

## Sulfate depletion in snow over sea ice near Syowa Station, Antarctica, in relation to the origin of sulfate depleted sea salt aerosol particles in winter

Kazuo Osada<sup>1</sup>, Keiichiro Hara<sup>1,2</sup>, Mizuka Kido<sup>1</sup>, Hiroki Kai<sup>3</sup>,  
Takashi Yamanouchi<sup>2</sup>, Gen Hashida<sup>2</sup>, Katsuji Matsunaga<sup>1</sup>  
and Yasunobu Iwasaka<sup>1</sup>

<sup>1</sup>STEL, Nagoya University, Chikusa-ku, Furo-cho, Nagoya 464-8601

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

<sup>3</sup>RESTEC, Office Tower X 21F, Harumi Island Triton Square, 1-8-10  
Harumi, Chuo-ku, Tokyo 104-6021

**Abstract:** Snow samples collected over sea ice near Syowa Station were analyzed for ionic constituents to understand sulfate depletion in sea salt aerosol particles, which have often been observed in winter in the coastal region of Antarctica. Ratios of  $\text{Cl}^-/\text{Na}^+$  in snow were higher than that in sea water, whereas  $\text{SO}_4^{2-}/\text{Na}^+$  ratios were lower in snow samples. The degree of  $\text{SO}_4^{2-}$  depletion relative to the sea water composition increased with increase in  $\text{Na}^+$  concentration. From comparison with a simple chemical mass balance model using the  $\text{SO}_4^{2-}/\text{Na}^+$  ratios in the samples, depletion of  $\text{SO}_4^{2-}$  in snow is considered to be largely attributed to the fractionation of sulfate by forming Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) during sea ice growth.

The  $\text{Br}^-/\text{Na}^+$  ratios of the snow predicted from the fractionation model differ significantly from the observed values: positive deviations were found in dark early July and negative deviations were seen in September. This could have resulted from  $\text{Br}_2$  release from the snow after local sunrise.

In winter aerosols collected at Syowa Station, depletion of  $\text{SO}_4^{2-}$  was also found. Based on statistics of meteorological data at Syowa Station, as appropriate conditions of meteorological and salt concentrations in drifting snow particle were fulfilled, the depletion of  $\text{SO}_4^{2-}$  in aerosol particles in winter can be explained by sublimation of salted drifting snow particles from the sea ice area.

### 1. Introduction

Sea salt is the major constituent of atmospheric aerosol particles in coastal Antarctica (e.g. Osada *et al.*, 1998; Wagenbach *et al.*, 1998) as well as all other oceanic regions (Andreae, 1995). In the coastal area of Antarctica,  $\text{SO}_4^{2-}/\text{Na}^+$  ratios of some aerosol samples are lower than that of sea water (Osada *et al.*, 1998; Wagenbach *et al.*, 1998). This phenomenon has been observed mainly in the austral winter. Although the majority of aerosols in winter consist of sea salt particles in this region, the source and transport processes of sea salt aerosols are not well known. The speculated source area of sea salt aerosols reaching the coastal Antarctica is the Southern Ocean, especially around the stormy fringe of the Antarctic continent. However, since a vast sea ice

zone (some 1000 km toward the north) is developed in winter to spring (Parkinson and Gloersen, 1993), an efficient transport mechanism must exist from north of the sea ice zone for the aerosols to reach the coast of Antarctica.

Previously, based on measurements of sea salt particles at Syowa Station (Kikuchi and Yaura, 1970), the concentration of sea salt particles was found to increase under conditions of not only cyclonic disturbances from the north but also southern wind without a snow storm. Their observation suggested that different processes of sea salt transport were acting at the coast of Antarctica, but details of the processes were not given.

Another set of measurements relating to sea salt at Syowa Station was performed on the electrical conductivity of fallen and drifting snow collected at Syowa Station and samples of snow cover on sea ice near Syowa (Osada *et al.*, 1988). In their results, the electrical conductivity of calmly fallen snow was from a few to  $18 \mu\text{S}/\text{cm}$  whereas the values for drifting snow were up to about one thousand, and the values of snow cover over sea ice were several hundred to ten thousand approaching the bare sea ice area. From these measurements, they concluded that the high conductivity of the drifting snow as well as snow cover resulted from uptake of brine over sea ice. In their analysis, however, considerations of chemical fractionation for salty snow were not given at all.

On the other hand, Aoki (1997) reported episodes of  $\text{O}_3$  depletion in the surface air at Syowa Station. Recent modeling of atmospheric chemistry and observation of reactive halogenated species in the Arctic have suggested that reactive brominated species in the surface air may cause  $\text{O}_3$  depletion in the Arctic boundary layer (McConnell *et al.*, 1992; Foster *et al.*, 2001). In processes that produce reactive brominated species in the atmosphere, heterogeneous reactions of HOBr with sea salt aerosols or sea salt in snow over sea ice are suggested as the major source of  $\text{Br}_2$  that has a central role in  $\text{O}_3$  catalysis with sunlight (Foster *et al.*, 2001). Furthermore, recent study of HCHO at Alert, Canadian Arctic, has suggested that  $\text{NO}_3^-$  in snow over sea ice has an important role to initiate radical chemistry with organic compounds present in the snow (Sumner and Shepson, 1999). Thus, the processes of ozone destruction in the surface air at the polar sunrise may include chemistry within the snowpack over sea ice. However, not only halogens but also the variability of salt composition have not been studied well for snow over sea ice.

To study the fractionation of sea salt in various types of snow and aerosols near Syowa Station, we measured ionic compositions and concentrations in snow samples obtained from hand dug pits over sea ice near Syowa Station in the austral winter to early spring of 1999.

## 2. Samples and chemical analysis

Snow samples over sea ice were collected from the wall of a hand dug pit at point T-10 along the route from Syowa Station ( $69^\circ 00'S$ ,  $39^\circ 35'E$ ) to Tottuki Point, East Antarctica, as shown in Fig. 1. Within close proximity to the hand dug pit at T-10, other vertical snow samples were collected from thinner snow cover near the bare sea ice area for comparison. Such thinner snow may contain higher sea salt concentration than that of the thicker snow surface due to uptake of brine from sea ice. The snow

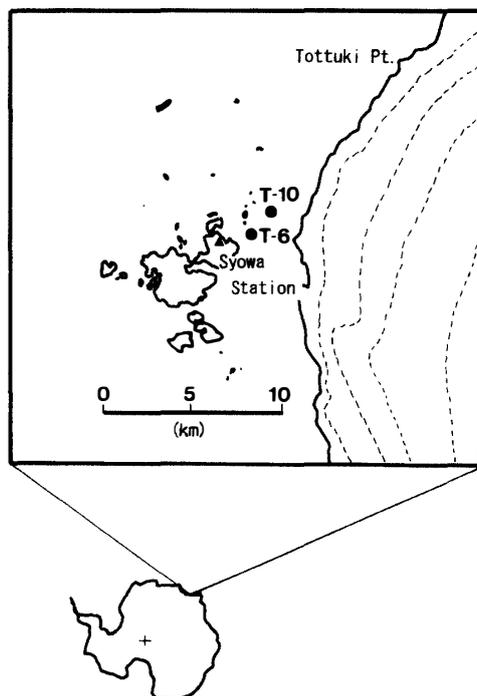


Fig. 1. A map showing snow pits T-10 and T-6 near Syowa Station, East Antarctica.

sampling was conducted on July 7, July 19, September 17 and September 29, 1999. The sampling of thinner snow cover in September was done at point T-6 because the snow cover near T-10 was uniformly thick. The sampling was done in dark winter and early spring as the sulfate depletion in aerosols was often observed at Syowa Station (Osada *et al.*, 1998). A polypropylene 50 ml centrifuge vial (Iwaki) pre-cleaned by ultra-pure water was pushed into the snow wall of the pit or scraped the upper most snow surface. The snow sample in the vial was sealed with an air tight cap immediately after the sampling to reduce air contamination.

Concentration levels of anions and cations were measured by an ion chromatograph (Shimazu, model LC-10A) equipped with IC-A3 analytical and IC-GA3 guard columns for anion separation, and IC-C3 analytical and IC-GC3 guard columns for cation separation. An automated sample injector was used for simultaneous analysis of anions and cations in the sample water. Electric conductivity of the sample water was measured by a conductivity meter (Horiba, C-172). Depending on the conductivity of the sample water, gravimetric dilution and changing injection volumes (50 and 500  $\mu$ l) were combined for optimizing analytical performance. However, trace amounts of  $\text{NO}_3^-$  and  $\text{Br}^-$  with very high  $\text{Cl}^-$  concentration could not be obtained for some samples.

### 3. Results and discussion

Figures 2 and 3 show vertical profiles of  $\text{Na}^+$  and  $\text{NO}_3^-$  concentrations with molar ratios to  $\text{Na}^+$  in the snow samples obtained in July and September, respectively. Values for snow samples of the uppermost few mm of thinner snow cover (except for the

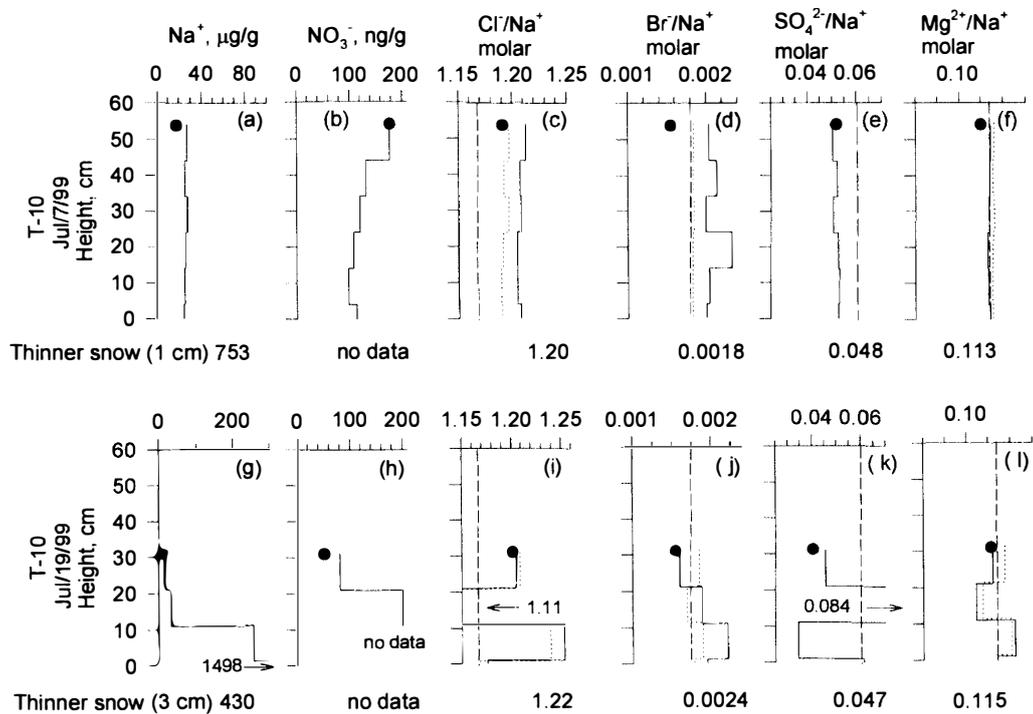


Fig. 2. Vertical profiles of ionic concentrations and ratios to  $\text{Na}^+$  in the samples obtained at T-10 in July, 1999. Filled circles represent values of the uppermost few mm of snow cover at T-10. Values of the uppermost snow sample from thinner area near T-10 are also indicated. Snow height of the thinner snow area is listed in parenthesis. Dashed and dotted lines represent the sea water ratio and the estimated values from  $\text{SO}_4^{2-}/\text{Na}^+$  ratio with Mirabilite fractionation, respectively.

September 29 sample) near T-10 and values of the uppermost few mm of the surface at T-10 (filled circles) are also shown in the figures.

$\text{Na}^+$  concentrations (Figs. 2a, 2g, 3a and 3g) ranged from 0.9 to  $1500 \mu\text{g/g}$  for T-10 and 1.5 to  $753 \mu\text{g/g}$  for thinner snow surface samples. The minimum values of  $\text{Na}^+$  concentrations are associated with newly fallen snow just before the sampling of September 29. The uppermost surface snow of T-10 contained much less  $\text{Na}^+$  than thinner snow. Except for the first (July 7) sample set,  $\text{Na}^+$  concentrations for T-10 were higher in the deeper part of the profiles: highest near the bottom of the snow cover. These lateral and vertical distributions of  $\text{Na}^+$  are considered to be caused by snow infiltration of salty brine from the sea ice surface (Martin, 1979; Takizawa, 1985).

Some of the  $\text{NO}_3^-$  concentrations could not be measured because of insufficient separation between  $\text{Cl}^-$  and  $\text{NO}_3^-$  peaks for samples of high  $\text{Cl}^-$  concentration such as thinner snow and the bottom snow of T-10. Except for these,  $\text{NO}_3^-$  concentrations (Figs. 2b, 2h, 3b and 3h) ranged from 50 to  $177 \text{ ng/g}$  with a median at around  $100 \text{ ng/g}$ . The concentration of  $\text{NO}_3^-$  in the snow samples over sea ice was higher than values obtained from ice cores (mostly below  $50 \text{ ng/g}$ ) at H15 (Kohno *et al.*, 1996) and S25 (Watanabe *et al.*, 1999) over the ice sheet near the coast of Dronning Maud Land, East Antarctica. According to the aerosol study at Syowa Station (Osada *et al.*, 1998) and at in the Norwegian Arctic (Hara *et al.*, 1999), deposition of gaseous precursors (such

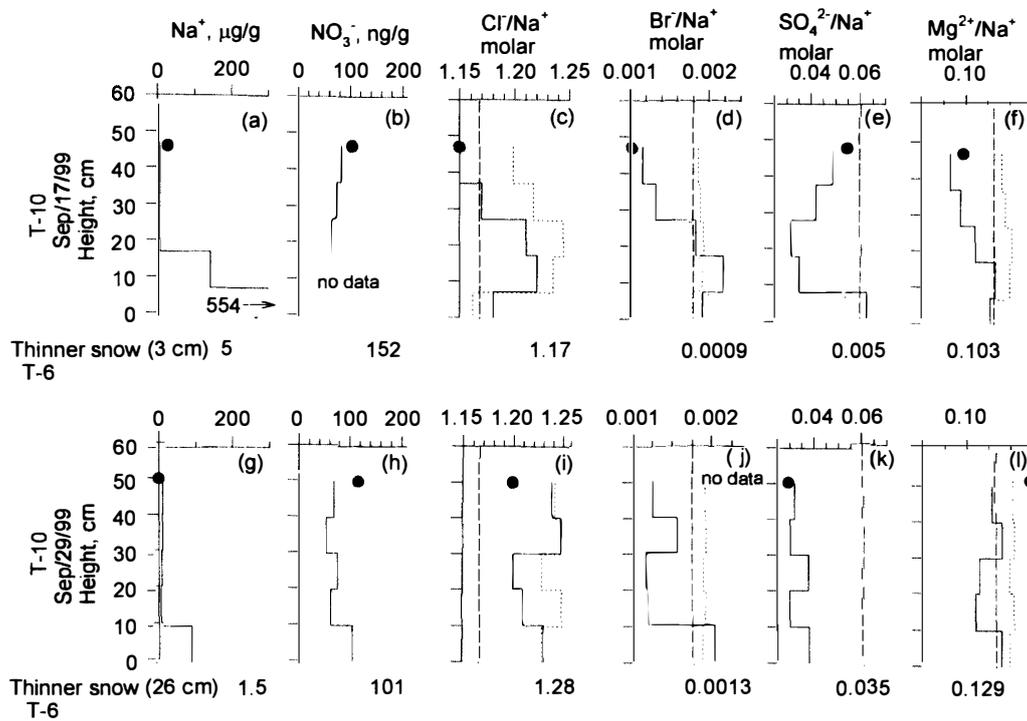


Fig. 3. Same as Fig. 2 but for September 1999. Note that the sampling location of thinner snow was changed to T-6.

as  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  etc) onto sea salt particles is presumed to be a major source of  $\text{NO}_3^-$  in coarse particles. Similarly, salty snow may contribute to dry deposition of the gaseous precursors. The vast sea ice area around Antarctica, and also over the Arctic Ocean, could be a huge sink for  $\text{NO}_3^-$  from various nitrogen oxides.

Most molar ratios of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Mg}^{2+}$  to  $\text{Na}^+$  in the snow samples deviated significantly from the ratio in sea water (Wilson, 1975, indicated as a dashed line in the figures).  $\text{Cl}^-/\text{Na}^+$  ratios (Figs. 2c, 2i, 3c and 3i) tend to be higher than the sea water ratio (1.17), whereas  $\text{Br}^-/\text{Na}^+$  ratios (Figs. 2d, 2j, 3d and 3j) are variable. Vertical profiles of the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio (Figs. 2e, 2k, 3e and 3k) seem to be mirror images of the  $\text{Cl}^-/\text{Na}^+$  ratio. A large positive deviation of  $\text{SO}_4^{2-}/\text{Na}^+$  at the middle of the profile on July 19 (Fig. 2k) is probably related to the existence of an ice layer (5-cm thick) in the snow cover. Trends in  $\text{Mg}^{2+}/\text{Na}^+$  profiles (Figs. 2f, 2l, 3f and 3l) resemble those in the  $\text{Cl}^-/\text{Na}^+$  ratios but the magnitude of the variation was small. Considering snow infiltration of brine and salt contribution from “salt flowers” over young sea ice (Martin, 1979; Ono *et al.*, 1980; Martin *et al.*, 1995; Rankin *et al.*, 2000), the deviations of  $\text{Cl}^-/\text{Na}^+$ ,  $\text{SO}_4^{2-}/\text{Na}^+$  and  $\text{Mg}^{2+}/\text{Na}^+$  ratios from the sea water ratios and their relationship may result from selective exclusion of salts, such as Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), during sea ice growth. As the ice is progressively cooled below freezing the volume ratio of brine to ice decreases, the salinity of the brine increases, and salts begin to precipitate. Mirabilite begins to precipitate at temperatures below  $-8^\circ\text{C}$ , the precipitate being incorporated into the sea ice matrix (Richardson, 1976). This leaves a surface brine that is depleted in  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ . Conversely, the ratios of  $\text{Cl}^-/\text{Na}^+$  etc in the surface brine increase from the value of sea water due to depletion

of  $\text{Na}^+$ . If the deviations of ratios such as  $\text{Cl}^-/\text{Na}^+$  are solely derived from the exclusion of Mirabilite, the deviations of these ratios should follow  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  depletion, namely the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio. Using the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio in the sample as an indicator of exclusion of Mirabilite, the ratios were calculated by a simple chemical mass balance between the brine and the ice matrix, as indicated by dotted lines in Figs. 2 and 3.

Trends of  $\text{Cl}^-/\text{Na}^+$  and  $\text{Mg}^{2+}/\text{Na}^+$  ratios predicted from the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio are consistent with observed ratios; some estimated values are quite close to the observed ratios, especially for the samples of July 19 (Figs. 2i and 2l) and part of September 29 (Fig. 3i). Differences between observed and estimated ratios should be partly due to exclusion of salts other than Mirabilite. Such salts include Hydrohalite ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ; Richardson, 1976). The daily mean air temperature at Syowa Station in winter sometimes decreases below  $-24^\circ\text{C}$ , which is the starting temperature for precipitation of Hydrohalite.

On the other hand, vertical profiles of the predicted  $\text{Br}^-/\text{Na}^+$  ratios (Figs. 2d, 2j, 3d and 3j) differ significantly from observed values: positive deviations in dark early July to negative deviations after local sunrise. This implies that addition and later volatilization of  $\text{Br}^-$  or brominated species may occur in the snow cover. Recent investigations (McConnell *et al.*, 1992; Foster *et al.*, 2001) of Arctic air/snow chemistry have suggested that heterogeneous reactions in the upper snow cover produce  $\text{Br}_2$  reducing  $\text{Br}^-$  concentrations in the snow, for example:



This reaction is able to sustain reactive Br atoms from photolysis of  $\text{Br}_2$  in the air during the polar sunrise when ozone in the surface air is destroyed by gas phase Br reactions. Although remarkable ozone depletion (below 10 ppbv) at Syowa Station was not reported for 1999, fluctuation of ozone concentration was observed after July (Kokuritsu Kyokuchi Kenkyu-jo, 2000). This could result from  $\text{Br}_2$  release associated with negative deviations of  $\text{Br}^-/\text{Na}^+$  in the snow.

Figure 4 shows scatter plots of  $\text{Na}^+$  versus  $\text{nssSO}_4^{2-}$  (Fig. 4a) and  $\text{nssCl}^-$  (Fig. 4b) concentrations in size-segregated aerosol particles obtained at Syowa Station during 1996 to 1998 (Osada *et al.*, 1998). The term non sea salt (nss) may not be appropriate in this case, but it is familiar to many atmospheric chemists. The non sea salt portions of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  in the aerosol samples were calculated from  $\text{Na}^+$  concentration in the sample and their sea water ratio to  $\text{Na}^+$ . Negative values in Fig. 4 indicate depletion.

A good linear correlation was obtained for the negative  $\text{nssSO}_4^{2-}$  versus  $\text{Na}^+$  concentrations, as shown in Fig. 4. Aerosol samples of high  $\text{Na}^+$  with negative  $\text{nssSO}_4^{2-}$  concentrations were mostly obtained in winter, whereas samples with positive  $\text{nssSO}_4^{2-}$  concentrations were obtained from spring to fall. The relationship between  $\text{Na}^+$  and  $\text{nssCl}^-$  was not so simple.

Figure 5 shows scatter plots of  $\text{Na}^+$  versus  $\text{nssSO}_4^{2-}$  (Fig. 5a) and  $\text{nssCl}^-$  (Fig. 5b) concentrations in the snow samples. Points indicated as # were samples of the bottom snow or ice layer in the snow cover. Excluding these samples with positive  $\text{nssSO}_4^{2-}$  values, the regression line for negative  $\text{nssSO}_4^{2-}$  versus  $\text{Na}^+$  concentrations is indicated as a dotted line. The regression line obtained from aerosol samples is drawn as a

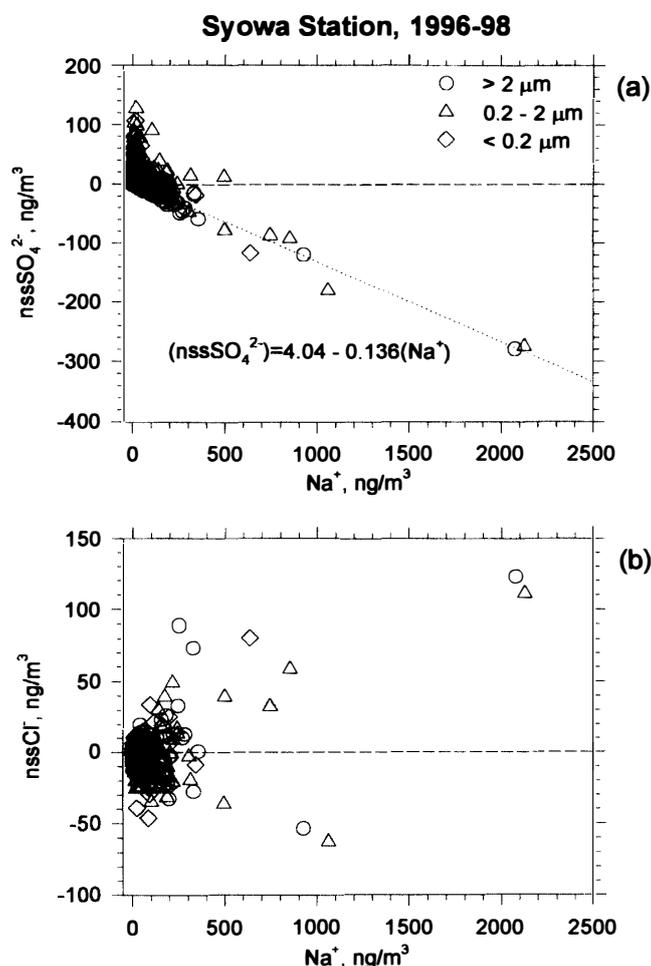


Fig. 4. Scatter plots of  $\text{Na}^+$  versus  $\text{nssSO}_4^{2-}$  (a) and  $\text{nssCl}^-$  (b) in size-segregated aerosol samples obtained from 1996 to 1998 (Osada et al., 1998). The regression line for negative  $\text{nssSO}_4^{2-}$  values is drawn as a dotted line.

dash-dotted line. The slope of the regression line for the snow samples was almost half of that for aerosols. Note that the aerosol and the snow samples were not taken in the same year. Even so, the connection of some snow data with the slope from aerosol data suggests that the depletion of  $\text{SO}_4^{2-}$  in the winter aerosols is implicated in brine formation of sea ice and that brine contribution to aerosol particles near Syowa Station may take place similarly every year.

In Fig. 5b, concentrations of  $\text{nssCl}^-$  increase with increasing  $\text{Na}^+$  concentration except for points labeled by #. Using the average  $\text{SO}_4^{2-}/\text{Na}^+$  ratio of the snow samples and the chemical mass balance for Mirabilite formation, the predicted  $\text{nssCl}^-/\text{Na}^+$  line is drawn as a long-dashed line. Except for the 3 points labeled, the observed relationship between  $\text{nssCl}^-$  and  $\text{Na}^+$  corresponds well with the expected line from the average  $\text{SO}_4^{2-}/\text{Na}^+$  ratio. This suggests that most deviations of  $\text{SO}_4^{2-}/\text{Na}^+$  and  $\text{Cl}^-/\text{Na}^+$  ratios from sea water are explained by Mirabilite formation during sea ice growth, and that residual brine from sea ice contributes to the sea salt composition of snow over the sea ice.

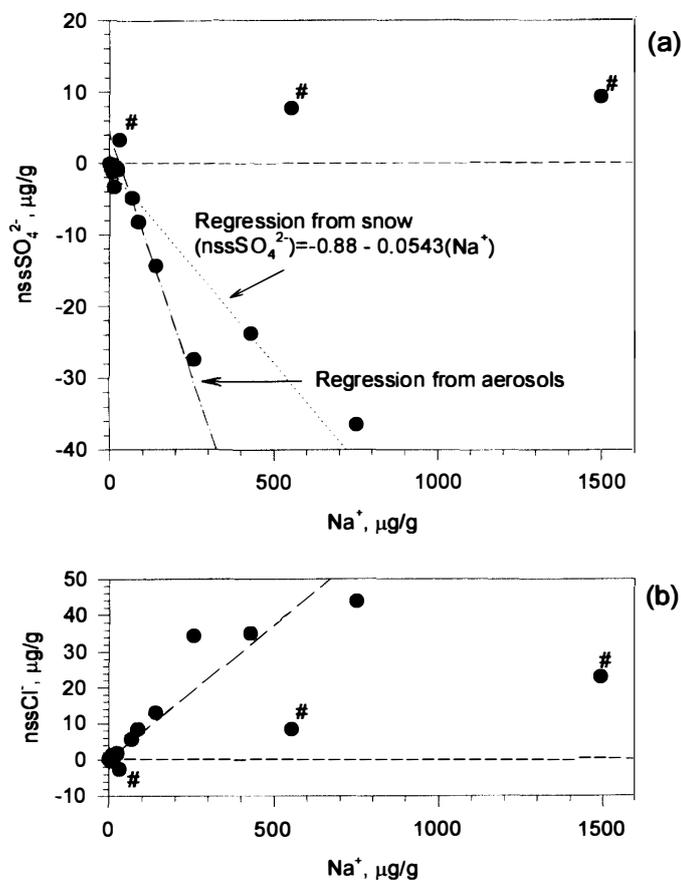


Fig. 5. Scatter plots of  $\text{Na}^+$  versus  $\text{nssSO}_4^{2-}$  (a) and  $\text{nssCl}^-$  (b) in snow samples obtained in 1999. A regression line for negative  $\text{nssSO}_4^{2-}$  values, except for samples labeled by #, is drawn as a dotted line. The dash-dotted line represents the regression line from Fig. 4. The long-dashed line in the lower panel indicates the relationship estimated from averaged  $\text{SO}_4^{2-}/\text{Na}^+$  ratios in snow (see text). Samples indicated by # represent snow influenced by melt water or brine at the snow bottom.

As mentioned earlier, the depletion of  $\text{SO}_4^{2-}$  of aerosols in winter is implicated in brine formation of sea ice. To connect fractionated sea salt composition in aerosols with snow over sea ice, sublimation of salted drifting and blowing snow particles is examined with respect to meteorological conditions at Syowa Station. As speculated earlier (Osada *et al.*, 1988), if the  $\text{SO}_4^{2-}$  depleted salts are captured by snow particles during saltation over a bare sea ice area or thin saline snow cover, the snow particles would contain  $\text{SO}_4^{2-}$  depleted salts as well. Drifting and blowing snow (existence of suspended snow particles in surface air) are phenomena that have been reported in meteorological observations (Japan Meteorological Agency, 1997–1999) at Syowa Station. Figure 6 shows the reported number of days per month (Fig. 6a) and monthly average of relative humidity over the ice (%) on days when drifting and blowing snow were observed (Fig. 6b). The meteorological statistics have been done for 3 years of aerosol observations.

The number of days of drifting and blowing snow is, in general, high in winter and low in summer. In August, the frequency of drifting and blowing snow decreases but

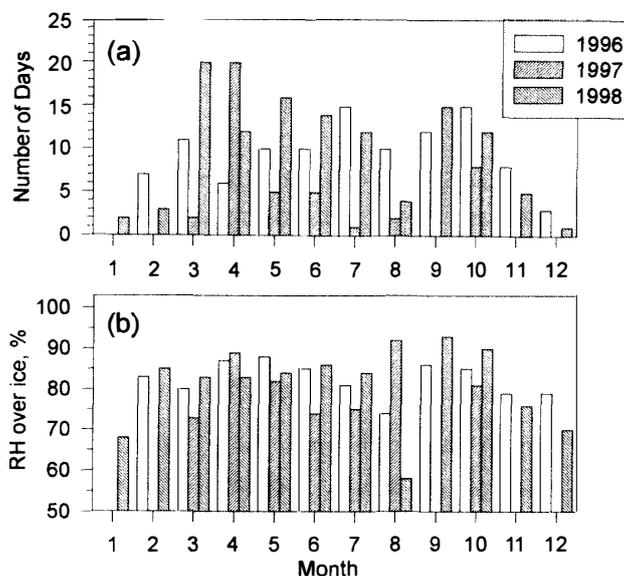


Fig. 6. Monthly number of days for drifting and blowing snow (upper panel) and monthly average of relative humidity over ice under drifting and blowing snow conditions.

it increases again in September. The monthly average frequency of drifting and blowing snow is about 1/3 to 1/2 of days in winter. Relative humidity over ice during drifting and blowing snow is mostly 75 to 90% in winter. This may allow water vapor to sublimate from snow particles during suspension in the air. Assuming that (1) typical salt concentration in a drifting snow particle is 50 mg/kg (about  $110 \mu\text{S}/\text{cm}$ ), (2) the radius of a drifting snow particle is 0.1 mm (Budd, 1966) and (3) the density of sea salt is  $2.2 \text{ g}/\text{cm}^3$ , an aerosol particle after sublimation may have a sphere of equivalent radius about  $2.8 \mu\text{m}$ . In reality, since the duration of suspension is usually not long, smaller but fewer snow particles below 0.1 mm in radius may sublimate. This prevents the atmospheric buildup of a huge amount of fractionated sea salts, which is consistent with the observation that occurrences of  $\text{SO}_4^{2-}$  depleted sea-salt aerosols are not so frequent as expected from Fig. 6. Thus, as appropriate conditions of meteorological and salt concentration in drifting snow particle are fulfilled, the depletion of  $\text{SO}_4^{2-}$  in aerosol particles in winter would be explained by the sublimation of salted drifting snow particles from the sea ice area. Formation of sea salt fractionated aerosol particles from the sublimation of salted drifting snow particles is considered to be an important process of sea salt transport without cyclonic storm activity.

#### 4. Summary and conclusions

To study the origin and fractionation of sea salt in snow and aerosols in the coastal region of Antarctica, ionic concentrations and their ratios were analyzed for snow samples obtained from hand dug pits over sea ice near Syowa Station in the austral winter of 1999. Vertical profiles of molar ratios of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Mg}^{2+}$  to  $\text{Na}^+$  in the snow samples deviated significantly from the ratio in sea water. The  $\text{SO}_4^{2-}/\text{Na}^+$  ratio in the sample was used as an indicator of exclusion of Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ )

during sea ice growth to calculate the chemical mass balance between the brine and the ice matrix. Trends of  $\text{Cl}^-/\text{Na}^+$  and  $\text{Mg}^{2+}/\text{Na}^+$  ratios predicted from the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio in the samples are consistent with observed ratios, suggesting that Mirabilite formation during sea ice growth causes such deviations in the ratios.

A similarity of the  $\text{SO}_4^{2-}$  depletion of atmospheric aerosols in winter was found in the snow data at Syowa Station. Statistics of meteorological data at Syowa station suggest that salted drifting snow particles may sublime during suspension. This leads to formation of salt fractionated sea salt particles in the winter atmosphere.

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