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Variations of constituents of individual sea-salt particles at Syowa station, Antarctica

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ABSTRACT

Sampling of atmospheric aerosol particles was carried out at Syowa station, Antarctica (39.58°E, 69.00°S) in 1998. For a better understanding of sea-salt chemistry in the coastal Antarctic regions, individual sea-salt particles were analysed using a scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM-EDX). Individual particle analysis indicates that more sea-salt particles were modified in fine particles (0.2–2 μm in diameter) through heterogeneous reactions mainly with gaseous sulfur species in the summer and reactive nitrogen oxides in the winter–spring. In particular, sea-salt particles in the coastal Antarctic atmosphere may be modified by heterogeneous reactions with not only SO_2 and H_2SO_4 but also volatile sulfur species (e.g. CH_3SO_3H, DMS and DMSO) derived from bioactivity on the ocean surface during the summer. Also, low air temperature and a larger extent of sea ice offshore Syowa probably enhanced release of fractionated sea-salt particles (S-rich, Mg-rich, K-rich and Ca-rich) from the surface of snow and sea ice, particularly in September–October 1998. In addition, we attempt to estimate the scavenging rate of atmospheric sulfur species and reactive nitrogen oxides by dry deposition of sea-salt particles. Our estimation suggests that the upper limit of the scavenging rate of atmospheric sulfur species by sea-salt particles could rise to approximately 0.5 nmol m^{-2} day^{-1} at Syowa station during the summer. This value corresponded to about 30% of the concentration of particulate sulfur species such as non-sea-salt (nss)-SO_4^{2-} and $CH_3SO_3^-$ and ~10% of total atmospheric sulfur species (nss-SO_4^{2-}, $CH_3SO_3^-$ and SO_2). In contrast, the estimated NO_3^- scavenging rate by sea-salt particles was ~0.2 nmol m^{-2} day^{-1}, which is similar to the dry deposition rate of $HNO_3+N_2O_5$ (approximately 0.2–0.3 nmol m^{-2} day^{-1}). Hence, sea-salt particles probably play an important role as scavengers of acidic species in the coastal Antarctic regions.

1. Introduction

In the lower troposphere, sea-salt particles can act as a source of reactive halogen species, cloud condensation nuclei (CCN) and cause atmospheric scattering of solar radiation. According to Quinn et al. (1996, 2000) and Murphy et al. (1998), sea-salt particles contribute significantly to aerosol optical properties in the remote marine boundary layer (MBL) and the Southern Ocean. Furthermore, some investigations have shown preferential Cl^- liberation (Mouri et al. 1997, 1999; Jourdain and Legrand, 2002; Hara et al., 2004) and Br^- liberation (Hara et al., 2004) from sea-salt particles in the Antarctic atmosphere in spite of its very clean air. Individual particle analysis of aerosol particles sampled in the coastal Antarctic area during the summer indicated that preferential Cl^- liberation occurred due to acidic sulfur species such as SO_4^{2-}, $CH_3SO_3^-$ and their precursors (Wouters et al., 1990; Hara et al., 1995; Mouri et al., 1997, 1999). In addition to acidic sulfur species, sea-salt modification (e.g. Cl^- modification) can be caused by heterogeneous reactions with reactive nitrogen oxides such as HNO_3 and N_2O_5 in the polar regions during transport (Hara et al., 1999). Since halides are liberated from sea-salt particles to the atmosphere (gaseous phase) via these heterogeneous reactions, sea-salt modification can thus simultaneously be an important source of gaseous and reactive inorganic halogen species.

From the viewpoint of the atmospheric cycles of acidic gases and reactive species, sea-salt modification (halogen liberation) with them can play an important role in both source and scavenging processes. The mode of sea-salt particles was distributed at approximately 2 μm (diameter) in the coastal Antarctic area during the summer (Kerminen et al., 2000; Jourdain and Legrand, 2002), although the mode in the summer was lower than in the MBL over the open water due to the presence of sea ice. Anticipating that the larger sea-salt particles will have a shorter lifetime due to dry deposition, it is expected that sea-salt particles will play a role as scavengers for acidic species through heterogeneous processes and dry deposition in the coastal

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Antarctic area. Sievering et al. (1992) also pointed out the possibility that the heterogeneous SO_2 oxidation in sea-salt particles constitutes a rapid cycling pathway by way of preferential dry deposition in the MBL. Indeed, individual particle analysis indicated that some sea-salt particles containing SO_4^{2-} and $CH_3SO_3^-$ in the coarse mode are present in the Antarctic atmosphere (Wouters et al., 1990; Hara et al., 1995).

Since the hypothesis was first proposed by Charlson et al. (1987), the climate-feedback system involving biogenic activity in the ocean has become of increasing interest in the remote MBL (particularly in the coastal Antarctic regions). With significant scavenging of the biogenic gases by aerosol particles, however, the scavenging of gaseous species such as DMS and its products by sea-salt particles can lead to reduced formation of new particles and hence a false estimate of the aerosol effect on climate change. Although the concentration of particulate acidic species in sea-salt particles has often been assumed by bulk aerosol analysis, actual mixing states between acidic species and sea-salt particles still remain uncertain. For accurate estimation of the scavenging rate of acidic gases by dry deposition of sea-salt particles, therefore, we must determine the concentrations of acidic species in individual sea-salt particles in addition to the ambient concentrations of acidic gas.

Because of lower air temperatures, fractionated sea-salt particles originating from sea-salt fractionation on the surface of sea-ice and snow are present in the Antarctic atmosphere, particularly in the austral winter–spring (Hall and Wolff, 1998; Wagenbach et al., 1998; Osada et al., 2001; Hara et al., 2004a). According to laboratory measurements (Richardson, 1976; Marion et al., 1999), formation of fractionated sea salts such as $Na_2SO_4 \bullet 10H_2O$ (mirabilite), KCl (sylvite), $MgCl_2 \bullet 12H_2O$, $CaSO_4 \bullet 2H_2O$ (gypsum) and $CaCl_2 \bullet 6H_2O$ (antarcticite) depend on the ambient temperature during freezing and sublimation. As these compounds have a quite different hygroscopicities (deliquescence point) from the major components of sea salts (NaCl, 76.3%), for example $MgCl \bullet 12H_2O$ (35%), $CaCl_2 \bullet 6H_2O$ (40%) and Na_2SO_4 (84.2%) (Pruppacher and Klett, 1978; Finlayson-Pitts and Pitts, 2000), sea-salt fractionation can result in changes of hygroscopicity and the ability to form CCN. However, the seasonal variations of their mixing states in individual aerosol particles have not been determined in the polar regions.

The present study aims to understand the variation of sea-salt constituents in individual sea-salt particles and the role of atmospheric chemical processes in the Antarctic atmosphere (coast of East Antarctica and East Dronning Maud Land). Here, we focus especially on sea-salt modification, fractionation and the scavenging of acidic gases by dry deposition of sea-salt particles in the coastal Antarctic regions.

2. Sample and analysis

2.1. Individual particle analysis of sea-salt particles

Aerosol samples for individual particle analysis were collected at Syowa station (39.58°E, 69.00°S, ca. 30 m above sea level) approximately once a week, from March until October 1999 using a two-stage low-volume impactor (LVI). In order to prevent contamination from station activity, the sampling loss of coarse sea-salt particles and sampling artefact arising, for example, from evaporation and vaporization of aerosol constituents, aerosol sampling using a portable LVI sampling system was carried out for 10 min to about 1 h at a flow rate of 1.2 l min^{-1} at a windward position in the ambient air (outside the building). For the LVI sampling, two kinds of sampling substrates were used: (1) carbon-coated collodion thin film for chemical analysis using energy dispersive X-ray spectrometry (EDX) and (2) Nitron-coated collodion thin film for identification of NO_3^- in aerosol particles. Details of sample treatment in the case of substrate (2) are given in Hara et al. (1999).

Collected aerosol samples were immediately stored in polyethylene capsules. Nitron samples were treated with octanol vapour after sampling. The polyethylene capsules containing the aerosol samples were packed into zipped polyethylene bags. They were subsequently placed in an airtight box with silica gel until the observation using a scanning electron microscope equipped with EDX (SEM-EDX) in order to prevent morphological chemical changes during sample storage.

To reduce sample damage due to electron beam radiation in SEM-EDX analysis, post-carbon coating was done on each aerosol sample. Individual sea-salt particles were observed and analysed using a SEM (SEM-EDX; S-3000N, Hitachi) and EDX (EMAX-500, Horiba) equipped with an ultra-thin window detector (S-798, Horiba). EDX area analysis was performed with an accelerating voltage of 20 kV for 30 s counting time. Although the EDX used in the present study was able to detect light elements such as C, N and O, high EDX background peaks from the collodion thin film used as the sampling substrate rendered the analysis uncertain. We therefore exclude these light elements (C, N and O) from our further discussion.

In the high-vacuum environment of SEM-EDX ($\sim 10^{-6}$ Torr), it is impossible to observe the ambient aerosol particles exactly as they are found in the atmosphere. Although evidence of a liquid phase in aerosol particles (e.g. sea-salt particles) in the winter/spring Arctic boundary layer was obviously observed by SEM-EDX measurements (Hara et al., 1999), a significant fraction of the liquid phase must be lost owing to the high vacuum in the SEM chamber. Fortunately, however, Sheridan et al. (1993) pointed out that the detectable X-ray signature of aerosol constituents (e.g. S, O, N) was insignificantly affected by water volatilization under the conditions of SEM-EDX. Furthermore, Pardess et al. (1992) also indicated that evaporation of aerosol constituents was negligible during exposure to the electron beam under analytical conditions with an accelerating voltage of 15–25 kV and 100 s counting time. Bearing in mind our analytical conditions (accelerating voltage 20 kV; counting time 30 s), we anticipate that the analytical artefact for the species of interest in the present study is probably negligible.

Here, we attempted to analyse more than 50 sea-salt particles in each sample (total >2100 particles) with EDX. Because Na^+ is the major component of sea-salt particles, sea-salt particles were identified by Na detection in EDX analysis. When aerosol particles containing Na^+ other than sea-salt particles (e.g. minerals) are internally mixed with sea-salt particles, the presence of non-sea-salt (nss-)Na can lead to incorrect estimation of Cl^- depletion and sea-salt fractionation. Thus, internal mixtures of sea-salt and minerals/dusts, which were identified by Na detection together with Al, Si and/or Fe, were excluded from discussion in the present study. These excluded sea-salt particles containing minerals/dusts made up less than 1% of the aerosol particles containing Na in the present study. Furthermore, to check analytical error and sensitivity, artificial particles of NaCl, Na_2SO_4 and mixtures of both were prepared and analysed using EDX according to our standard procedure.

2.2. *Size-segregated aerosol samples for bulk analysis*

The sampling site was located on the windward side of the prevailing wind at Syowa station. Ambient air was sampled using a Tetlon braid tube (length about 3 m; internal diameter about 9 mm) situated 5 m above the ground surface, and then distributed into the sampling systems and other instruments (e.g. optical particle counters and condensation nuclei counters). Unfortunately, air sampling at Syowa stopped in October 1998 as a result of mechanical problems. Considering that aerosol sampling was carried out inside the room, aerosol particles were probably collected on the filter under dry and heated (room temperature, 10–20 °C) conditions.

Size-segregated aerosol samples were also collected using a two-stage mid-volume impactor (MVI), made from conductive plastics, with cut-off diameters of 2.0 and 0.2 μm at a flow rate of 27 l min^{-1}, and a back-up filter for 2 to 3 d, depending on the local weather conditions. Nucleopore filters (25 mm Ø, 0.2 μm pore size; Costar Co.) and a Teflon membrane filter (PTFE, 1.0 μm pore size, 47 mmϕ, Advantec) were used as sampling substrates for the MVI and back-up filter, respectively. After sampling, each filter was immediately placed in a precleaned polypropylene 15 ml centrifuge vial with an airtight cap in order to prevent contamination during sample storage. Sample vials were packed in polyethylene bags and were kept at about −20 °C in a freezer until chemical analysis in Japan. For a qualitative check of aerosol samples, procedural blank samples were taken from each sampler periodically (twice a month).

For extraction of the water-soluble aerosol constituents, ultrapure water (18.3 MΩ, Milli-Q water; 14 ml) was added to each sample vial. Concentrations of the water-soluble constituents were determined with an ion chromatograph (Dionex, DX-300) using a 500 μl injection loop for each flow system equipped with an AS11A analytical column and an AG11 guard column for anion separation, and a CS12 analytical column and CG12 guard column for cation separation. The atmospheric concentrations of each species were corrected using procedural blank levels.

2.3. *Acidic gas samples*

Sampling of acidic gases was carried out simultaneously with size-segregated aerosol sampling at Syowa station. Acidic gases and non-size-segregated aerosol particles were simultaneously collected using a filter holder (NILU) with a PTFE filter (1.0 μm pore size, 47 mm Ø, Advantec) in series of two-stage alkaline impregnated filters (300 μl of 1 wt% Na_2CO_3 + glycerol) for 2 to 3 d, depending on local weather conditions, at a flow rate 11.5–12 l min^{-1}. Storage of acidic gas samples (alkaline impregnated filters) was carried out in the same way as for the MVI samples.

For extraction of acidic gaseous species, ultra-pure water (18.3 MΩ, Milli-Q water, 10 ml) and H_2O_2 solution (300 μl; 3%) were added to each sample vial. The concentrations of acidic gases were measured by an ion chromatograph (TOA, ICA-5000) using a 500 μl injection loop equipped with an AS12A analytical column, an AG12A guard column and an autosuppression system (ASRS-I, all columns and equipment manufactured by Dionex). Our analytical method cannot identify each gaseous halogen species (HX, HOX, XNO_2, XY, X_2, $XONO_2$ and XNO; X or Y = Cl or Br) individually because of the release of Cl^- and Br^- during the aqueous extraction step from the alkaline-impregnated filters. Atmospheric concentrations of each species were corrected using procedural blank levels.

3. Results and discussion

The main points to be discussed in the present study are sea-salt constituents in individual sea-salt particles at Syowa (Section 3.1), variations of sea-salt constituents in individual sea-salt particles (Section 3.2), variations of sea-salt modification (Cl^- liberation) and release of gaseous chlorine species (Section 3.3) and scavenging of atmospheric acidic species by sea-salt particles (Section 3.4). In particular, the discussion of the release of gaseous chlorine species and scavenging of acidic species will be based on the results obtained from individual particle analysis of sea-salt particles using SEM-EDX. We elaborate on these points in the following discussion.

3.1. *Constituents of individual sea-salt particles at Syowa station*

Figure 1 indicates typical examples of EDX spectra of individual sea-salt particles collected at Syowa. Major sea-salt constituents such as Na, Cl, Mg, K, Ca and S were determined by EDX analysis. As shown in Figs. 1a and b, the intensity of the Cl peak is slightly lower relative to Na in the summer. Also, higher S peaks are observed in both coarse and fine sea-salt particles collected in the summer (Figs. 1a and b), so that acidic sulfur species in sea-salt particles probably contributed to liberation of Cl^- from

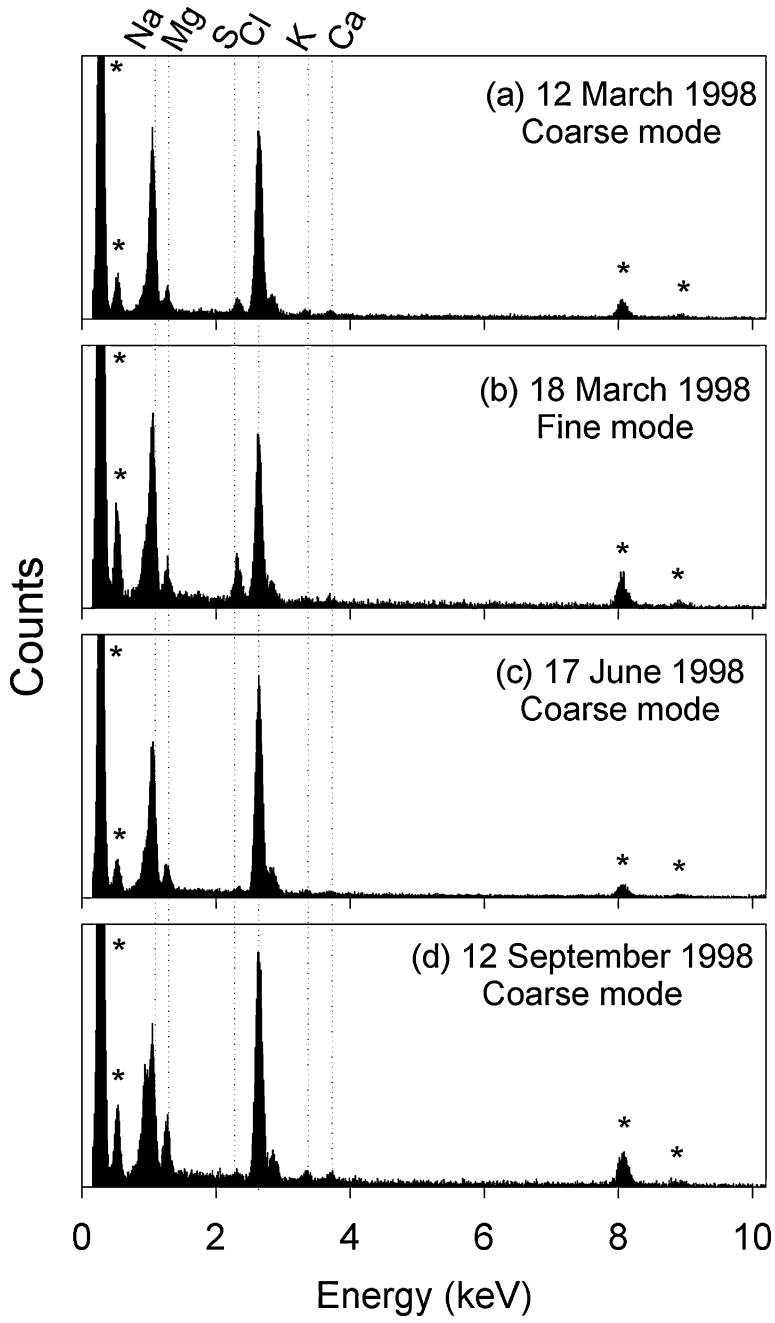

Fig. 1. Typical examples of EDX spectra of sea-salt particles collected at Syowa station, Antarctica.

sea-salt particles in the summer Antarctic atmosphere. Unlike sea-salt particles in the summer, sea-salt particles sampled in the winter have a higher Cl peak and a lower S peak, as shown in Figs. 1c and d. Suggestive of less sea-salt modification (Cl^- liberation) in the Antarctic winter (Mouri et al., 1999; Hara et al., 2004a), this type of sea-salt particle can be identified as being relatively fresh or less modified (less Cl^- liberated). Although sea-salt particles in the spring also have a higher Cl peak and a lower S peak similar to the less-modified sea-salt particles in the winter (Fig. 1c), the peak intensities of Mg, K and Ca increased markedly as shown in Fig. 1d.

3.2. Seasonal variations of sea-salt constituents in individual particles at Syowa station

For quantitative estimation of sea-salt constituents, we attempt to evaluate seasonal variations of the constituents in individual sea-salt particles as shown in Fig. 2. The relative percentage of Na in individual sea-salt particles in the coarse mode was distributed around about 50 mol% on average throughout the year with the exception of a slight decrease and large variability in the standard deviation in September–October at Syowa. The larger variability strongly suggests heterogeneity of sea-salt

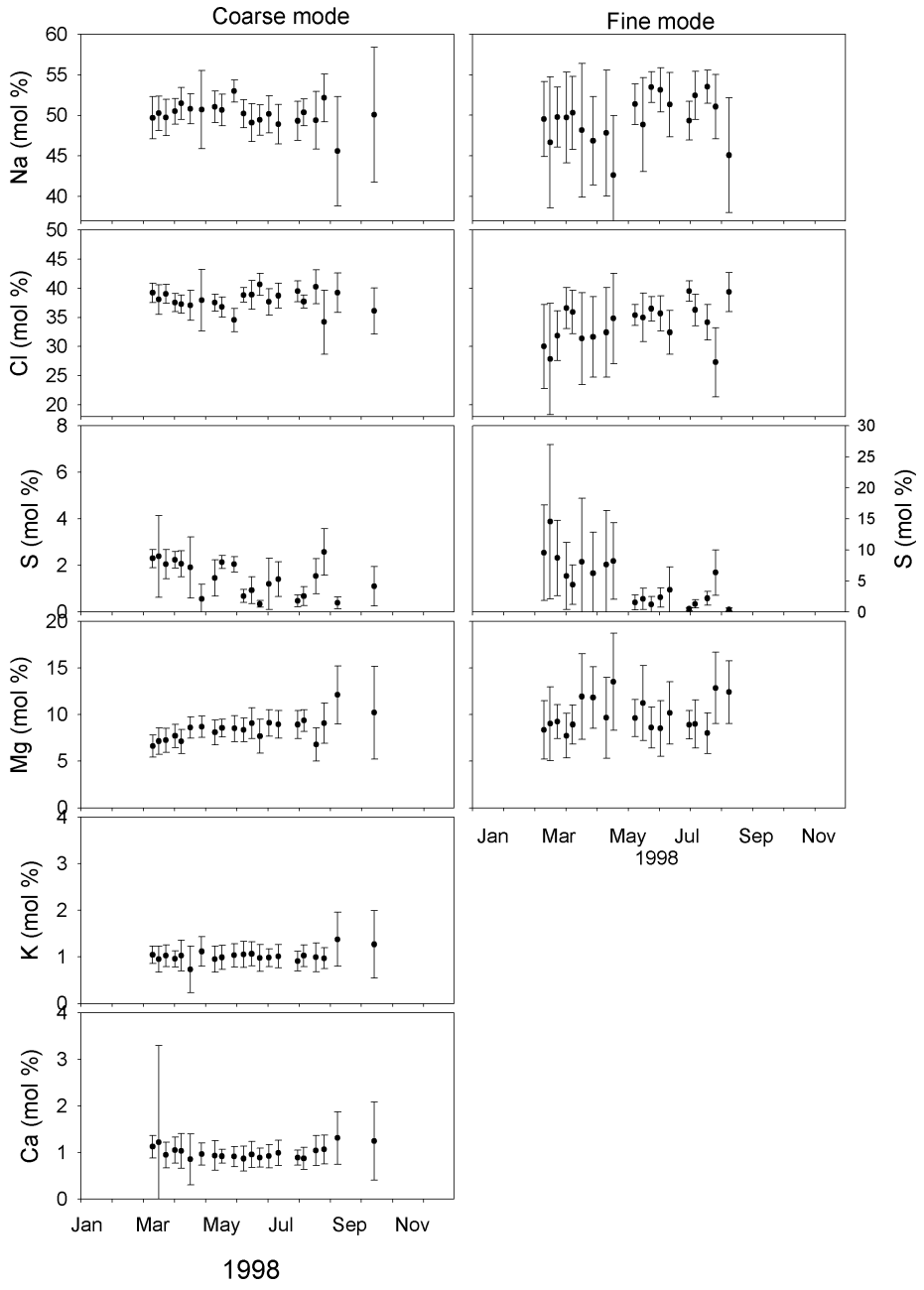

Fig. 2. Mean mass ratio of sea-salt constituents in each sea-salt particle. Error bars indicate standard deviation.

constituents in each sea-salt particle in the atmosphere. The mean Cl percentage is high in the winter in both coarse and fine modes and decreases in the summer to <40 mol% in the coarse mode and to <30 mol% in the fine mode. With the increase in percentage of S in sea-salt particles, the percentage of Cl tended to vary greatly and decrease in the fine sea-salt particles. Thus, the large variability may be due to the heterogeneity of sea-salt constituents, in other words, external mixing of aged (modified) and relatively less modified sea-salt particles in the summer atmosphere around Syowa (details to be discussed later).

Furthermore, the wintertime Cl/Na mol% ratio was approximately 0.8 lower than the sea water ratio (SWR) in the literature (e.g. Wilson, 1975). The following are considered to be possible reasons for this: (1) analytical bias in EDX analysis in the present study and (2) ambient sea-salt constituents showing the lower Cl/Na ratio (about 0.8) during the winter due to liberation of Cl^- from sea-salt particles and sea-salt fractionation.

As check on the analytical reliability of EDX, we determined the chemical composition of artificial particles of NaCl, Na_2SO_4 and mixtures using the same procedure. Since the grains (about

10 μm) of pure NaCl and Na_2SO_4 of analytical grade showed a molar ratio of Cl/Na $\approx$1.0 and S/Na $\approx$0.6, respectively, in EDX analysis under our analytical condition (e.g. area analysis and sample preparation), the EDX spectrometer in the present study was apparently well calibrated. Hence, any analytical bias in EDX analysis will produce only insignificantly lower Cl/Na ratios.

Although sea-salt fractionation, yielding mirabilite ($Na_2SO_4 \bullet 10H_2O$), can change the Cl/Na ratio in sea-salt particles under low-temperature conditions, the Cl^-/Na^+ molar ratio in the bulk analysis of wintertime samples mostly ranged in the typical sea water ratio (1–1.2) (Hara et al., 2004a). Also, Mouri et al. (1999) indicated that sea-salt particles had constituents similar to less modified or fresh sea-salt particles at Syowa in the winter. Although the causes of the slightly lower molar ratio of Cl/Na in the present study are still unclear, the percentage of sea-salt constituents in the less modified coarse sea-salt particles was evaluated on the basis of the constituents of coarse aerosol particles in June at Syowa in the present study, as shown in Table 1. This ratio will be used in the later discussion (Section 3.3.2).

The relative percentage of S in individual sea-salt particles increased up to 13.7 mol% in the coarse mode and to 48.9 mol% in the fine mode in March 1999, whereas the mean S percentage was <3 mol% in both modes with small variability in June. In particular, the larger variability in the percentage of S was obtained in the fine sea-salt particles sampled in the period from March until May. Dominant sea-salt modification (Cl^- liberation) in the fine sea-salt particles was also observed in Syowa and the MBL of the Antarctic Ocean in the austral summer (Mouri et al., 1997, 1999). According to individual particle analysis by means of LAMMS (laser microprobe mass spectrometry) (Hara et al., 1995; Wouters et al., 1990), the modified sea-salt particles contained Na_2SO_4 and CH_3SO_3Na at coastal Antarctica during the summer. Thus, the particulate sulfur components in sea-salt particles are probably composed of $CH_3SO_3^-$ and SO_4^{2-} in the present study. This mixing state suggests heterogeneous formation of $CH_3SO_3^-$ and SO_4^{2-} in sea-salt particles from precursors such as SO_2, $CHSO_3H(g)$ and $H_2SO_4(g)$ (details will be described in a later section).

Although the mean relative percentages of Mg, K and Ca in coarse sea-salt particles ranged from 6.6–9.4, 0.7–1.1 and 0.8–1.2 mol%, respectively, from March until August, these percentage increased slightly to 10.2–12.1, 1.3–1.4 and 1.2–1.3 mol%, respectively, in September–October, as shown in Fig. 1d. Also, LAMMS analysis of Antarctic aerosol particles showed that Mg-rich and Ca-rich particles were in the form of chloride at Syowa station in September–October 1991 (Hara et al., unpublished data). Also, Iwai et al. (1981) showed that Mg and Ca in sea-salt particles were in the form of $MgCl_2 \bullet 6H_2O$, $MgSO_4 \bullet 6H_2O$ and $CaSO_4 \bullet 2H_2O$ at Syowa station. Enrichments of Mg, K and Ca were obvious in bulk aerosol constituents at Syowa in September–October 1998 corresponding to a lower air temperature and the largest extent of sea ice offshore of Syowa (Hara et al., 2004a). Furthermore, the anomaly of molar ratio (K^+/Na^+, Mg^{2+}/Na^+ and Ca^{2+}/Na^+) was correlated with a higher Na^+ concentration resulting from strong winds and ejection of the fractionated sea-salt particles from the surface of the sea ice and snow (Hara et al., 2004a). So far, formation of mirabilite due to sea-salt fractionation has been widely reported from the coastal Antarctic stations (Hall and Wolff, 1998; Wagenbach et al., 1998; Osada et al., 2001; Hara et al., 2004a), whereas the fractionation processes of other sea salts have not been discussed. According to some laboratory measurements on sea-salt freezing (Richardson, 1976; Marion et al., 1999), KCl (sylvite), $MgCl_2 \bullet 12H_2O$, $CaSO_4 \bullet 2H_2O$ (gypsum) and $CaCl_2 \bullet 6H_2O$ (antarcticite) can be formed (fractionated) from sea water below -20 °C. Thus, the fractionated sea-salt particles such as Mg^{2+}-rich, K^+-rich and Ca^{2+}-rich sea-salt particles, in addition to mirabilite, might result from fractionation of sea salt on the surface of sea ice and snow through freezing and sublimation under lower-temperature conditions which then become suspended in the coastal Antarctic atmosphere, especially in September–October.

Table 1. Comparison of the molar ratio between the literature and the EDX analysis

Ratio	Literature*	This study (EDX analysis)
Cl/Na	1.16	0.825
S/Na	0.06	0.007

*Wilson (1975).

3.3. *Sea-salt modification at Syowa station*

3.3.1. Sea-salt modification in individual sea-salt particles. As shown in Fig. 2, the relative percentage of Cl^- was reduced in the summer at Syowa. In order to discuss quantitatively the liberation of Cl^- from sea-salt particles at Syowa, Figs. 3-4 illustrates variations in the relative molar ratio of Na, S and Cl in individual sea-salt particles. Dashed lines trace the stoichiometric change in chemical composition from NaCl to Na_2SO_4 and CH_3SO_3Na. When NaCl (the major sea-salt component) is gradually modified with H_2SO_4 and SO_2, for example, each molar ratio should be distributed around the line (NaCl–Na_2SO_4).

Ternary plots indicate that during summer fine sea-salt particles are preferentially modified (Cl^- liberated) at Syowa. In contrast to the summer, Cl^- liberation is insignificant in the winter at Syowa. A similar seasonal feature of Cl^- liberation was reported by Mouri et al. (1999) and Hara et al. (2004a). In the summer, fine sea-salt particles containing particulate sulfur species (probably SO_4^{2-} and $CH_3SO_3^-$) often had larger sulfur ratios relative to the NaCl–Na_2SO_4 stoichiometric line. Noticeably, some fine sea-salt particles were distributed near the NaCl–CH_3SO_3Na stoichiometric line or larger sulfur ratios, especially on 12 and 18 March 1998. Analogous sulfur-excess sea-salt particles were

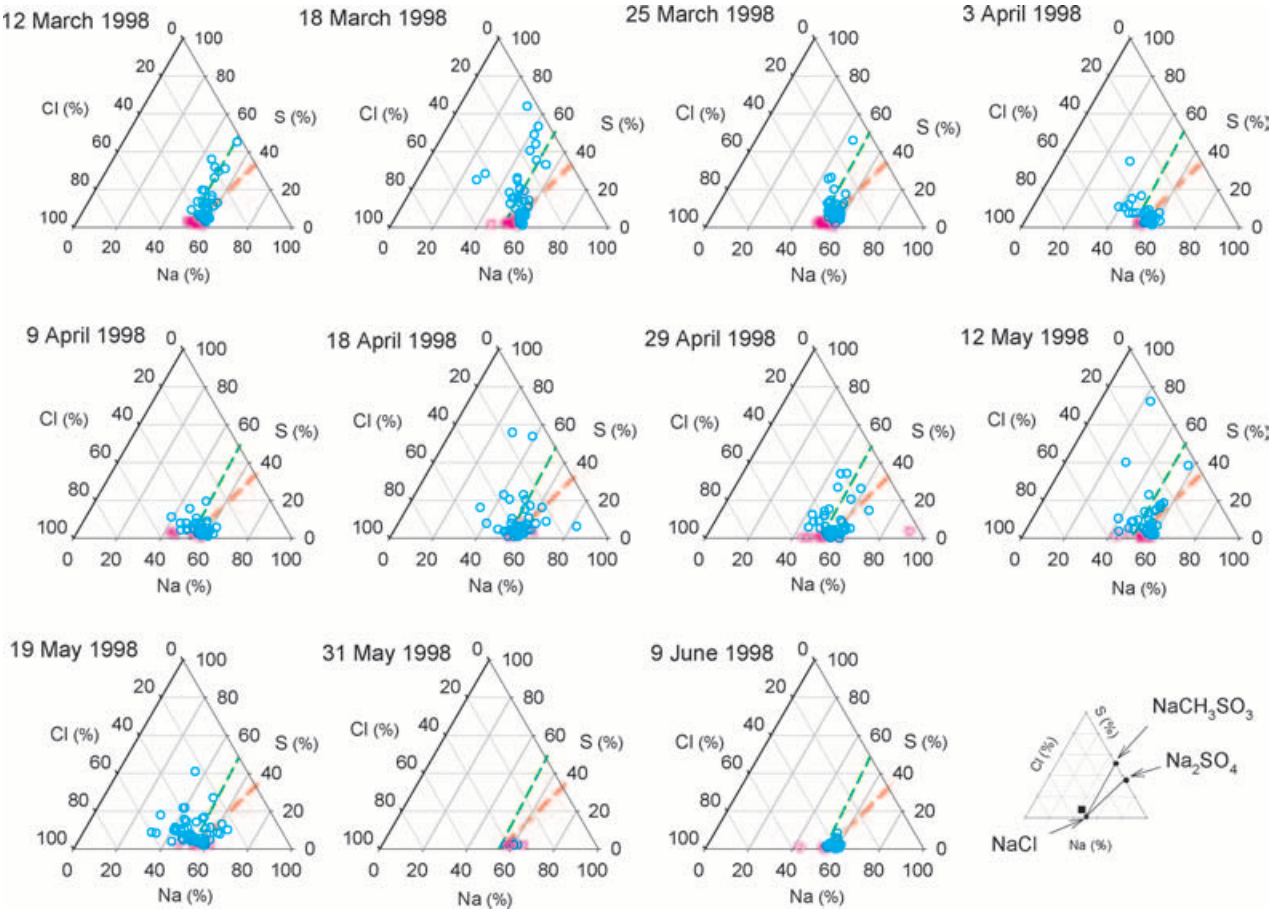

Fig. 3. The relative molar ratio of Na, S and Cl in individual sea-salt particles collected at Syowa station, 12 March-17 June, 1998. Red and blue circles indicate the molar ratio in each sea-salt particle in coarse ($d \geq 2$ μm) and fine (2 μm $\geq d \leq 0.2$ μm) modes, respectively. Red and green dash lines show the stoichiometric lines of NaCl–Na_2SO_4 and NaCl –CH_3SO_3Na.

also observed at Syowa station in 1993 by Mouri et al. (1999), though they focused only on sea-salt modification by sulfate. Under the Arctic haze conditions carrying higher anthropogenic SO_2, however, the modified sea-salt particles were mostly distributed along the NaCl–Na_2SO_4 line (Hara et al., 2002a). In spite of the presence of modified sea-salt particles with a sulfur-excess relative to the NaCl– Na_2SO_4 line also in the spring in the Arctic, such particles were obtained only in wholly Cl^--liberated sea-salt particles (relative mass percentage Cl $\approx$0) (Hara et al., 2002a). Consequently, sulfur species other than SO_2 and H_2SO_4 may also enhance sea-salt modification (Cl^- liberation) in the coastal Antarctic atmosphere during the summer. Considering internal mixing states of $CH_3SO_3^-$ and nss-SO_4^{2-} in sea-salt particles in the summer Antarctic atmosphere (Hara et al., 1995), these results suggest that the modified sea-salt particles contained excess sulfur species and that $CH_3SO_3^-$ and precursors such as DMS and DMSO can also make an important contribution to sea-salt modification (Cl^- liberation) in coastal Antarctic regions. Therefore, Cl^- liberation from sea-salt particles is likely to occur through heterogeneous reactions with SO_4^{2-}, $CH_3SO_3^-$ and their precursors such as SO_2, DMS and DMSO, which are strongly related to biogenic activity in the coastal Antarctic ocean during the summer. Since EDX analysis was unable to identify SO_4^{2-} and $CH_3SO_3^-$, we need to make a comparison with the bulk analysis data in order to obtain information on $CH_3SO_3^-$ in coarse sea-salt particles.

Figure 5 shows the seasonal variations of the molar ratio of $[CH_3SO_3^-]/[\text{nss-}SO_4^{2-}]$ (R_s) in coarse and fine particle modes at Syowa. Concentrations of nss-SO_4^{2-} were calculated using the following equation:

$$\left[\text{nss} - SO_4^{2-}\right] = \left[SO_4^{2-}\right]_{\text{aerosol}} - \text{SWR} \times [Na^+]_{\text{aerosol}} \quad (1)$$

where SWR is the sea-water ratio (Wilson, 1975). During summer (February to the end of April), R_s was higher in both modes. Surprisingly, molar ratios >1 were observed in coarse aerosol particles at Syowa in the summer. In coastal Antarctic stations, non-size-segregated R_s increased by approximately 0.3 (Dumont d'Urville) and 0.4–0.5 (Neumayer) similar to R_s in the fine mode at Syowa (Fig. 5), though R_s increased occasionally up to 0.8 (Neumayer) (Legrand and Pasteur, 1998a; Jourdain and Legrand,

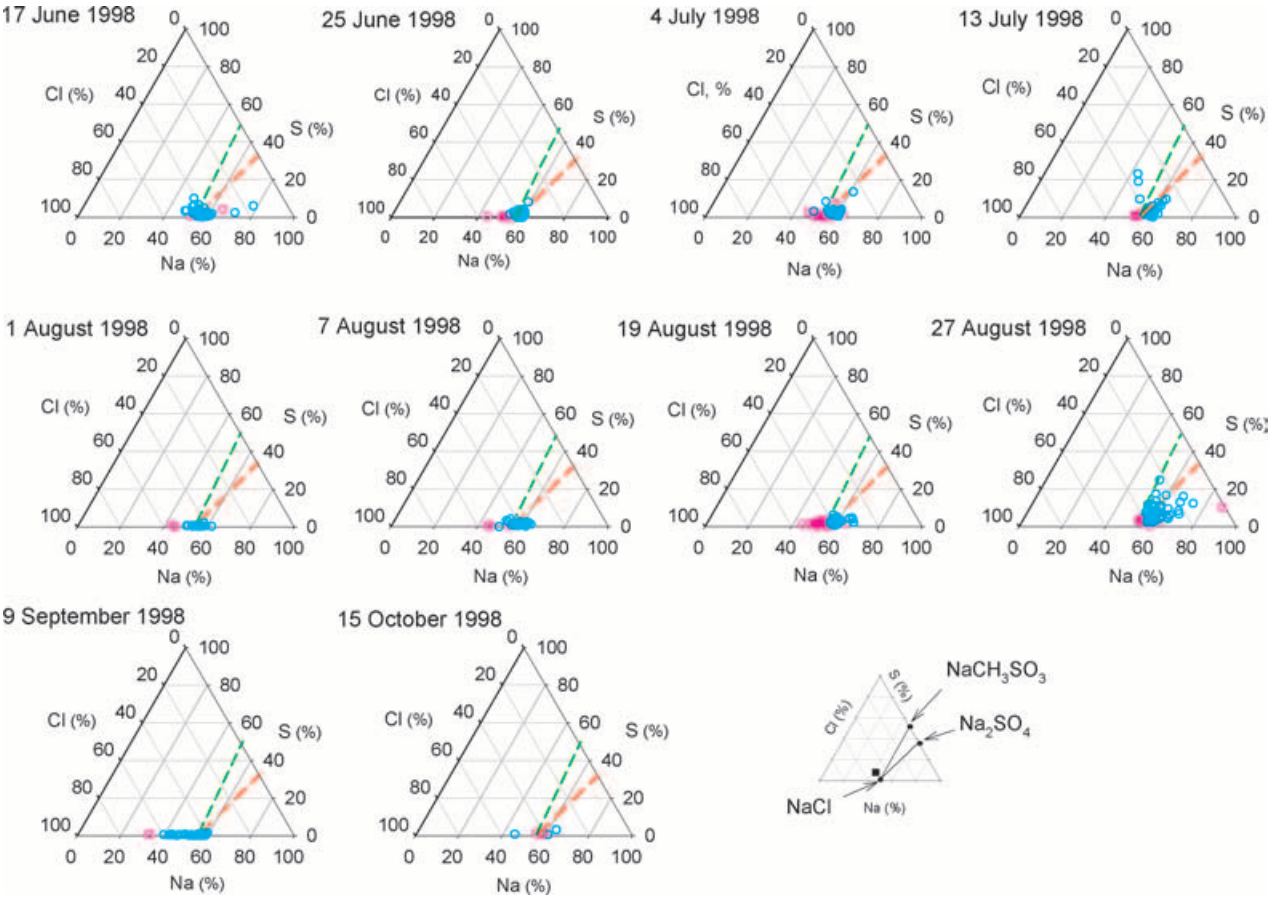

Fig. 4. The relative molar ratio of Na, S, and Cl in individual sea-salt particles collected at Syowa station 25 June-15 October, 1998. Plot style is as Figure 3.

2001). Thus, so far, we have identified the following internal mixing states of $CH_3SO_3^-$ and nss-SO_4^{2-} in aerosol particles in the Antarctic boundary layer during summer: (1) an internal mixture of $CH_3SO_3^-$ and nss-SO_4^{2-} and (2) sea-salt particles containing $CH_3SO_3^-$ and nss-SO_4^{2-} (Hara et al., 1995; Wouters et al., 1990). Although, in bulk analysis, it is difficult to divide each mixing state, SEM-EDX analysis showed that the coarse aerosol particles observed at Syowa during the summer were composed dominantly of sea-salt particles and rarely sulfate/methanesulfonate particles. On the other hand, fine aerosol particles were dominantly composed of sulfate/methanesulfonate particles. Since the sea-salt particles were also larger than sulfate particles in the Antarctic boundary layer during the summer (Osada et al., 1998; Kerminen et al., 2000; Teinilä et al., 2000; Jourdain and Legrand, 2001; Rankin and Wolff, 2003), the anomaly of R_s in coarse particles may be associated with sulfur-excess in sea-salt particles as indicated in Fig. 3.

According to the observations of gaseous H_2SO_4 and CH_3SO_3H at Palmer station (64.46°S, 64.03°W) in summer (February) (Jefferson et al., 1998a,b), the ratio of CH_3SO_3H to H_2SO_4 revealed a diurnal variation in the range of 0.2–0.3 at midday and sometimes increased up to about 1.6 in the dark. Because the larger mass accommodation coefficient (α) of H_2SO_4, $\alpha \geq 0.5$ (Jefferson et al., 1997) compared with that of CH_3SO_3H, $\alpha \approx 0.15$ (De Bruyn et al., 1994) leads to preferential uptake of H_2SO_4 onto aerosol particles, uptake processes of H_2SO_4 and CH_3SO_3H cannot account for the R_s anomaly in coarse sea-salt particles. Recent laboratory work has suggested that the rapid heterogeneous oxidation of DMS and DMSO (finally to $CH_3SO_3^-$) in the aqueous phase has important potential for $CH_3SO_3^-$ formation in aerosol particles (e.g. Barcellos da Rosa et al., 2000; Gershenzon et al., 2001; Bardouki et al., 2002, references therein). Thus, a preferential $CH_3SO_3^-$ formation pathway, which makes important contribution in the summer Antarctic atmosphere, appears to be available on sea-salt particles but not on sulfate particles. Since EDX analysis was unable to identify SO_4^{2-} and $CH_3SO_3^-$, the contribution of $CH_3SO_3^-$ and the precursors to sea-salt modification during the Antarctic summer remain as matters to be discussed. Also, a better understanding will require additional laboratory measurements and model

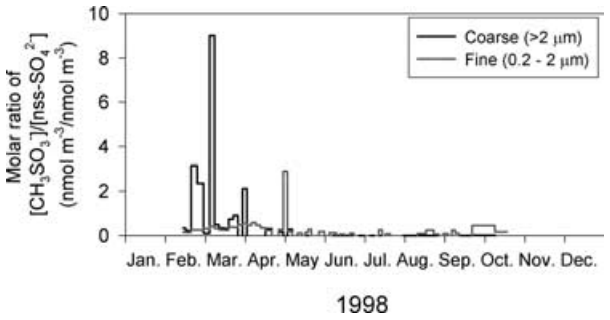

Fig. 5. Seasonal variation of molar ratio of $CH_3SO_3^-$ to nss-SO_4^{2-} in aerosol particles at Syowa station.

estimations associated with the heterogeneous sulfur chemistry in aerosol particles.

Although most of the sea-salt particles were identified as less modified particles during the winter at Syowa, relatively high percentages of S were observed on 13 July and 27 August (Fig. 5). The following possibilities are considered for the sulfur-rich sea-salt particles in the winter: (1) sea-salt modification through heterogeneous reactions with acidic sulfur species derived from biogenic activity in the open sea and (2) sea-salt fractionation on the surface of sea ice and snow.

Atmospheric sulfur cycles are strongly affected by oceanic biogenic activity in the coastal Antarctic regions during summer, but less so in the winter (e.g. Minikin et al., 1998; Moore and Abbott, 2002). Indeed, the seasonal variation of the $CH_3SO_3^-$ concentration showed a minimum during the winter (Osada et al., 1998; Minikin et al., 1998; Jourdain and Legrand, 2001). According to the 5-d backward trajectory analysis shown in Fig. 6, air masses came from the sea-ice area (13 July 1998) and Antarctic continent (27 August 1998). If sulfur species originating from oceanic biogenic activity contribute significantly to the higher S percentage in sea-salt particles during the winter, the higher S ratio of sea-salt particles in the continental air mass (27 August) cannot be explained. Consequently, sulfur species of oceanic origin may make only an insignificant contribution to the relatively high S percentage in sea-salt particles observed during the winter.

As already noted, low-temperature processes can enhance sea-salt fractionation (e.g. mirabilite formation) on the surface of snow and sea ice. Also, recent field observations suggested mirabilite formation at Dome Fuji (inland) station (Hara et al., 2004) and sulfate depletion through the sublimation processes on the continental snow surface (Iizuka et al., 2004) in addition to sea-salt fractionation in coastal areas (Hall and Wolff, 1998; Wagenbach et al., 1998; Osada et al., 2001; Hara et al., 2004). Hence, the sulfur rich sea-salt particles observed on 13 July and 27 August 1998 probably result from sea-salt fractionation.

Some sea-salt particles in winter–spring had a lower Cl ratio with an increasing of the S ratio. When significant sea-salt fractionation (SO_4^{2-} depletion) occurs, sea-salt constituents enhance Cl^- enrichment relative to the SWR as obtained on 9 September 1998 (Fig. 4). Thus, it is expected that the sea-salt modification results from acidic species other than sulfur species in coastal Antarctic regions during the winter–spring. Chemical tests using the Nitron thin film technique, which provides direct evidence of particulate NO_3^- (Hara et al., 1999), indicated that some sea-salt particles collected during late June to October, contained NO_3^-. Indeed, the concentrations of NO_3^- in aerosol particles and $HNO_3+N_2O_5$ at Syowa increased in winter and spring (Osada et al., 1998). Therefore, heterogeneous NO_3^- formation from reactive nitrogen oxides (e.g. HNO_3 and N_2O_5) onto sea-salt particles might cause significant Cl^- liberation in sea-salt particles at Syowa during winter–spring. Also, internal mixing of oxalate in sea-salt particles was suggested in the boundary layer of polar regions by Kerminen et al. (2000) and Hara et al. (2002b). In spite of a higher concentration of oxalate in aerosol particles during spring at coastal Antarctic stations (Legrand and Pasteur, 1998; Osada et al., 1998), the oxalate concentration at Syowa (Osada et al., 1998) was probably too low (by a factor of about 0.02 relative to NO_3^-) to make a significant contribution to sea-salt modification in comparison with NO_3^- concentration in winter–spring. Consequently, Cl^- liberation from sea-salt particles in the winter–spring probably results mainly from heterogeneous reactions with reactive nitrogen oxides such as HNO_3, N_2O_5 and NO_3 during the transport, as suggested by Hara et al. (1999).

Furthermore, a decrease in the surface O_3 concentration resulting from the bromine catalytic system in the boundary layer was often observed at Syowa in August 1998 (Hara et al., 2004). Fortunately, the aerosol samples for SEM-EDX analysis were collected during one such phase. Dominant sea-salt modification with NO_3^- and reactive nitrogen oxides in August suggests that atmospheric nitrogen chemistry involving sea-salt particles and reactive bromine species result in O_3 depletion in the boundary layer during the polar sunrise. Interestingly, a similar relationship between NO_3^- formation on sea-salt particles and gaseous inorganic bromine species was suggested in the Arctic boundary layer during the winter–spring (Hara et al., 2002c).

On 9 September (Fig. 4), most sea-salt particles contained excess Cl in both coarse and fine particles relative to NaCl. As shown in Figs. 1 and 2, the fractionated (Mg-rich, K-rich and Ca-rich) sea-salt particles were observed on 9 September in the present study. Hence, it appears that the excess Cl relative to Na seen in Fig. 4 may be not due to sea-salt modification with acidic species but rather arises from mixing of KCl, $MgCl_2$ and $CaCl_2$ derived from sea-salt fractionation.

3.3.2. Estimation of amount of Cl^- liberated from sea-salt particles. In order to evaluate the amount of gaseous inorganic chlorine species (g_Cl) released from the ambient sea-salt particles, we attempt to estimate the amount of Cl^- liberated directly from individual sea-salt particles. For the estimation of

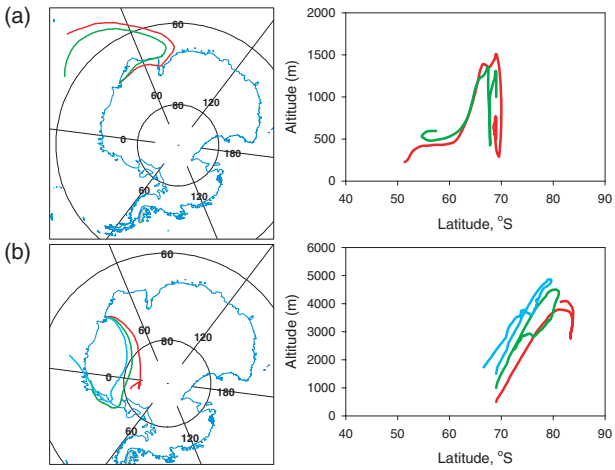

Fig. 6. 5-day backward trajectory from Syowa station in (a) 13 July 1998 and (b) 27 July 1998. Backward trajectory was calculated by vertical motion mode (kinetic) of HYSPLIT4 (NOAA, Draxler and Rolph, 2003).

the amount of Cl^- liberation at Syowa, we calculate the amount of Cl^- liberated from each coarse and fine sea-salt particle as follows:

$$\left(\frac{Cl}{Na}\right)_{liberation} = \left(\frac{Cl}{Na}\right)_{fresh\ sea\ salt} - \left(\frac{Cl}{Na}\right)_{ambient\ sea\ salt} \quad (2)$$

where $(Cl/Na)_{liberation}$, $(Cl/Na)_{fresh\ sea\ salt}$, and $(Cl/Na)_{ambient\ sea\ salt}$ are the molar ratios for liberated Cl^-, fresh sea-salt particles and ambient sea-salt particles in each sea-salt particle, respectively. Here, the molar ratio ($Cl/Na \approx 0.825$) in sea water as given in Table 1 was used as that of fresh sea-salt particles, as stated above. The percentage of Cl^- liberated from sea-salt particles (R_{Cl^-}) can be estimated using the molar ratio of liberated Cl^- to total Cl^- in sea-salt particles and eq. (2) using the following equation:

$$R_{Cl^-} = \frac{\sum \left(\frac{Cl}{Na}\right)_{liberation}}{\sum \left(\frac{Cl}{Na}\right)_{fresh\ sea\ salt}} \times 100. \quad (3)$$

Seasonal variations of R_{Cl^-} in coarse and fine sea-salt particles are shown in Fig. 7. R_{Cl^-} in March–April at Syowa ranged from 13.6–30.7% (mean 21.6%) in fine sea-salt particles and from 5.4–10.8% (mean 8.4%) in coarse sea-salt particles. In June to mid-August, R_{Cl^-} in the coarse mode decreased to 2.9–9.2% (mean 6.0%), whereas R_{Cl^-} in the fine mode remained in the range of 4.7–23.2% (mean 15.7%) (as shown in Fig. 2).

For estimation and discussion of the amount of liberated Cl^- from sea-salt particles and ambient g_Cl concentration, we must compare the individual aerosol analysis data with the bulk analysis data. However, the bulk aerosol sampling occasionally contains sampling artefacts such as volatilization of particulate species and gas uptake on aerosol particles during the sampling. In contrast, aerosols sampled for individual particle analysis have negligible sampling artefacts since sampling times are so short under the clean air conditions. For that reason, we compare the amount of liberated Cl^- between our bulk analysis and individual particle analysis in order to understand the contribution of potential sampling artefacts in our bulk aerosol sampling.

Using the R_{Cl^-} values and the ambient Na^+ concentration in coarse and fine modes, total amount of Cl^- liberated was calculated. The amount of Cl^- liberated was following:

$$[\text{liberated Cl}^-]_{coarse} = R_{Cl^-\,coarse} \times [Na^+]_{coarse},$$

$$[\text{liberated Cl}^-]_{fine} = R_{Cl^-\,fine} \times [Na^+]_{fine}$$

and

$$[\text{liberated Cl}^-]_{total} = [\text{liberated Cl}^-]_{coarse} + [\text{liberated Cl}^-]_{fine}.$$

On the other hand, the amount of liberated Cl^- in MVI was calculated using the Na^+ concentration in MVI and the SWR (Wilson, 1975). Figure 8 indicates the relationship between the amount of Cl^- liberated in the fine mode of MVI and the estimated amount of Cl^- liberated in the fine mode using SEM-EDX (individual particle) analysis. Although the aerosol samples containing the fractionated sea-salt particles on 13 July 1998 led to the overestimation of the amount of Cl^- liberated, probably due

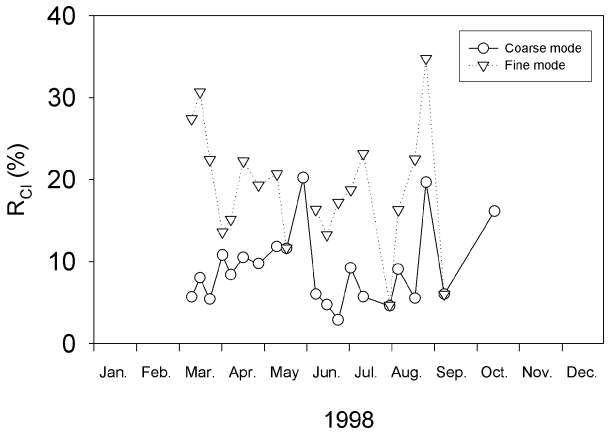

Fig. 7. Seasonal variations of Cl^- liberated ratio (R_{Cl^-}) in coarse and fine modes.

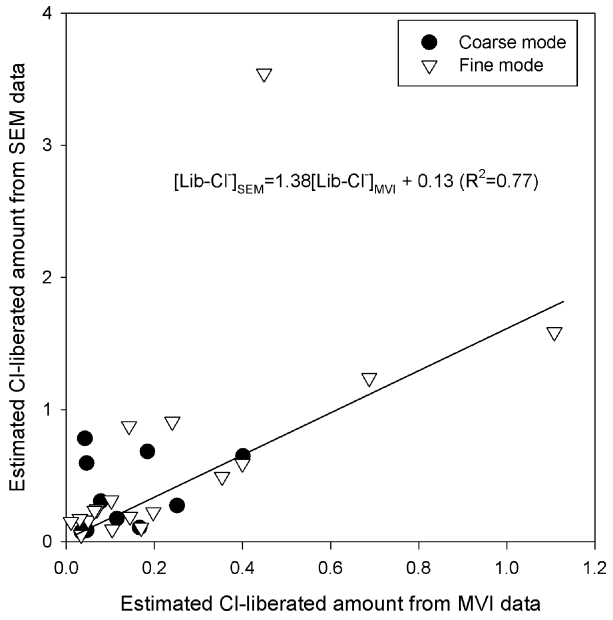

Fig. 8. Relationship between Cl^- liberated amount estimated from SEM-EDX analysis and MVI samples.

to significant mixing of fractionated sea-salt particles, the relatively high correlation, with the exception of 13 July 1998, was obtained in the fine mode as follows:

$$[\text{liberated Cl}^-]_{\text{SEM}} = 1.38 \times [\text{librated Cl}^-]_{\text{MVI}} + 0.13 (R^2 = 0.77).$$

Despite high correlation ($R^2 = 0.77$) between liberated Cl^- amount in SEM-EDX and the amount in MVI, the slope (1.38) of the correlation is slightly larger than 1. The large slope (1.38) might result from size dependency of Cl^- liberation of sea-salt particles even in the remote MBL as suggested by McInnes et al. (1994). However, the high correlation suggests that our bulk aerosol sampling system has an insignificant sampling artefact, at least associated with sea-salt particles.

As indicated in Fig. 9, the estimated amount corresponded well with the ambient g_Cl concentration at Syowa during the summer when preferential Cl^- liberation occurred (Figs. 2 and 3), while the ambient g_Cl concentration (mainly HCl) was markedly higher than the estimated amount during the winter–spring. As mixing of mirabilite-containing particles into winter–spring samples (e.g. 13 July) probably led to overestimation of the liberated Cl^-, this tendency cannot account for the different concentrations. Although the presence of SO_4^{2-}-depleted sea-salt particles, which have higher Cl^- relative to the SWR, can result in an underestimation, the molar ratio of $[Cl^-]/[Na^+]$ in the bulk analysis indicated approximate equivalence to the SWR ($[Cl^-]/[Na^+] \approx 1.2$) during the winter–spring (Hara et al., 2004a). While the presence of some fractionated sea salts such as KCl, $MgCl_2 \bullet 12H_2O$ and $CaCl_2 \bullet 6H_2O$ can cause underestimation of the liberated Cl^-, these particles were observed only in September– October in the present study. Thus, the exceeded g_Cl concentration relative to the amount of Cl^- liberated was probably not due to sea-salt fractionation but to accumulation of g_Cl in the boundary layer during Antarctic winter–spring. This suggests preferential Cl^- liberation during the summer at Syowa, and that the contrast between the summer and winter values might depend on the residence time of g_Cl in the boundary layer of the coastal Antarctic region.

The residence time of g_Cl in the boundary layer probably depends on the chemical compositions of g_Cl species such as HCl and ClX (e.g. X = Cl, Br, I and so on). The major compound involved in liberation of Cl^- is HCl, which, on account of its high solubility in water (Brimblecombe and Clegg, 1988; Sander, 1999) can be driven to deposition/uptake on wet surfaces and aqueous phases (e.g. aerosol particles, open sea and wet sea ice). In particular, the seasonal variation of the extent of sea ice in the coastal Antarctic area has a drastic annual feature (the largest extent of sea ice is in September–October offshore of Syowa) (Cavalieri et al., 1999, updated 2002). Thus, it can be speculated that, in addition to the wet surface of aerosol particles, seasonal variation in the extent and condition of sea ice may make an important contribution to seasonal features of g_Cl lifetime around Syowa. For a better understanding of sea-salt modification and the lifetime of g_Cl in the Antarctic regions, we ought to identify each g_Cl species and discuss the relationship to the seasonal variation in the extent and condition of sea ice in the near future.

3.4. Scavenging of acidic species by sea-salt particles at Syowa station

Plausible dry deposition processes of acidic gases (e.g. SO_2 and HNO_3) are (1) direct deposition onto sea ice and snow and dry deposition together with (2) sea-salt particles and (3) sulfate particles through heterogeneous reactions. Due to the larger dry deposition velocity in coarse particles they can be removed preferentially from the atmosphere. If fresh and slightly aged sea-salt particles, having alkaline and often deliquescent surfaces, preferentially scavenge the acidic gases, it is expected that sea-salt particles, especially coarse sea-salt particles, could play an important role in the scavenging of acidic gases from the atmosphere, as pointed by Sievering et al. (1992).

The mode of sea-salt particles in the coastal Antarctic stations was approximately smaller than 2 μm in diameter (Teinilä et al., 2000; Kerminen et al., 2000; Jourdain and Legrand, 2002), though the mode of coarse particles is larger in the MBL. Thus, the mode would become smaller than 2–5 μm in the MBL due to preferential deposition of coarse sea-salt particles. In spite of shorter lifetime of coarse sea-salt particles in the atmosphere, particulate sulfur species (nss-SO_4^{2-} and $CH_3SO_3^-$) were enriched in coarse and fine sea-salt particles relative to fresh and less modified sea-salt particles during the summer at Syowa, as shown in Fig. 3. In the present study, we attempt to estimate the dry deposition velocity of acidic sulfur species and NO_3^- by the sea-salt particles.

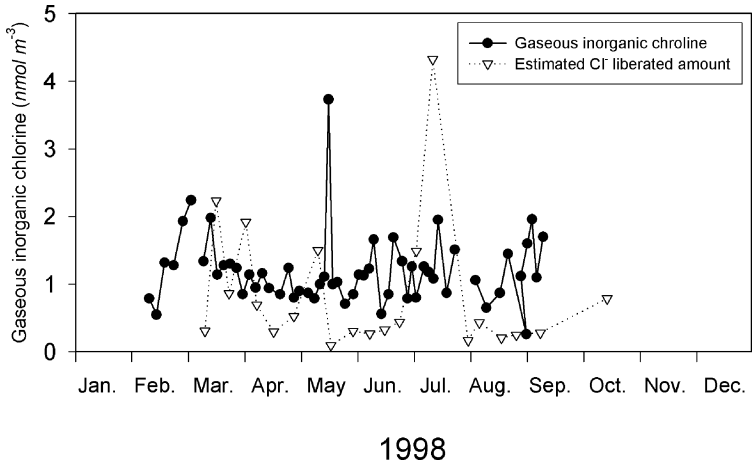

Fig. 9. Seasonal variations of the ambient concentrations of gaseous inorganic chlorine species (g_Cl) and the estimated amount of liberated Cl^- from sea-salt particles.

The dry deposition velocity of acidic sulfur species (nss-SO_4^{2-}, $CH_3SO_3^-$, H_2SO_4(g) and CH_3SO_3H(g)) and HNO_3+N_2O_5 by sea-salt particles was calculated from the relative concentrations of excess S and NO_3^- in each sea-salt particle and the dry deposition velocity of sea-salt particles. The mean relative excess S concentration in each sea-salt particle (ΔS_{mean}) was estimated in the coarse and fine modes from SEM-EDX analysis as follows:

$$\Delta S_{\mathrm{mean}} = \frac{\sum \left(\frac{S}{\mathrm{Na}}\right)_{\mathrm{excess}}}{n} = \frac{\sum \left[\left(\frac{S}{\mathrm{Na}}\right)_{\mathrm{ambient}} - \left(\frac{S}{\mathrm{Na}}\right)_{\mathrm{SWR}}\right]}{n}, \quad (4)$$

where n is the number of analysed sea-salt particles. In the present study, the NO_3^- mixing ratio in each sea-salt particle was not determined. Our previous investigations indicated that most particulate NO_3^- was internally mixed in sea-salt particles in the Antarctic (Hara et al., 2004a) and Arctic (Hara et al., 1999) boundary layer. As the enrichment factors of NO_3^- to sea water relative to Na^+ in aerosol particles is in the region of $>10^3$ (Parungo et al., 1987), NO_3^- in sea-salt particles must also be due to heterogeneous reactions even in the Antarctic area, as suggested by Hara et al. (2004a). Assuming that particulate NO_3^- is internally mixed with sea-salt particles in the Antarctic troposphere, the mean relative NO_3^- concentrations in each sea-salt particle ($\Delta NO_{3\ \mathrm{mean}}^-$) for coarse and fine modes were calculated using the bulk analysis data obtained from the MVI samples, as follows:

$$\Delta NO_3^- = \frac{[NO_3^-]}{[Na^+]}. \quad (5)$$

The amount of sea-salt particles and acidic gases deposited by dry deposition was estimated using the dry deposition velocity and Na^+ concentration obtained from the MVI by the following equation:

$$\Delta C_{\mathrm{sea\ salt\ particles}} = \frac{V_i C_i}{H}, \quad (6)$$

where H, V_i and C_i are the height of mixing layer (1000 m), the dry deposition velocity of aerosol particles and the Na^+ concentration in each mode, respectively. Here, a dry deposition velocity ranging from 432–1500 m d^{-1} for the coarse particles and 10–100 m d^{-1} for fine particles was assumed for the estimation (Seinfeld and Pandis, 1998). Although sea salts are also present in the Aitken mode in the Antarctic atmosphere, dry deposition (sedimentation) of Aitken particles probably only makes an insignificant contribution because of efficient loss by Brownian motion and coagulation. Thus, we exclude the scavenging by sea-salt particles in Aitken modes from our estimation. Therefore, the scavenging rate of acidic gases by sea-salt particles can be obtained as follows:

$$\text{scavenging rate} = \Delta C_i \times \Delta S_{\mathrm{mean}\,i}$$

for acidic sulfur species (e.g. SO_2) and

$$\text{scavenging rate} = \Delta C_i \times \Delta NO_3^-$$

for $HNO_3 + N_2O_5$. On the other hand, the following dry deposition velocities for acidic gases were assumed in the present study: V_{SO_2} = 43.2–86.4 m d^{-1}, $V_{CH_3SO_3H(g)} = V_{H_2SO_4(g)}$ = 1730 m d^{-1} and V_{HNO_3} = 1730 m d^{-1} onto sea ice and the snow surface (Ibrahim et al., 1983; Barrie and Hoff, 1984; Johansson and Granat, 1986; Ganzeveld et al., 1998; Kerminen and Leck, 2001). The scavenging rates of acidic gases were calculated in the same manner using eq. (6). Although the concentrations of other volatile organic sulfur species (DMS, DMSO and $DMSO_2$) in the summer Antarctic atmosphere are higher relative to other regions (Berresheim et al., 1998; Davis et al., 1998), their dry deposition velocities are uncertain. A discussion of the dry deposition of these organic sulfur species will not be given in the present study.

Figure 10 indicates the seasonal variations of the scavenging rates of acidic sulfur species by sea-salt particles at Syowa station. With the exception of the apparently incorrect deposition velocity on 13 July 1998, due to mixing of fractionated sea-salt particles, the sulfur-scavenging rate of sea-salt particles tends to show lower rates in the winter. During the summer at Syowa, the scavenging rate of atmospheric sulfur species by sea-salt

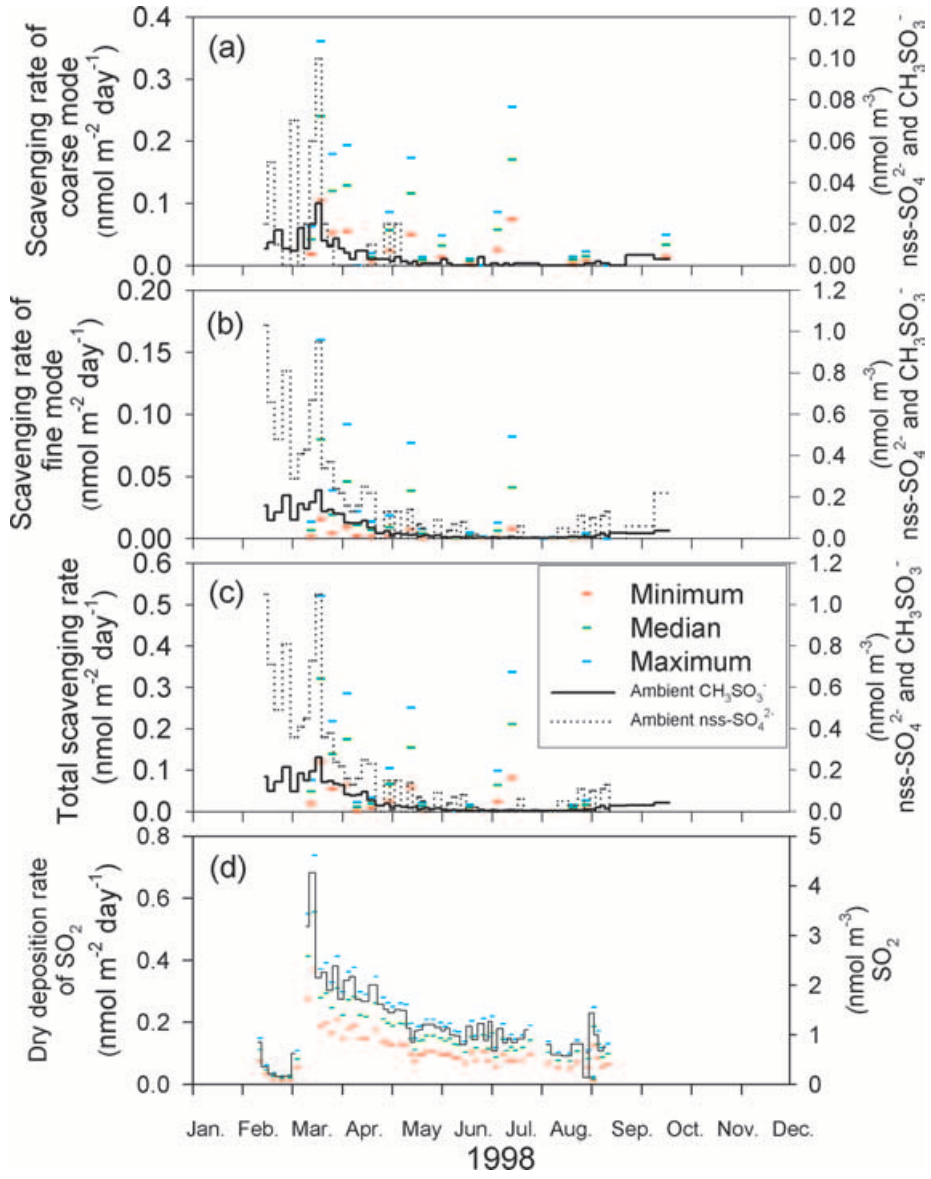

Fig. 10. Seasonal variations of (a–c) scavenging rate of acidic sulfur species together with sea-salt particles and (d) direct dry deposition of SO_2 onto snow and sea-ice at Syowa station. Colored bars indicate the estimated scavenging rate for each assumed dry deposition velocity (highest, blue; median, green; lowest, red). Thick and broken lines in (a–c) show the variations of ambient concentrations of $CH_3SO_3^-$ and nss-SO_4^{2-}. Line in (d) shows seasonal variation of ambient SO_2 concentration.

particles ranged from about 0.05–0.5 nmol m^{-2} d^{-1}. In addition, the scavenging rate by sea-salt particles was governed dominantly by coarse sea-salt particles. This scavenging rate corresponded to approximately 17% of the ambient concentrations of particulate sulfur species (nss-SO_4^{2-} and $CH_3SO_3^-$) and ~10% of atmospheric sulfur species (nss-SO_4^{2-} and $CH_3SO_3^-$ and SO_2).

In contrast to the scavenging by sea-salt particles, the dry deposition velocity of SO_2 ranged from <0.02–0.75 nmol m^{-2} d^{-1} at Syowa, as shown in Fig. 10. Assuming the concentrations of H_2SO_4(g) (8.2×10^{-4}–1.1×10^{-3} nmol m^{-3}) and CH_3SO_3H(g) (3.3×10^{-4}–1.3×10^{-3} nmol m^{-3}) obtained by (Jefferson et al., 1998a,b), the estimated deposition rates are in the range of $1.2 \times 10^{-3} - 1.9 \times 10^{-3}$ nmol m^{-2} d^{-1} for H_2SO_4(g) and $5.7 \times 10^{-4} - 2.3 \times 10^{-3}$ nmol m^{-2} d^{-1} for CH_3SO_3H(g). Therefore, dry deposition of SO_2 is likely to make an important contribution to the removal of atmospheric sulfur species, whereas H_2SO_4(g) and CH_3SO_3H(g) contribute insignificantly to dry deposition of acidic species on the surface of snow and sea ice. As a result, sea-salt particles may play an important role in scavenging acidic sulfur species in the atmosphere under conditions of non-precipitation.

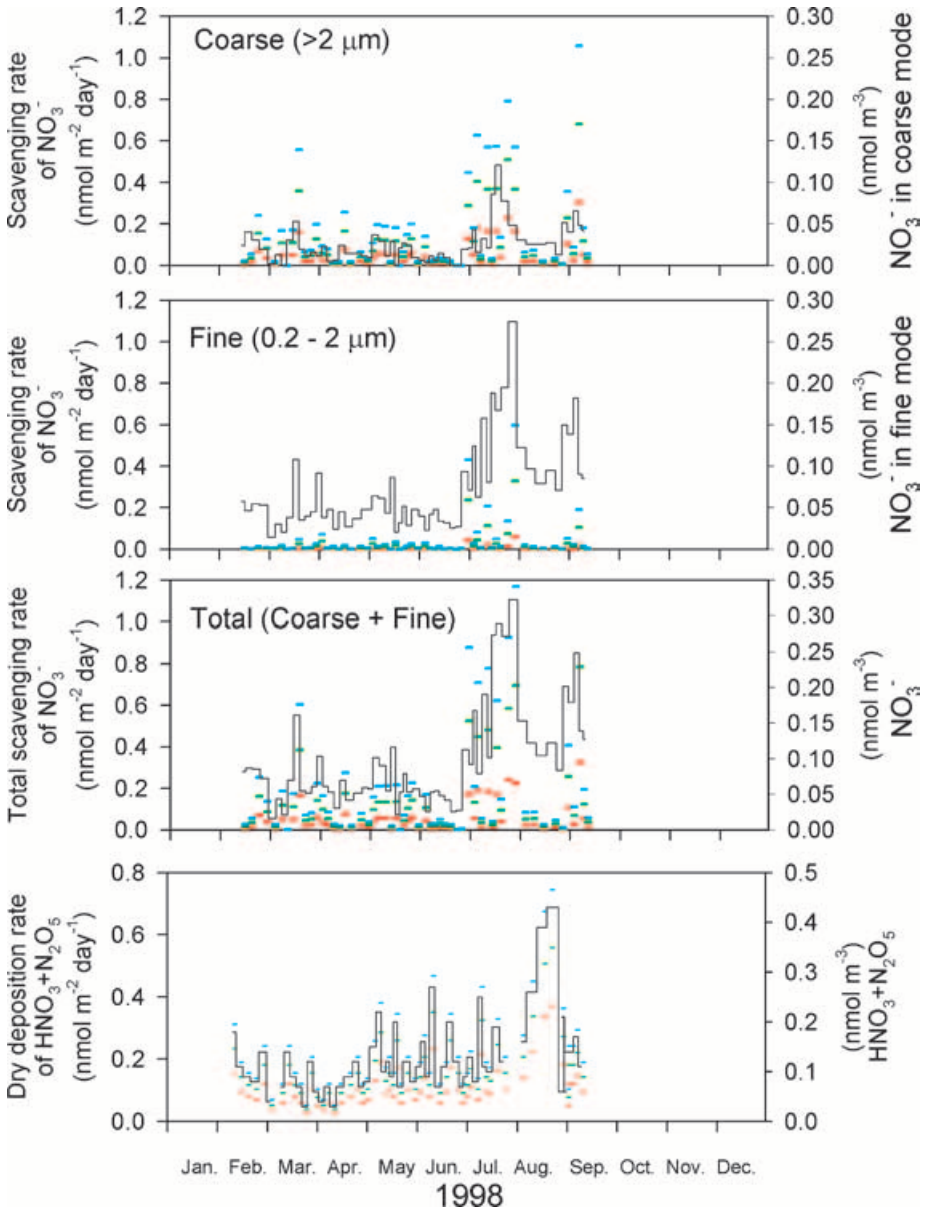

Fig. 11. Seasonal variations of (a–c) scavenging rate of NO_3^- and the precursors by sea-salt particles and (d) direct dry deposition of $HNO_3+N_2O_5$ onto snow and sea-ice at Syowa station. Thick lines indicate variations of ambient NO_3^- concentrations or $HNO_3+N_2O_5$ concentration at Syowa station.

Likewise, the mean scavenging rate of NO_3^- by sea-salt particles was in the range of ~0.2 nmol m^{-2} d^{-1} and the scavenging rate occasionally reached up to 1.2 nmol m^{-2} d^{-1} approximately as shown in Fig. 11. The scavenging rate of NO_3^- by sea-salt particles depended on coarse sea-salt particles due to preferential dry deposition, though the NO_3^- concentration was higher in fine-particle mode at Syowa. On the other hand, the mean dry deposition rate of $HNO_3+N_2O_5$ was approximately 0.2–0.3 nmol m^{-2} d^{-1}, slightly greater than the scavenging by sea-salt particles. By comparison with the ambient concentrations of NO_3^- and $HNO_3+N_2O_5$ at Syowa, these species may be removed efficiently from the atmosphere through scavenging by sea-salt particles and direct deposition onto the surface of snow and sea ice.

Under conditions with little or no precipitation the scavenging processes and direct deposition may become relatively more important, although wet deposition processes (precipitation) can make significant contributions to deposition onto the surface of snow and sea ice. As shown by Yamanouchi et al. (1999), the number concentration of aerosol particles in the free

troposphere over coastal areas (Syowa–Mizuho) was enhanced by low-pressure activity. If the concentrations of sea-salt particles increased in the free troposphere by low-pressure activity, sea-salt particles would also be expected to play a role as important scavengers of acidic gases in the Antarctic free troposphere. The more information we can obtain on deposition processes (e.g. the contribution of each type of deposition), the more accurate will be our interpretation of atmospheric processes from ice-core records in polar regions. For a better understanding of the deposition and removal processes of atmospheric species in the polar regions, we need to compare the scavenging of acidic gases and reactive species by aerosol particles with wet deposition such as diamond dust and snow, and the spatial distribution of aerosol particles (especially constituents) in the future.

4. Conclusions

Aerosol measurements were carried out at Syowa station, Antarctica, in 1998. Individual particle analysis by means of SEM-EDX indicated that liberation of Cl^- occurred preferentially via heterogeneous reactions mainly with acidic sulfur species (nss-SO_4^{2-} and $CH_3SO_3^-$) during the summer and with reactive nitrogen oxides in the winter–spring at Syowa station. In particular, more sea-salt particles tended to be modified in the fine aerosol particle mode (0.2–2 μm). As $CH_3SO_3^-$ was enriched in coarse sea-salt particles, it is expected that heterogeneous $CH_3SO_3^-$ formation from precursors such as DMS and DMSO preferentially occurred on sea-salt particles in the coastal Antarctic regions during summer. During the winter–spring, sulfur-rich sea-salt particles probably arising from sea-salt fractionation (i.e. mirabilite formation) were often observed in the air mass originating from the coastal Antarctic area and the Antarctic plateau. Also, Mg, K and Ca may be enriched in sea-salt particles in September–October via sea-salt fractionation by low-temperature processes.

The amount of Cl^- liberated from sea-salt particles was calculated from analysis of individual particles by means of SEM-EDX. This estimates corresponded well to the ambient g_Cl concentration at Syowa station during the summer, whereas ambient g_Cl concentration exceeded the estimated amount. This contrast between summer and winter might result from the seasonal variation in the lifetime of g_Cl in the atmosphere. It is expected that seasonal variation of the extent of sea-ice makes an important contribution to the seasonal variation of residence time of g_Cl in the coastal Antarctic regions.

In spite of the short lifetime of coarse sea-salt particles due to their large dry deposition velocity, coarse sea-salt particles contained excess sulfur species during the summer at Syowa. We also attempted to estimate the scavenging rate of atmospheric sulfur species by dry deposition together with sea-salt particles in the present study. The upper limit of the scavenging rate of atmospheric sulfur species by sea-salt particles reached approximately 0.5 nmol m^{-2} d^{-1} at Syowa station in the summer of 1998. This scavenging rate corresponded to about 17% of the concentration of particulate sulfur species such as nss-SO_4^{2-} and $CH_3SO_3^-$ and ~10% of total atmospheric sulfur species (nss-SO_4^{2-} and $CH_3SO_3^-$ and SO_2). Because the scavenging rate of sulfur species by sea-salt particles was similar to the direct dry deposition velocity of SO_2 onto the surface of snow and sea ice, sea-salt particles may play an important role in scavenging sulfur species from the atmosphere via heterogeneous reactions on sea-salt particles in the Antarctic regions. The mean NO_3^- scavenging rate was ~0.2 nmol m^{-2} d^{-1}, similar to the dry deposition rate of $HNO_3+N_2O_5$ (approximately 0.2–0.3 nmol m^{-2} d^{-1}), though the scavenging rate by sea-salt particles occasionally reached 1.2 nmol m^{-2} d^{-1} during our observations at Syowa. Since the scavenging rates of sulfur species and NO_3^- by sea-salt particles are dominantly governed by coarse sea-salt particles, sea-salt particles probably play an important role in the scavenging of acidic species and reactive species through heterogeneous reactions on sea-salt particles in the coastal Antarctic regions.

5. Acknowledgment

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