, 7.5, 26.7, 8.5, 17.4, 17.0, and 10.0 for Cl^-, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, respectively), suggesting more efficient transport of $nssSO_4^{2-}$. In other words, atmospheric $nssSO_4^{2-}$ from the open ocean can be efficiently transported to at least as far inland as ~800 km from the coast (~2800 m above sea level; site P2).

~~Similar to the surface snow, the modification processes to sea salt aerosols is negligible in snow pit P1, while the ubiquitous modification process to sea salts throughout the year was found in the interior areas (P2 and P3; Fig. S3). Thus, Cl^- in inland Antarctica, often deviating from the seawater dilution line remarkably in both summer and winter, is not a quantitative indicator of sea salts in snow.~~

5 Conclusions

Snow chemistry~~Surface snow and snow pit samples collected~~ on a traverse from coastal Zhongshan Station to ~~the ice sheet summit~~Dome A, ~~East Antarctica, during five campaigns were used to comprehensively~~ was investigated~~ spatial and temporal variations in snow chemistry~~. It is shown that the non-sea-salt fractions of K^+, Mg^{2+}, and Ca^{2+} are mainly associated with terrestrial particle mass, while $nssCl^-$ is linked to the deposition of HCl. Spatially, the proportions of non-sea-salt fractions of ions to the totals are higher in the interior areas than on the coast, and seasonally, the proportions are generally higher in summer than in winter, due to the high sea salt inputs during wintertime. Negative $nssSO_4^{2-}$ observed on the coast indicates sea salts mainly originating from the sea ice in winter, while positive $nssSO_4^{2-}$ is present throughout the year in the interior areas, suggesting the dominated role of marine biogenic emissions. The $nssSO_4^{2-}$ can be transported efficiently to at least as far inland as the ~2800 m contour line.

~~Cl^-, Na^+, K^+, and Mg^{2+} concentrations are high within the narrow coastal region, falling off strongly further inland, while NO_3^- exhibits an opposite trend and no clear spatial trends were found for SO_4^{2-}, NH_4^+, and Ca^{2+}. In inland snow, Cl^-, K^+, and Mg^{2+} are slightly enriched relative to Na^+ with respect to the composition of seawater. $nssCl^-$ is associated with the deposition of HCl produced from dechlorination of sea salt aerosols, and $nssK^+$ and $nssMg^{2+}$ are possibly linked to terrestrial particle mass. Ca^{2+} and SO_4^{2-} are significantly enriched versus Na^+, and terrestrial dust mass and marine biogenic emissions are responsible for the enrichments respectively. Snow NH_4^+ is related to marine biological activities, and multivariate statistical analysis suggests, at least in part, the NH_4^+ transport is via free troposphere.~~

~~On the coast, parts of the winter snow showed a depletion of SO_4^{2-} versus Na^+, indicating sea salt aerosols sourced from sea ice. In the interior areas, SO_4^{2-} in both summer and winter snow is dominated by marine biogenic emissions, with no negative $nssSO_4^{2-}$ values observed. In general, the contribution proportions of $nssCl^-$ to total Cl^- are higher in interior snow than in coastal snow. Ternary plots of Cl^-, Na^+, and SO_4^{2-} in snow suggest the modification process to sea salts is negligible on the coast, while the degree of modification to sea salts is higher in inland throughout the year, which results in Cl^- not being a quantitative indicator of sea salts. Ion flux assessment suggests an efficient transport of $nssSO_4^{2-}$ to at least as far inland as the ~2800 m contour line.~~

Data availability. This dataset, chemical data on ion concentrations in snow on the traverse from coast (Zhongshan Station) to Dome A, is in the process of being hosted on a public server by the Chinese National Arctic and Antarctic Data Center (https://www.chinare.org.cn/).

Author contributions. GS, ZC, YL and BS designed the experiments and GS, HM, ZH, CA, SJ, TM,

JY, DW and SL carried them out. GS and MH prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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Table 1 Rotated component matrix of the major ions in surface snow. (Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in 4 iterations.) Factor loadings were calculated from the eigenvalues of the three components and their corresponding eigenvectors, and the values greater than 0.7 are shaded.

Chemical ions	PC1	PC2	PC3	Communalities
Cl^-	0.93	-0.01	0.27	0.93
NO_3^-	0.04	-0.06	0.95	0.90
SO_4^{2-}	0.55	0.08	0.42	0.49
Na^+	0.98	-0.01	-0.06	0.96
NH_4^+	0.10	0.81	0.04	0.66
K^+	0.71	0.25	0.12	0.57
Mg^{2+}	0.96	0.05	-0.09	0.92
Ca^{2+}	0.03	0.79	-0.07	0.62
Initial eigenvalues	3.67	1.33	1.06	
Percentage of variance	46	17	13	
Cumulative percent	46	63	76	

Table 2 Pearson correlation matrix of major ions in surface snow

—	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1.00	0.24**	0.47**	0.94**	0.05	0.74**	0.91**	0.09
NO_3^-		1.00	0.21**	-0.02	-0.04	0.09*	-0.04	-0.05
SO_4^{2-}			1.00	0.34**	0.08	0.30**	0.31**	0.03
Na^+				1.00	0.05	0.77**	0.98**	0.12*
NH_4^+					1.00	0.19**	0.10*	0.30**
K^+						1.00	0.75**	0.15**
Mg^{2+}							1.00	0.15**
Ca^{2+}								1.00

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

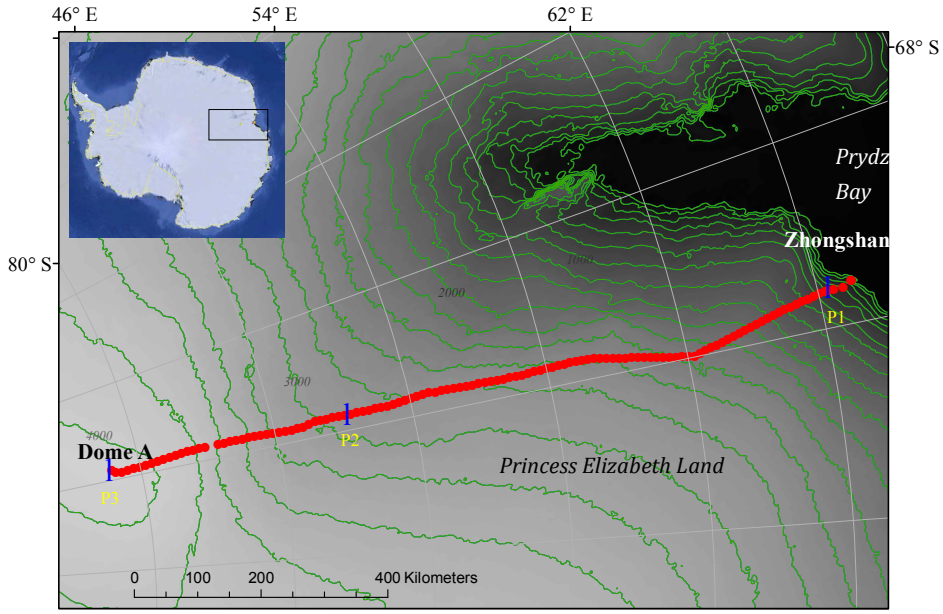
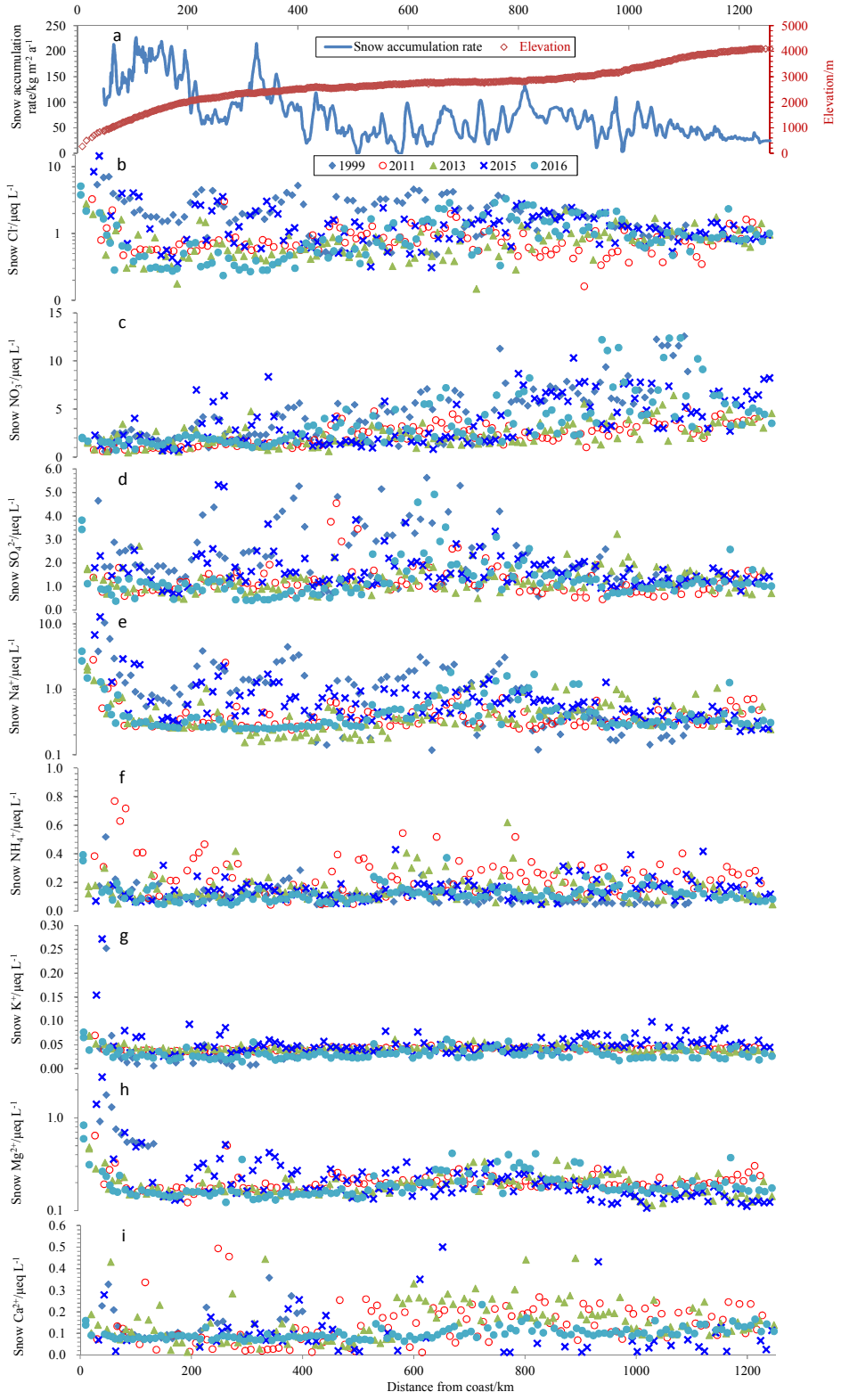
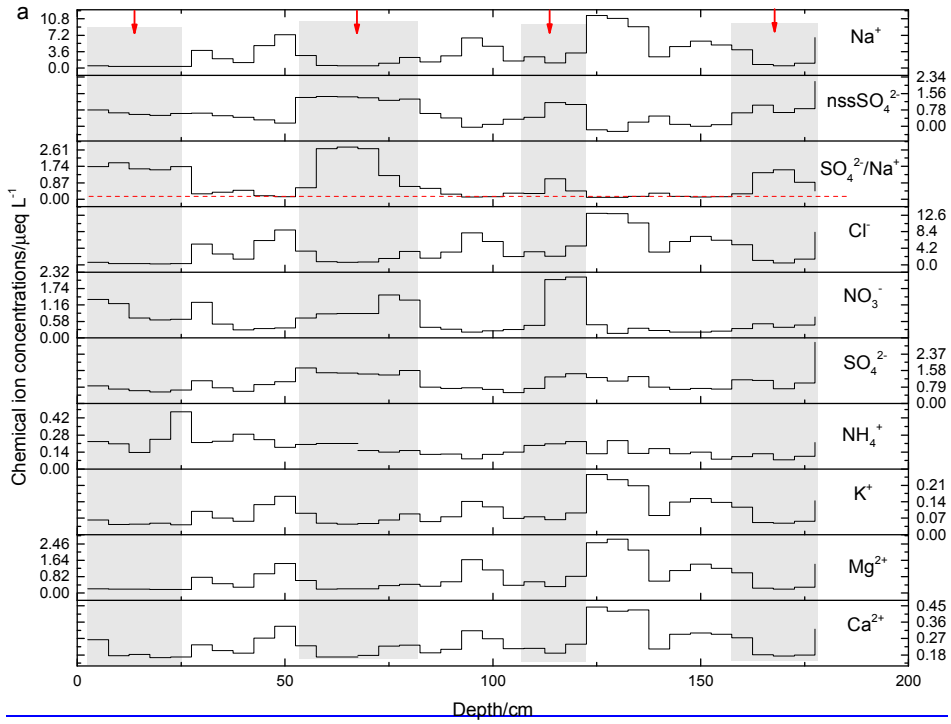


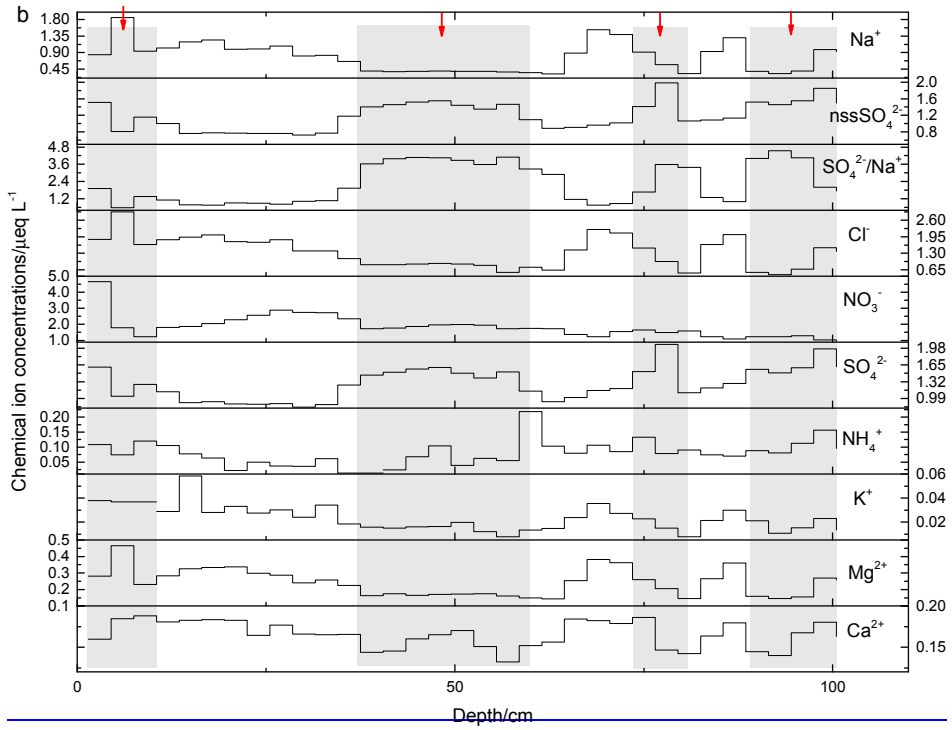
Figure 1. The Chinese inland investigation traverse from the coast (Zhongshan station) to the ice sheet summit, Dome A, East Antarctica. The traverse is generally along the 77.0 °E longitude.


a
Snow accumulation rate
Elevation
Snow accumulation rate/kg m^{-2} a^{-1}
Elevation/m
b
1999
2011
2013
2015
2016
Snow Cl$^-$/μeq L^{-1}
c
Snow NO$_3^-$/μeq L^{-1}
d
Snow SO$_4^{2-}$/μeq L^{-1}
e
Snow Na$^+$/μeq L^{-1}
f
Snow NH$_4^+$/μeq L^{-1}
g
Snow K$^+$/μeq L^{-1}
h
Snow Mg^{2+}/μeq L^{-1}
i
Snow Ca^{2+}/μeq L^{-1}
Distance from coast/km

730

Figure ~~2~~ 1. Annual snow accumulation rate, elevation (a) and ion concentrations in surface snow collected during five seasons (b-i). Annual snow accumulation rate is obtained from field bamboo stick measurements, updated to 2016 from Ding et al. (2011). The closed diamond, open circle, closed triangle, cross and closed circle denote ion concentrations in the years 1999, 2011, 2013, 2015, and 2016, respectively. Note that a base-10 log scale is used for the *y*-axis of Cl^- (b), Na^+ (e), and Mg^{2+} (h).





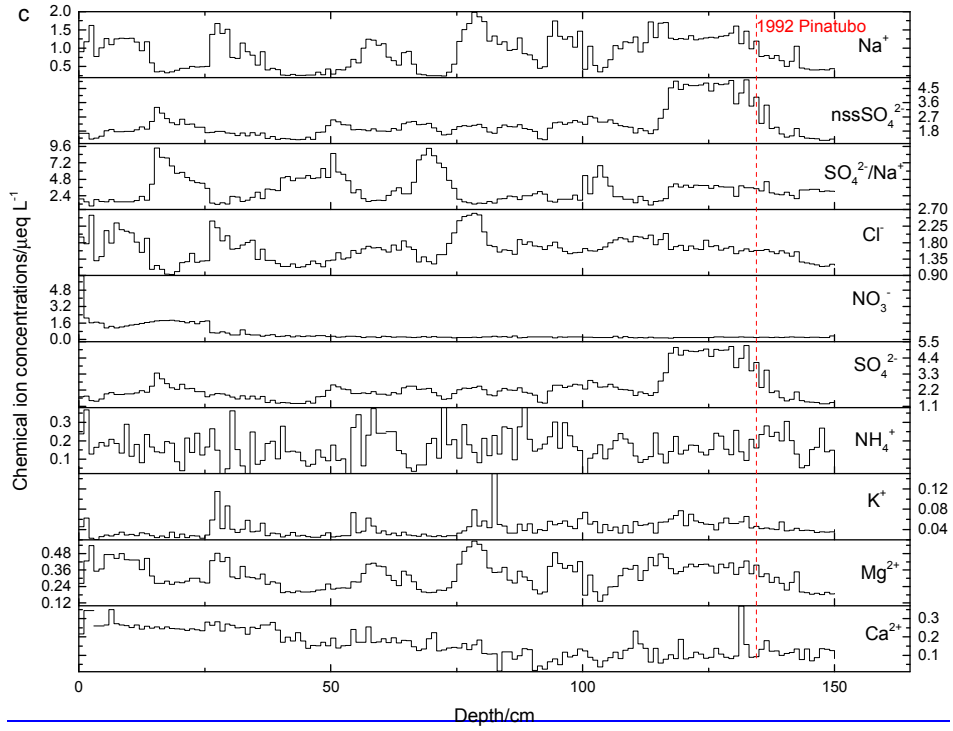


Figure 3. Profiles of chemical ions in snow pits P1 (a), P2 (b), and P3 (c). Snow pits P1 and P2 were sampled in the summer season in 2015-2016, and P3 was sampled in January 2010. The ratios of

~~SO_4^{2-}/Na^+ in snow samples were also present. Red arrows in panels (a) and (b) represent the middle of the identified summer, and shaded areas denote summer seasons (see text). The red dashed line in panel (a) represents the ratio of SO_4^{2-}/Na^+ in bulk seawater, while the red dashed line in panel (c) signifies the first snow sample significantly influenced by the Pinatubo eruption. One seasonal cycle generally represents local Na^+ minima and $nssSO_4^{2-}$ and SO_4^{2-}/Na^+ maxima.~~

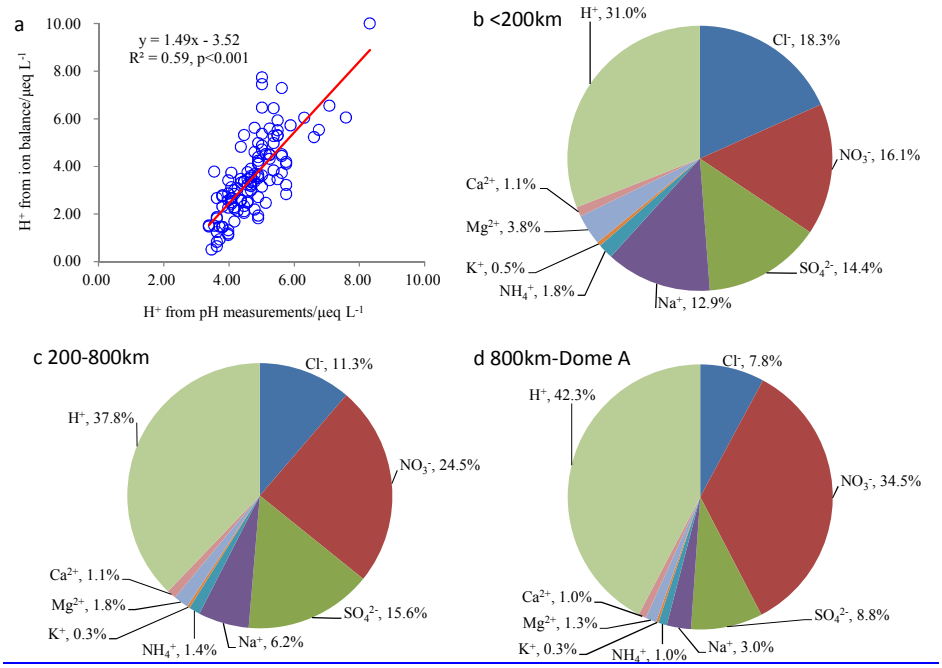


Figure 4. Major ions in surface snow on the Chinese inland Antarctic traverse. Concentrations of H^+ derived from pH versus those from the ion balance method are shown in panel (a), and contribution percentages of each ion to the total in different regions on the traverse are shown in panels (b)-(d), in μeq L^{-1}. The percentages of each ion in individual regions were calculated from the averages of all sites within the region.

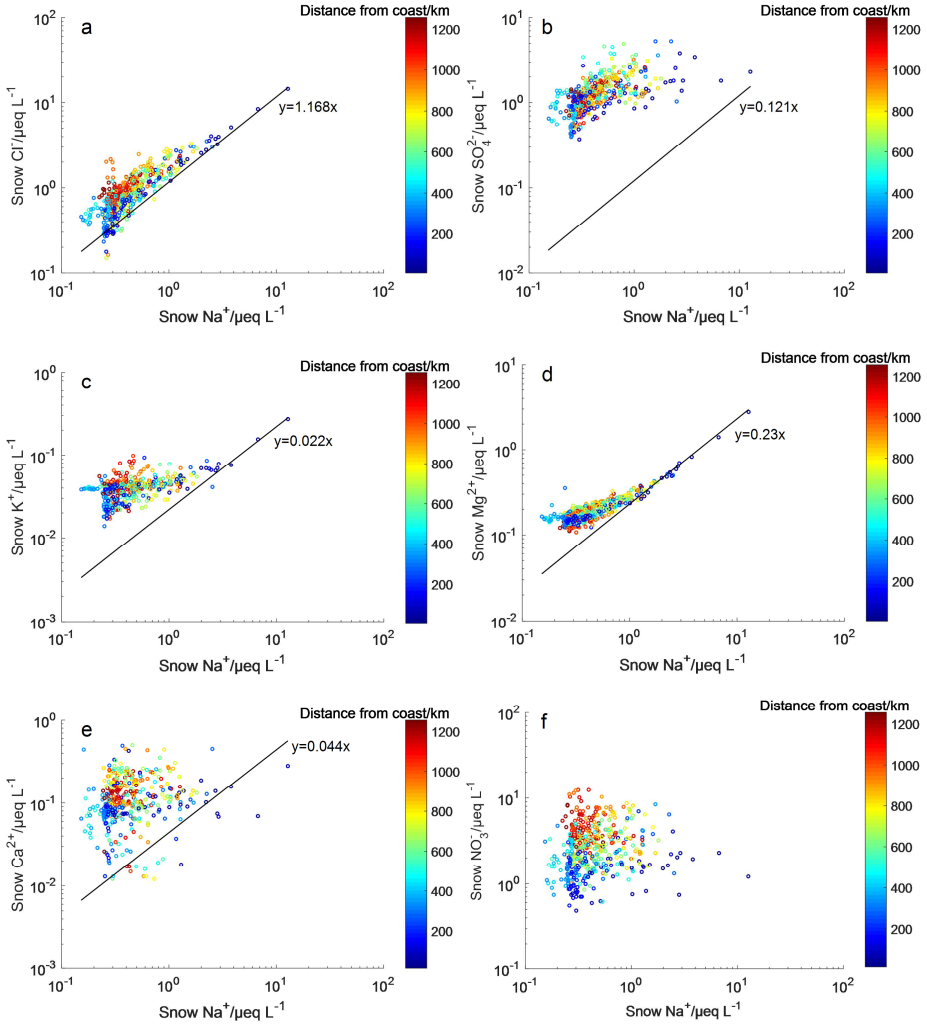


Figure ~~5~~2. Correlation plots of Cl^-, SO_4^{2-}, K^+, Mg^{2+}, Ca^{2+}, and NO_3^- versus Na^+ in surface snow. The black solid line represents the seawater dilution line, with slopes of typical ions versus Na^+ ratios in seawater (in μeq L^{-1}). The concentration of NO_3^- in seawater is too variable among the seas, and a representative ratio of NO_3^-/Na^+ cannot be presented. Note that a base-10 log scale is used for ion concentrations.

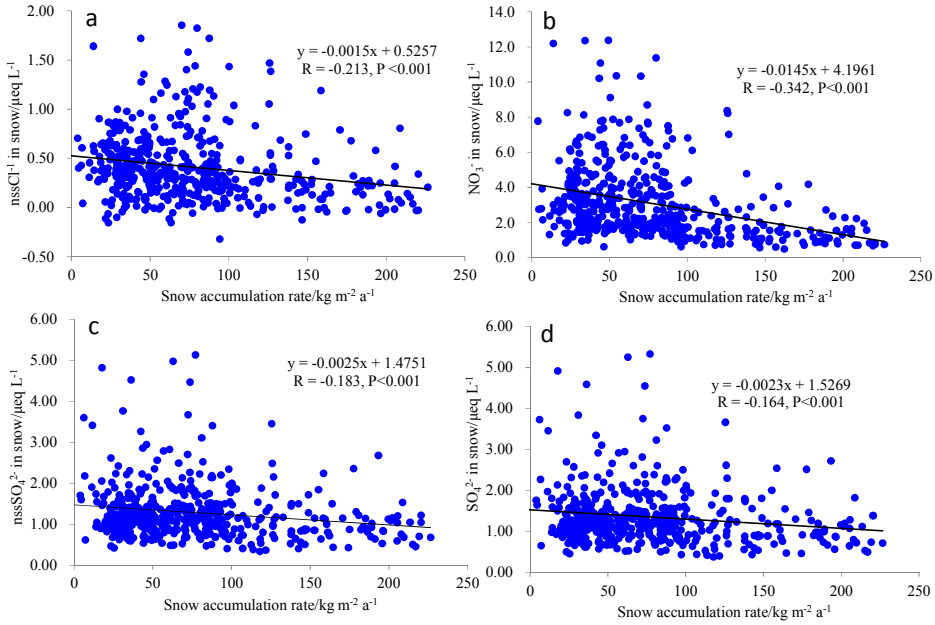


Figure 6. Relationship between chemical ions in surface snow and snow accumulation rate on the traverse.

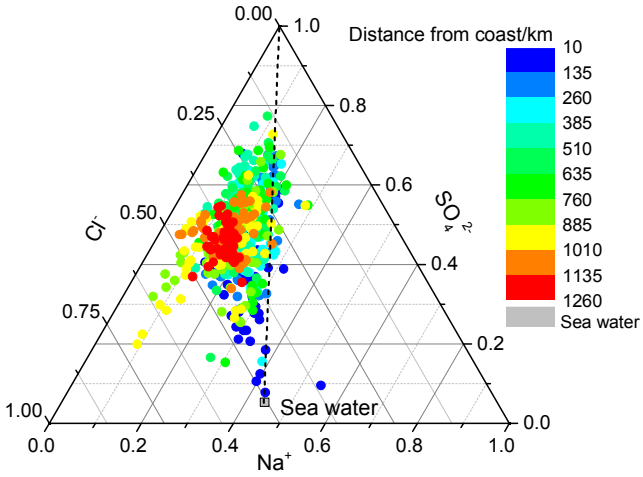


Figure 7. Ternary plot of Cl^-, Na^+, and SO_4^{2-} in surface snow samples. Bulk seawater composition is denoted by a grey square. The dashed line extending between the sea salt reference value and the SO_4^{2-} summit represents the composition of sea salt with increasing SO_4^{2-}.

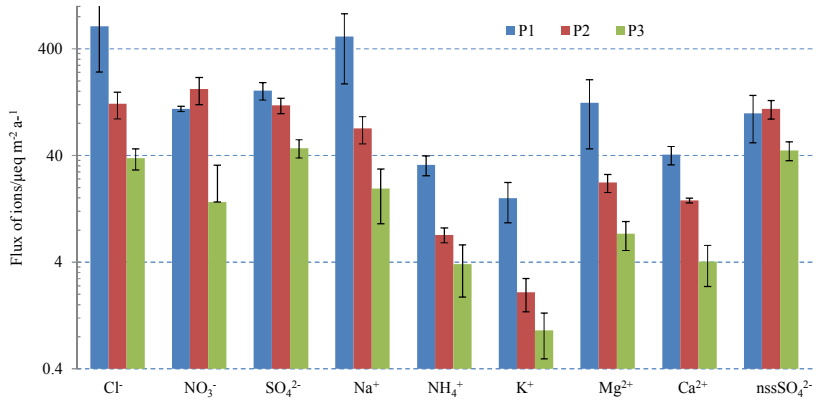


Figure 8. Ion fluxes at the three pits (P1, P2, and P3). The error bars represent one standard deviation of fluxes in different years. Note that a base-10 log scale is used for the *y*-axis.

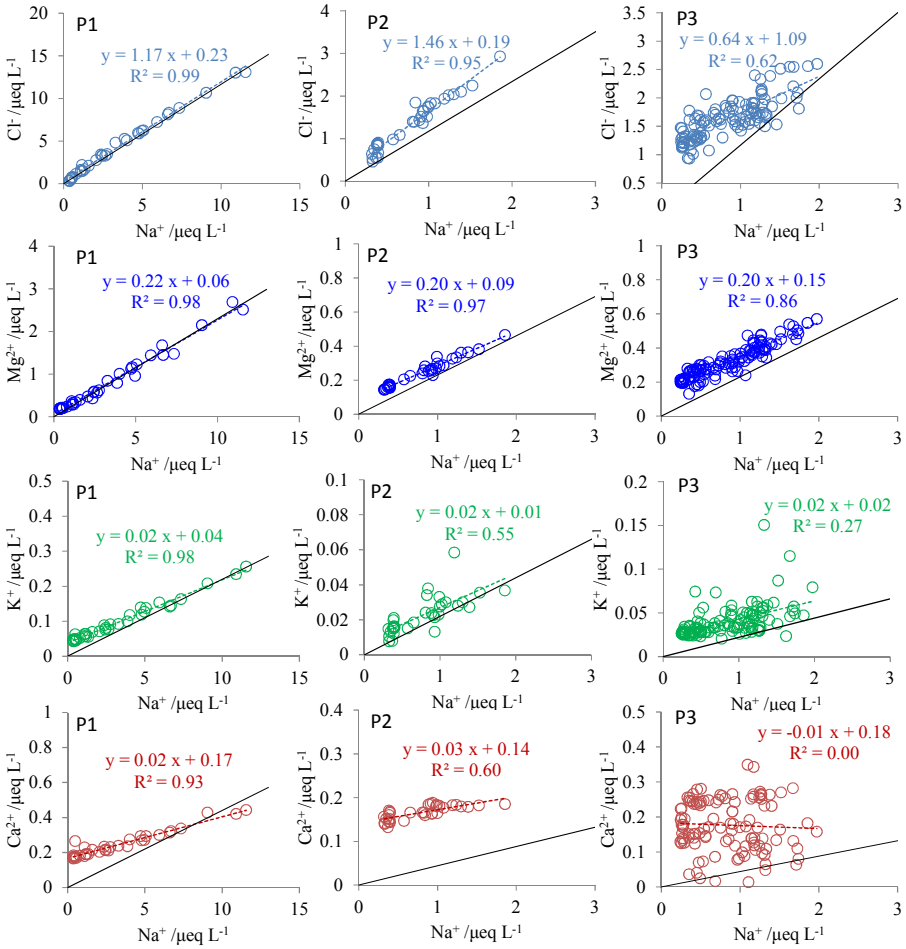


Figure 93. Relationships between Na^+ and Cl^-, K^+, Mg^{2+}, Ca^{2+} in the three snow pits (P1, P2, and P3). Also shown are the linear regressions between them (dashed line), with all of the linear correlation significant at $p<0.001$ except Ca^{2+}/Na^+ at P3. The black solid line represents seawater dilution line. Note that the data of the bottom ~30 cm layer of P3 was excluded in the plots, since it represents a snow layer clearly impacted by volcanic (Pinatubo) eruption emissions.