

Spatial variability of chemical tracers in surface snow along the traverse route from the coast to 1000 km inland at east Dronning Maud Land, Antarctica

Toshitaka Suzuki¹, Yoshinori Iizuka², Teruo Furukawa², Kenichi Matsuoka³, Kokichi Kamiyama² and Okitsugu Watanabe²

1 Yamagata University, Kojirakawa-cho 1-chome, Yamagata 990-8560

2 National Institute of Polar Research, Kaga 1-chome, Itabashi-ku, Tokyo 173-8515

3 Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo 060-0819

Received February 21, 2002

Abstract We measured the spatial variability of Cl^- , Na^+ , SO_4^{2-} , NO_3^- and ^7Be concentrations in snow cover along the traverse route from S16 to Dome Fuji station in east Dronning Maud Land, Antarctica. The concentrations of Cl^- and Na^+ at the coast exponentially decreased with distance from the coast up to 200 km inland. Between 200–1000 km inland, the concentrations of Na^+ were nearly constant. On the other hand, the concentrations of Cl^- increased with distance beyond 750 km inland. Furthermore, the contribution factors between Cl^- and Na^+ decreased and the $\text{Cl}^- / \text{Na}^+$ ratio and the $\text{nssCl}^- / \text{Cl}^-$ ratio increased toward the interior of the continent. These results indicate that sea salt aerosols are transported from the coastal region toward the inland region of the Antarctic continent, and that a source of Cl^- other than sea salt exists in the inland plateau of Antarctica. The concentrations of SO_4^{2-} , NO_3^- and ^7Be in snow were relatively high in the coastal region and the inland plateau region compared with those in the katabatic wind region.

Key words Antarctica, snow, chemistry, spatial variability, atmospheric transport.

1 Introduction

Antarctic ice sheet is a burial ground for atmospheric deposition. Since there is continuous interaction between the ice sheet and the atmosphere, various atmospheric substances are injected to the ice sheet sequentially in time and space. Therefore, vertical analyses of the ice sheet provide us with information about past climatic change (Delmas 1992; Legrand and Mayewski 1997) and horizontal analyses of the ice sheet provide us with knowledge regarding long-range transport of airborne materials (Kamiyama *et al.* 1989; Kreutz and Mayewski 1999). The Japanese Antarctic Research Expeditions (JARE) have conducted many glaciological observations including the Dome Fuji Project (Dome-F Coring Group 1998) on the ice sheet in east Dronning Maud Land during the past several decades. The study route from the coast to Dome Fuji station, 1000 km inland, has been established through these observations (Ageta *et al.* 1989; Kamiyama *et*

al. 1996). The 40th JARE (1998-2000) carried out three inland expeditions for glaciological investigation along this study route. In this report, we show and discuss the regional distributions of Cl^- , Na^+ , SO_4^{2-} , NO_3^- and ^7Be concentrations in snow cover along the route during the austral summer and winter seasons.

2 Methods

A map of east Dronning Maud Land, with the study route from S16 to Dome Fuji station, is shown in Fig. 1. The traverse from the coast, S16 ($69^\circ 02' \text{S}$, $40^\circ 04' \text{E}$, 591 m a. s. l.), to Dome Fuji station ($77^\circ 19' \text{S}$, $39^\circ 42' \text{E}$, 3810 m a. s. l.) was carried out during the austral summer, from December 27, 1998 to February 15, 1999. From August 23 to September 13, 1999, the traverse in the winter season was performed from S16 to Mizuho station ($70^\circ 42' \text{S}$, $44^\circ 20' \text{E}$, 2230 m a. s. l.). Snow samples in this study were collected during these two inland expeditions. In the research area along the route, samples for ion analyses were taken from the snow cover at a depth of 0–2 cm by pushing a 100-ml pre-cleaned plastic bottle into the snow. The sample collection was performed every 10 km along the route. During the return traverse of the expedition, each sampling site was shifted 5 km further along the route than those of the outward traverse. On the traverse to Dome Fuji station in the summer season, snow samples for ^7Be measurement were also obtained at 50 km intervals. Samples for ^7Be analyses were taken from the snow cover at a depth of 0–2 cm by using a stainless shovel to fill a 4-l pre-cleaned plastic bottle. Samples were analyzed at Syowa station ($69^\circ 00' \text{S}$, $39^\circ 35' \text{E}$, 29 m a. s. l.) immediately after the inland expeditions. The concentrations of ionic species and the activities of ^7Be were measured by ion chromatography and spectrometry, respectively. Beryllium-7, with a half-life of 53 days, is a naturally occurring cosmogenic radionuclide, which is produced by nuclear spallation reactions between high energy cosmic ray and atmospheric nuclei. The production rate of ^7Be increases with altitude and reaches a maximum at 15 km at higher latitudes, and approximately 70% of the production of ^7Be occurs in the stratosphere (Lal *et al.* 1958; 1960).

3 Results and discussion

The concentrations of Cl^- and Na^+ in snow cover along the study route are shown in Fig. 2. Variation of the altitude is also indicated in the figures. There were no remarkable differences between the results of outward and return traverses to and from Dome Fuji station. This implies that the temporal variation of Cl^- and Na^+ concentrations in snow were not significant during the period of the inland expedition. The concentrations of Cl^- and Na^+ at the coast were approximately 0.6 mg kg^{-1} and 0.3 mg kg^{-1} , respectively. These values decreased one order of magnitude until about 200 km inland (2.0 km a. s. l.) from S16 point. This result indicates that sea salt aerosols are transported from the coastal region toward the inland region of the Antarctic continent (Kreutz and Mayewski, 1999). Delmas (1992) suggested that sea salt deposition in polar snow is very high in coastal areas but decreases rapidly inland as a function of elevation rather than of the distance from the sea, because the Na^+ concentrations found at J9 on the Ross Ice Shelf (0.06 km a. s. l.) and at D 80 in Ad•lie Land (2.5 km a. s. l.) both located about 430 km from the ice front :

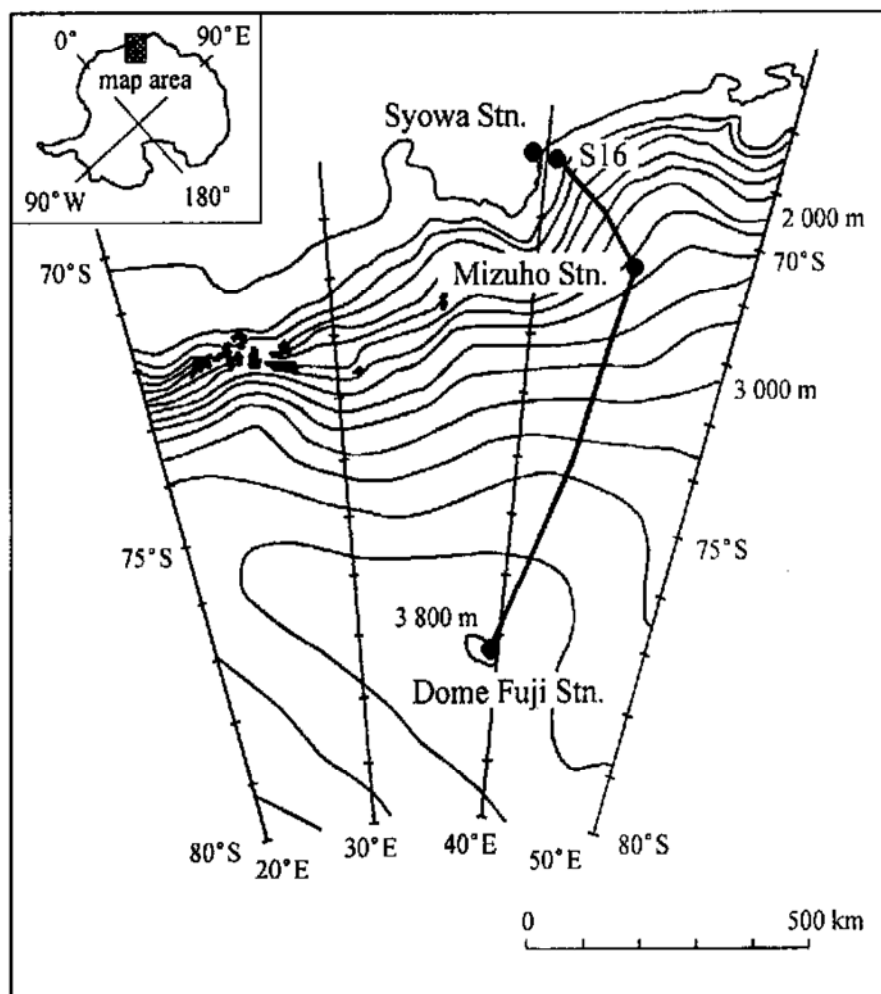


Fig. 1. Map showing the study route in East Dronning Maud Land, Antarctica.

$0.1 \text{ mg} \cdot \text{kg}^{-1}$ (Herron and Langway 1979) and $0.02 \text{ mg} \cdot \text{kg}^{-1}$ (Legrand and Delmas 1985), respectively. On the other hand, Minikin *et al.* (1994) found an exponential decrease of the Cl^- concentration on the Filchner-Ronne ice shelf which is essentially flat. These findings indicate that sea salt concentrations in snow at the coast of Antarctica are dependent both on altitude and distance from the coast. In Fig. 3, the concentrations of Na^+ in snow are plotted against (a) the distance from S16 up to 300 km and (b) the altitude up to 2.5 km. Regression analyses using an exponential formula were performed on these data sets based on the assumption that sea salt aerosols in the atmosphere are removed to the ice sheet in proportion to its concentration in the atmosphere, i. e. a first-order removal process. The half-decrease distance of sea salt in the ice sheet expected from the exponential term of the equation in Fig. 3a is approximately 100 km. In the same way, from Fig. 3b, we can recognize that the concentration of sea salt in the ice sheet decrease to half with increasing altitude every 0.6 km.

From 200 km to 1000 km inland, the concentrations of Na^+ were nearly constant (Fig. 2b). On the other hand, the concentrations of Cl^- increased with distance beyond 750 km inland (3.6 km a. s. l.) (Fig. 2a). These results suggest that a source of Cl^- other than sea salt exists in the inland plateau of Antarctica. The study route can be divided into three sections on the basis of the characteristics of snow surface features: 0 – 200 km, a coastal region (0.6 – 2 km a. s. l.), characterized by a high frequency of small sastrugi

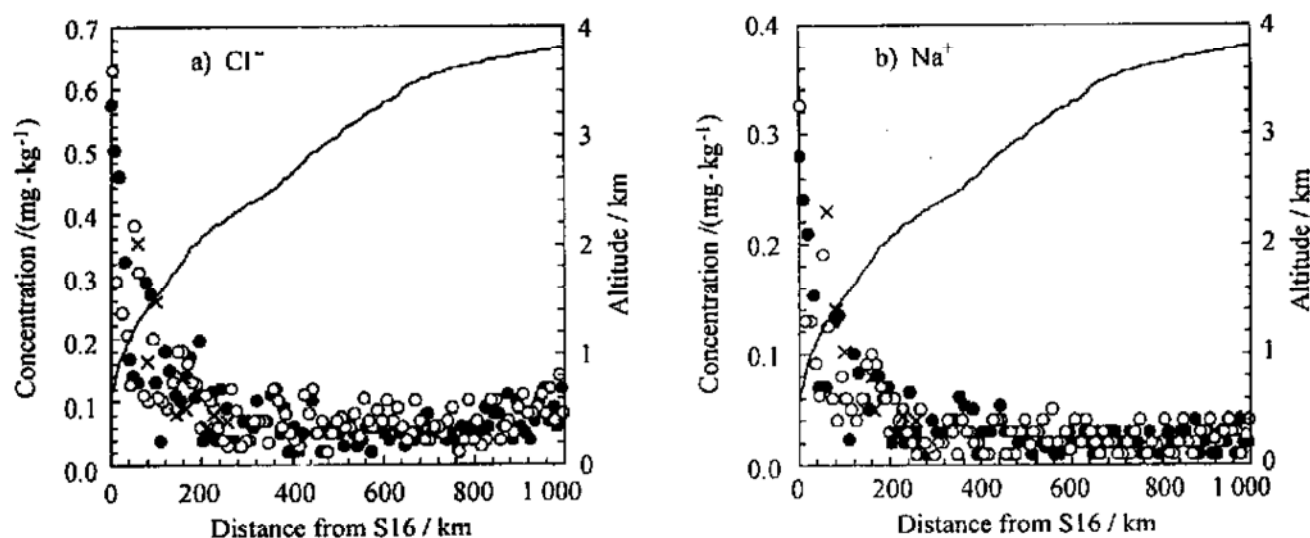


Fig. 2. The distributions of the concentrations of a) Cl^- and b) Na^+ in snow cover along the study route. Solid circles and open circles express the data obtained in outward and return traverses during the summer expedition performed from December 27, 1998 to February 15, 1999, respectively. The crosses represent data obtained in the winter expedition performed from August 23 to September 13, 1999. Variation of the altitude is also indicated by the solid line.

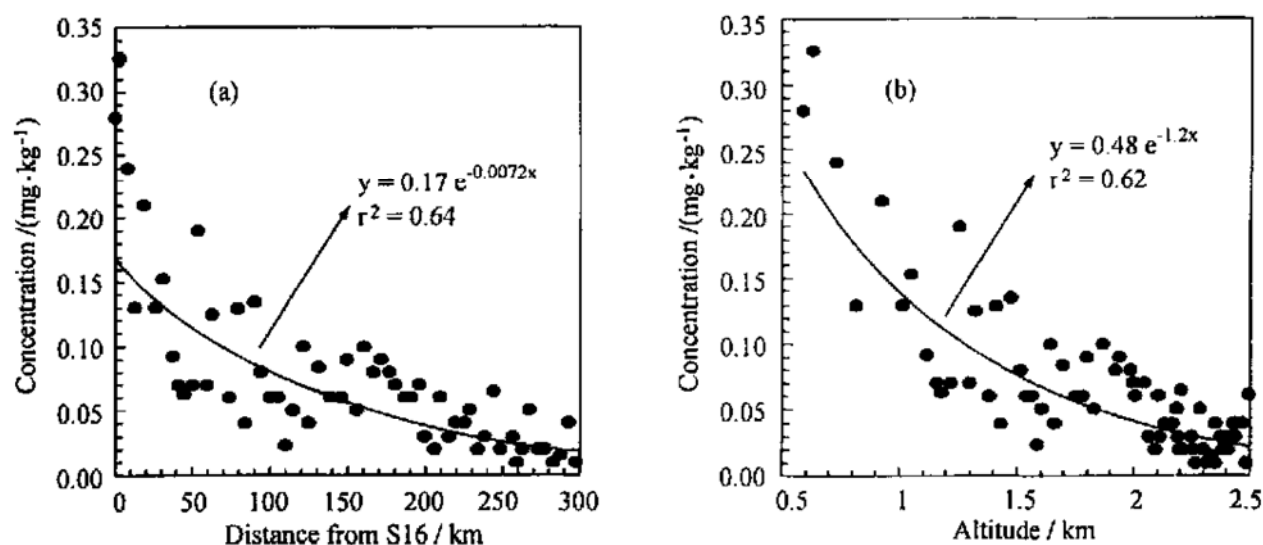


Fig. 3. The concentrations of Na^+ in snow obtained in the summer expedition plotted against a) the distance from S16 and b) the altitude. The curves in the figures are obtained by the least squares method.

and low frequency of dunes; 200–750 km, a katabatic wind region (2.0–3.6 km a. s. l.) characterized by the coexistence of small and large sastrugi, dunes and a glazed surface; and 750–1000 km, an inland plateau region (3.6–3.8 km a. s. l.) characterized by low frequencies of small sastrugi and dunes (Furukawa *et al.* 1996). Each section was also defined as a uniform accumulation zone by offshore cyclones, a sporadic accumulation zone with katabatic winds and a calm accumulation zone with weak winds, respectively. Number of samples, the contribution factors ($r^2 \times 100$) between Cl^- and Na^+ , the average Cl^-/Na^+ ratios and the average $\text{nssCl}^-/\text{Cl}^-$ ratios in each section are summarized in

Table 1. The concentrations of nssCl^- (non-sea-salt Cl^-) were obtained as follows:

$$[\text{nssCl}^-] = [\text{Cl}^-] - 1.8[\text{Na}^+] \quad (1)$$

where 1.8 is the Cl^-/Na^+ ratio in bulk sea water (Broecker and Peng 1982), considering that Na^+ is the best reference element for sea salt. The contribution factors between Cl^- and Na^+ were 97% in the coastal region, 61% in the katabatic-wind region and 33% in the inland plateau, respectively. The decrease in the contribution factor indicates that the correlation between the concentration of Cl^- and Na^+ is weakened toward the inland region. In the coastal region, the average value of the Cl^-/Na^+ ratio, 2.0 ± 0.3 , was close to the ratio in bulk sea water, 1.8, and the proportion of nssCl^- to total Cl^- was less than 10%. On the other hand, the Cl^-/Na^+ ratio in the inland plateau region, 3.4 ± 1.5 , was approximately twice the value of the ratio in sea water, and roughly 40% of Cl^- in this section was the non-sea-salt fraction. Not only the average values of Cl^-/Na^+ and $\text{nssCl}^-/\text{Cl}^-$, but also their standard deviations, increased toward the interior of the continent. These results indicate that the intensity and instability of unknown source of Cl^- become strong toward the inland plateau. The increase in the concentration of Cl^- in the snow inland may be due to an inflow of nssCl^- into the Antarctic boundary layer from the stratosphere and the upper troposphere along with atmospheric convergent flow in the interior of the Antarctic continent (James 1989; Parish and Bromwich 1991). Although we cannot identify the origin of nssCl^- in this study, the anthropogenic Cl^- which is injected into the upper atmosphere in the mid-latitude region and/or naturally occurring Cl^- which is produced by the chemical reaction in the Antarctic atmosphere, e. g. HCl production from sea salt aerosol as suggested by Legrand and Delmas (1988), are possibilities. Wagnon *et al.* (1999) clarified that volatile chemical species in the upper snow layers of the inland region suffer very serious post-depositional change. If the influence of post-depositional migration and redeposition process increases with altitude or distance from the coast, thus the enrichment of Cl^- in the surface snow by this phenomenon will be important to interpret our results. However, Kamiyama *et al.* (1994) reported that not only the concentration of Cl^- and NO_3^- but also the concentration of SO_4^{2-} , non-volatile species, in the surface snow have also increased on the inland plateau of east Dronning Maud Land. Further observations of the regional distribution of the upper atmospheric tracers and the extent of post-depositional migration of the volatile species needed to identify the source of nssCl^- in the interior of Antarctica.

The distribution of the concentrations of SO_4^{2-} and NO_3^- in snow along the study route are shown in Fig. 4. For both ions, relatively high concentrations were observed in the coastal region and the inland plateau compared with the katabatic-wind region. Although this trend roughly resembles the result for Cl^- , the fluctuations in the concentrations of SO_4^{2-} and NO_3^- were large compared with that of Cl^- . The fluctuation, if not due to analytical errors, may be due to spatial and/or temporal variability of the atmospheric fluxes of these species. In addition, the concentration of the volatile species NO_3^- may be affected by post-depositional migration and re-deposition of the gaseous species (Wagnon *et al.* 1999). The regional distribution of the ratio of concentration of nssSO_4^{2-} to that of total SO_4^{2-} is shown in Fig. 5. The concentrations of nssSO_4^{2-} (non-sea-salt SO_4^{2-}) were obtained as follows:

$$[\text{nssSO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.25[\text{Na}^+] \quad (2)$$

where 0.25 is the $\text{SO}_4^{2-}/\text{Na}^+$ ratio in bulk sea water (Broecker and Peng 1982). The proportion of the nssSO_4^{2-} to SO_4^{2-} was larger than 75% in all samples. This indicates that almost all the SO_4^{2-} in the snow cover along the study route originated from a source other than sea salt. The result also indicates that the contribution of sea salt aerosols is relatively high in the coastal region.

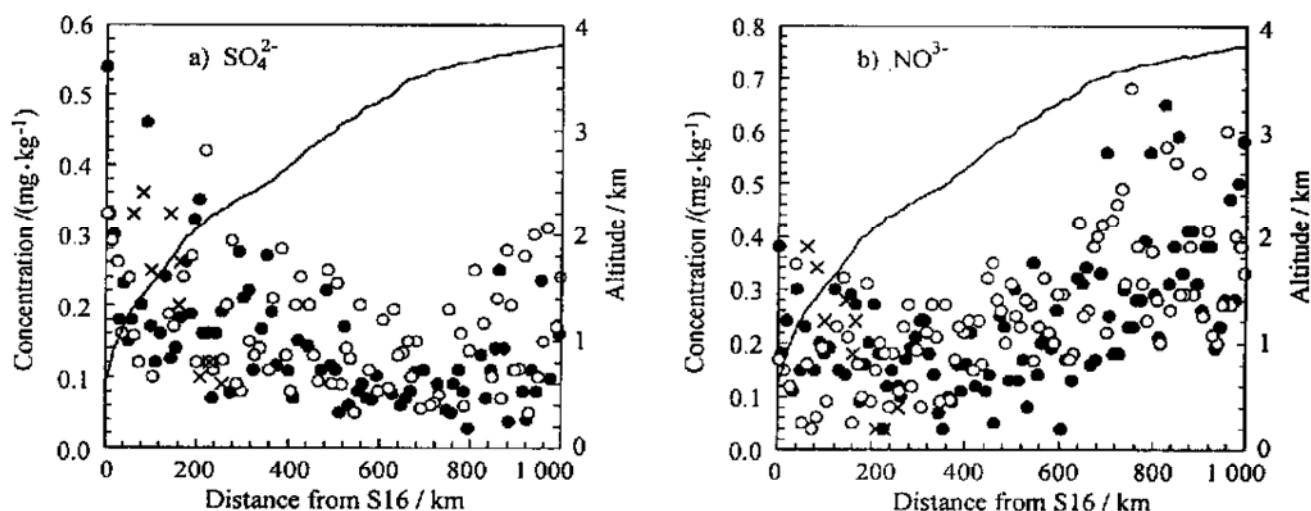


Fig. 4. The distribution of the concentrations of a) SO_4^{2-} and b) NO_3^- in snow cover along the study route. Meanings of symbols and solid line in the figures are same as those of Fig. 2.

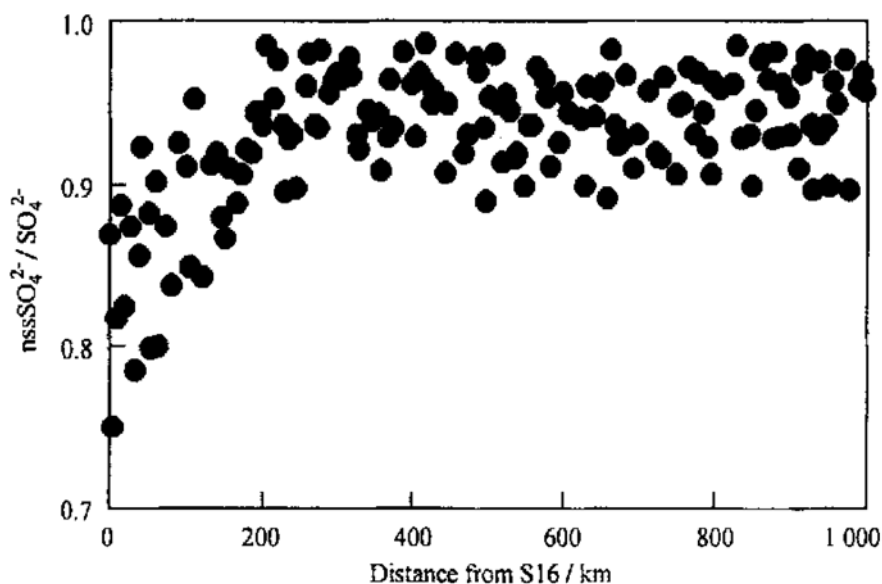


Fig. 5. The regional distribution of the concentration ratios of nssSO_4^{2-} to total SO_4^{2-} .

The concentrations of ^7Be in the snow cover along the study route are shown in Fig. 6. The regional variation of the concentration was also high in the coastal region and the inland plateau region. The high concentration of ^7Be observed in the coastal region cannot be explained by the mechanism whereby the ^7Be descends from the upper atmosphere in-

side of a polar vortex and is transported along the continental slope by the katabatic wind. If ^7Be is deposited onto the sea surface and then re-suspended into the atmosphere together with sea salt aerosols, the high concentration of ^7Be in snow at the coastal region would be expected. Let us calculate the concentration of ^7Be in sea salt aerosols. The concentration of Na^+ in the coastal region obtained in this study is approximately $0.2 \text{ mg} \cdot \text{kg}^{-1}$ (Fig. 2b). This value can be converted to $18 \text{ mg-sea salt kg}^{-1}$ because the concentration of Na^+ in seawater is $11000 \text{ mg} \cdot \text{kg}^{-1}$ (Broecker and Peng 1982). The concentration of ^7Be in the surface water of the South Pacific is $\sim 10^{-8} \text{ Bq mg}^{-1}$ (Young and Silker 1980). Consequently, the concentration of ^7Be in snow originating from sea salt is calculated to be $\sim 1.8 \times 10^{-7} \text{ Bq kg}^{-1}$; but this value does not substantially contribute to the total concentration of ^7Be in snow of the coastal region. Radioactive decay is another possible cause to explain the regional distribution of ^7Be . The production rate of ^7Be in the latitude belt of our study area ($69^\circ - 77^\circ\text{S}$) is nearly constant (Junge 1963). The activity of ^7Be , with a half-life of 53 days, in the katabatic-wind region should be lower than that in the other regions because the accumulation of fresh snow is disturbed by strong winds. At the present time, we do not have any supporting data to explain the regional distribution of ^7Be . Measurement of ^{10}Be , with a half-life of 1.6×10^6 years, may provide us with some knowledge that may help us to interpret the distribution.

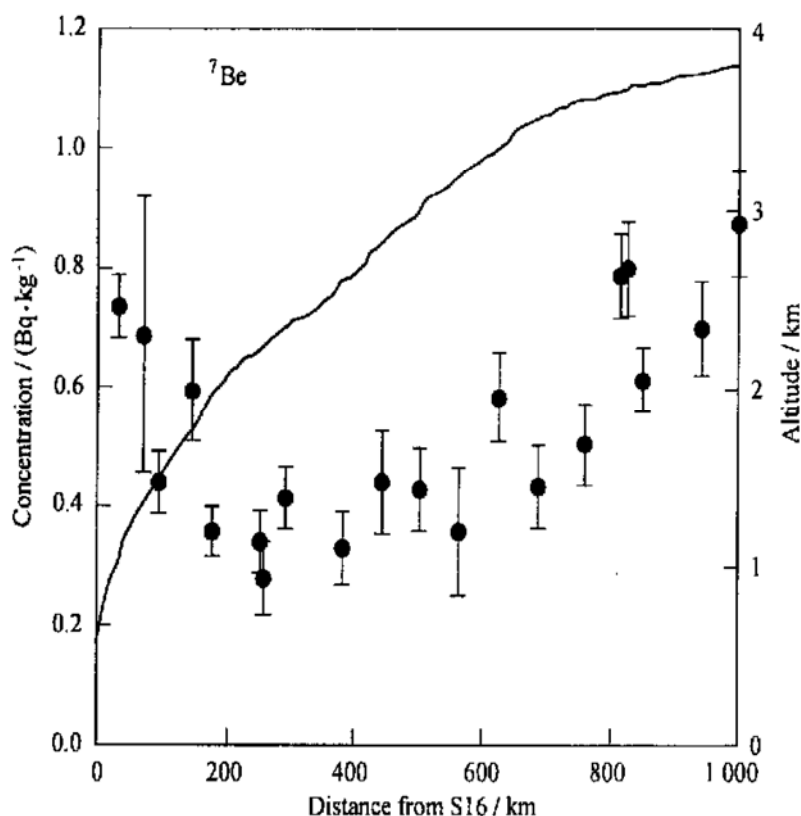


Fig. 6. The distribution of the concentrations of ^7Be in snow cover along the study route. Error bars are given for each point.

4 Concluding Remarks

We measured the spatial variability of Cl^- , Na^+ , SO_4^{2-} , NO_3^- and ^7Be in snow cov-

er along the study route from S16 to Dome Fuji station in east Dronning Maud Land, Antarctica, and obtained the following results.

(1) The concentrations of Cl^- and Na^+ at the coast rapidly decreased up to 200 km inland (2.0 km a. s. l.). This result may be due to the fact that sea salt aerosols are transported from the coast toward the interior of the continent and are removed onto the Antarctic ice sheet.

(2) From 200 km to 1000 km inland, the concentrations of Na^+ were substantially constant. On the other hand, the concentrations of Cl^- increased with distance beyond 750 km inland. Moreover, the contribution factors between Cl^- and Na^+ decreased and the Cl^-/Na^+ ratio and the $\text{nssCl}^-/\text{Cl}^-$ ratio increased toward the interior of the continent. These results suggest that a source of Cl^- other than sea salt exists in the inland plateau of Antarctica.

(3) The concentrations of Na^+ in snow cover in the ice sheet within the coastal region decreased to half with every 100 km of distance from the coast and 0.6 km of the altitude.

(4) Although the concentrations of SO_4^{2-} and NO_3^- in snow were relatively high in the coastal region and the inland plateau, the fluctuations in the concentrations were large compared with those of Cl^- and Na^+ .

(5) The concentrations of ^7Be in snow were also high in the coastal region and the inland plateau region. This may be due to the activity of ^7Be in the katabatic wind region should be lower than that in the other regions because the accumulation of fresh snow is disturbed by strong winds.

Table 1. The contribution factors between Cl^- and Na^+ , the Cl^-/Na^+ and the $\text{nssCl}^-/\text{Cl}^-$ ratios in three sections of the study route

Distance from S16 / km	c. f. ^a / (%)	Cl^-/Na^+ ^b	$\text{nssCl}^-/\text{Cl}^-$ ^b
0– 200	97	2.0 ± 0.3	0.09 ± 0.13
200– 750	61	2.6 ± 1.0	0.22 ± 0.24
750– 1000	33	3.4 ± 1.5	0.38 ± 0.24

^aContribution factors between Cl^- and Na^+ .

^bErrors are ± 1 standard deviation.

Acknowledgments We are very grateful to the members of the 40th Japanese Antarctic Research Expedition, conducted by Prof. K Shiraishi of the National Institute of Polar Research, for their support in the field operations and in performing the chemical analyses at Syowa station. We express our special thanks to the members of the inland expedition, Mr. K Ikarashi, Dr. H Kusagaya, Mr. Y Tsuchiya, Mr. E Murakata, Mr. S Matsunaga, Mr. N Endo, Mr. H Horimoto, Mr. Y Kitakaze and Mr. K Yanagiya, for giving various support for the snow sampling.

References

- Ageta Y, Kamiyama K, Okuhira F *et al.* (1989): Geomorphological and glaciological aspects around the highest dome in Queen Maud Land. East Antarctica. Proc. NIPR Symp. Polar Meteorol. Glaciol., 2: 88–96.
 Broecker WS, Peng TH (1982): Tracers in the sea. New York: Eldigio Press, 26.

- Delmas RJ (1992): Environmental information from ice core. *Rev. Geophys.*, 30: 1 - 21.
- Dome F Coring Group (1998): Deep ice core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica. *Ann. Glaciol.*, 27: 333 - 337.
- Furukawa T, Kamiyama K, Maeno H (1996): Snow surface features along the traverse route from the coast to Dome Fuji Station, Queen Maud Land, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, 10: 13 - 24.
- Herron MM, Langway Jr. CC (1979): Dating of Ross Ice Shelf cores by chemical analysis. *J. Glaciol.*, 24: 345 - 357.
- James IN (1989): The Antarctic drainage flow: implications for hemispheric flow on the Southern Hemisphere. *Antarc. Sci.*, 1: 279 - 290.
- Junge CE (1963): *Air Chemistry and Radioactivity*. New York: Academic Press, 235.
- Kamiyama K, Ageta Y, Fujii Y (1989): Atmospheric and depositional environments traced from unique chemical compositions of the snow over an inland high plateau, Antarctica. *J. Geophys. Res.*, 94: 18515 - 18519.
- Kamiyama K, Motoyama H, Fujii Y *et al.* (1996): Distribution of hydrogen peroxide in surface snow over Antarctic ice sheet. *Atmos. Environ.*, 30: 967 - 972.
- Kamiyama K, Watanabe O (1994): Substances deposited on an inland plateau, Antarctica. *Nankyo Shiryō (Antarctic Record)*, 38: 232 - 242 (in Japanese).
- Kreutz KJ, Mayewski PA (1999): Spatial variability of Antarctic surface snow glaciochemistry: implications for palaeoatmospheric circulation reconstructions. *Antarc. Sci.*, 35: 105 - 118.
- Legrand M, Delmas RJ (1985): Spatial and temporal variations of snow chemistry in Terre Adélie (Antarctica). *Ann. Glaciol.*, 7: 20 - 25.
- Legrand M, Delmas RJ (1988): Formation of HCl in the Antarctic atmosphere. *J. Geophys. Res.*, 93: 7153 - 7168.
- Legrand M, Mayewski PA (1997): Glaciochemistry of polar ice cores: A review. *Rev. Geophys.*, 35: 219 - 243.
- Lal D, Arnold JR, Honda M (1960): Cosmic ray produced rates of Be^7 in oxygen, and P^{32} , P^{33} , S^{35} in argon at mountain altitudes. *Phys. Rev.*, 118: 1626 - 1632.
- Lal D, Malhorta PK, Peters B (1958): On the production of radioisotopes in the atmosphere by cosmic radiation and their application to meteorology. *J. Atmos. Terrest. Phys.*, 12: 306 - 328.
- Minikin A, Wagenbach D, Graf W *et al.* (1994): Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf, Antarctica. *Ann. Glaciol.*, 20: 283 - 290.
- Parish TH, Bromwich DH (1991): Continental-scale simulation of the Antarctic katabatic wind regime. *J. Climate*, 4: 135 - 146.
- Wagon P, Delmas RJ, Legrand M (1999): Loss of volatile acid species from upper firn layers at Vostok, Antarctica. *J. Geophys. Res.*, 104: 3423 - 3431.
- Young JA, Silker WB (1980): Aerosol deposition velocities on the Pacific and Atlantic oceans calculated from ^7Be measurements. *Earth Planet. Sci. Lett.*, 50: 92 - 104.