Tellus (1999), 51B, 603–611
Printed in UK. All rights reserved

TELLUS
ISSN 0280–6509

Individual-particle analyses of coastal Antarctic aerosols

By H. MOURI[1]*, I. NAGAO[2], K. OKADA[1], S. KOGA[3] and H. TANAKA[2], [1]*Meteorological Research Institute, 1-1 Nagamine, Tsukuba 305, Japan;* [2]*Institute for Hydrospheric-Atmospheric Sciences, Nagoya University, Nagoya 464, Japan;* [3]*National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba 305, Japan*

(Manuscript received 2 March 1998; in final form 9 July 1998)

ABSTRACT

Samplings of aerosol particles were made almost monthly throughout a year at a coastal Antarctic station Syowa (69°00′S, 39°35′E). With X-ray spectrometry, elemental composition of the individual particles is studied. The dominant aerosol constituents are sulfur species and sea salt. They are internally mixed with each other in most cases. We find seasonal variations in (1) the relative importance of sulfur and sea salt, and (2) the modification of sea salt by acidic materials. In the austral-summer samples, the number fractions of sulfur-rich particles and modified sea-salt particles are high, because the production of marine organosulfer was enhanced. In the austral-winter samples, the number fraction of unmodified sea-salt particles is high, because severe storms enhanced the production of sea salt.

1. Introduction

Aerosol particles over Antarctica are under a unique environment. Since Antarctica is nearly completely covered with snow and ice, there is no ground-level aerosol production, apart from small areas of exposed rock. Also, Antarctica is far from anthropogenic sources in the lower latitudes. Hence the only significant aerosol source is the Antarctic Ocean, which is highly productive from the biological point of view (Andreae, 1986). Accordingly, Antarctic aerosol has been a subject of intensive research (Wolff et al., 1998).

To study aerosol chemistry, there are two approaches: bulk analyses such as ion-chromatography and individual-particle analyses such as X-ray spectrometry. These approaches complement each other. The bulk analyses provide an average chemical composition of the aerosol collected on long timescales, while the individual-particle analyses provide chemical variability between particles collected on short timescales. However, Antarctic aerosol has been studied preferentially with bulk techniques (Legrand and Delmas, 1988; Wagenbach et al., 1988, 1998; Artaxo et al., 1992; Savoie et al., 1992a; Legrand et al., 1998). Only the summertime aerosol particles have been studied individually (Cadle et al., 1968; Parungo et al. 1979; Saxena et al., 1985; Harvey et al., 1991). The exceptions are the year-round analyses of Parungo et al. (1981) and Artaxo et al. (1992). They studied individual particles collected at the South Pole and the Antarctic Peninsula, respectively.

This paper reports the results of individual-particle analyses made on a series of 12 aerosol samples. They were taken roughly once a month during a year at a coastal Antarctic station. With X-ray spectrometry, we examine about 100 particles in each of the samples. Those particles are from 0.1 μm to 1.0 μm in dry radius, which are important to the total mass of the aerosol (Ito, 1985).

The subsequent discussion is focussed on several

* Corresponding author.

issues. First, seasonal variations of the aerosol characteristics are discussed, by comparing our results with those of ion-chromatography for the filter samples obtained at the same site. Second, the relative importance of sea salt and sulfur species is discussed. The bulk analyses have revealed that they are the principal constituents of Antarctic airborne particles at >0.1 μm in radius (Wagenbach et al., 1988; Savoie et al., 1992a). Nevertheless, only individual-particle analyses can clarify whether these two components exist as distinguished particles (external mixture) or coexist within particles (internal mixture). For atmospheric sulfur, the accumulation onto sea-salt particles is a fast removal mechanism, since coarse sea-salt particles are removed quickly from the atmosphere (Chameides and Stelson, 1992). Third, we discuss the modification of sea-salt particles, i.e., chemical reactions with acidic materials where Cl^- is replaced by SO_4^{2-} or NO_3^-. This process is the major source for gaseous chlorine in the atmosphere (Legrand and Delmas, 1988; Keene et al., 1990).

2. Experimental

2.1. Sampling procedures

The aerosol samples were obtained during 1993 at the Japanese Antarctic station, Syowa (69° 00′S, 39° 35′E, 18 m above the sea level). The station is located in East Ongle Island on Lützow-Holm Bay, Antarctica. The location is shown in Fig. 1 (a filled circle). We collected aerosol particles always at the upwind place from the main station. There are 12 samples in total. The time and the weather conditions are summarized in Table 1.

The aerosol particles were collected on carbon-coated nitrocellulose (collodion) films supported on copper grids, by using impactors of 1-mm and 0.5-mm diameter jets. In the case of the 1-mm impactor, the flow rate of air was 1.3 l min^{-1}, and the sampling time was 10 min. In the case of the 0.5-mm impactor, the flow rate was 1.0 l min^{-1}, and the sampling time was 5 min. For spherical particles with 2 g cm^{-3} density, the 1-mm impactor has a collection efficiency of 50% at 0.5 μm radius and 100% at $\geqslant 0.7$ μm radius. The 0.5-mm impactor has an efficiency of 50% at 0.15 μm radius and 100% at $\geqslant 0.25$ μm radius.

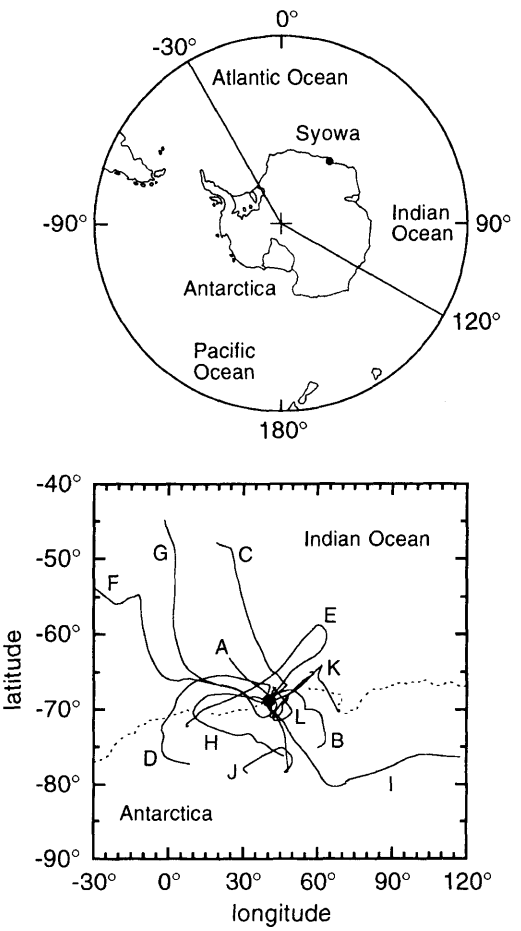

Fig. 1. Map with the location of Syowa Station (a filled circle). Solid lines in the lower panel are the five-day backward trajectories of air masses which arrived at the 750 hPa height over the station during the individual samplings (A–L).

2.2. Individual-particle analyses

The aerosol particles collected were examined with an energy-dispersive X-ray analyzer (Kevex, Delta 5 or Sigma II) attached to a transmission electron microscope (Hitachi, H-600). This system can quantify elements with atomic numbers $Z \geqslant 11$. For all the particles in several areas on the individual carbon films, X-ray spectra were taken at an accelerating voltage of 50 kV and a counting time of 50 s, with the electron beam being irradiated at the centers of the individual particles. The intrinsic diameter of the electron beam is about

Table 1. *Sampling time, weather, pressure at mean sea level (P), wind speed (V), temperature (T), humidity (H), and particle number*

Sample	Day (GMT)	Hour (GMT)	Weather	P (hPa)	V (m/s)	T (°C)	H (%)	Particle number							
								total		mineral		$S>90\%$		Na>10%	
A	17 Feb.	19	fine	980.5	3.0	−5.4	62	72	26	0	0	21	18	39	8
B	6 Mar.	12	snowy	990.2	0.3	−4.1	73	67	32	1	0	14	6	51	26
C	29 Mar.	18	cloudy	1005.8	3.7	−7.8	80	35	48	0	0	0	3	35	45
D	15 Apr.	12	cloudy	990.4	9.4	−7.3	76	53	33	0	0	0	2	53	31
E	8 May	14	cloudy	971.8	7.1	−6.1	79	53	36	0	0	5	4	46	32
F	24 May	11	cloudy	996.6	6.0	−18.9	56	52	47	1	1	2	5	48	41
G	7 Jul.	12	cloudy	982.6	5.4	−15.4	64	84	16	0	0	1	1	83	15
H	21 Jul.	15	fine	982.5	7.4	−19.7	59	31	43	0	0	0	0	31	43
I	26 Aug.	07	fine	987.7	4.8	−30.8	53	59	31	0	0	1	0	58	31
J	8 Oct.	14	fine	973.8	3.8	−20.1	48	67	32	4	0	3	0	60	32
K	16 Nov.	07	fine	986.6	9.0	−9.0	57	58	39	1	0	2	7	52	31
L	19 Dec.	07	fine	990.6	9.1	−2.9	59	60	37	1	2	4	3	54	32

The meteorological data are from the Japan Meteorological Agency (1994); the numbers of the particles analyzed (total), the mineral particles excluded from our study (mineral), the particles with the weight ratio $S/(Na+Mg+S+Cl+K+Ca)>0.9$ ($S>90\%$), and the particles with the weight ratio $Na/(Na+Mg+S+Cl+K+Ca)>0.1$ ($Na>10\%$) are shown; the left column gives the numbers of the particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$, and the right column gives the numbers of the particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$.

0.1 μm. Within the particles, the beam could become wider.

Nearly all the spectra exhibited characteristic X-rays from elements with $Z \geqslant 11$ (e.g., Na, Mg, Al, Si, S, Cl, K and Ca). The software Kevex Quantex was used, and the weight fractions of those elements were computed by means of a thin-film method (Cliff and Lorimer, 1975). The accuracy of our analyses was assessed with artificial NaCl particles. Their weight ratios Cl/Na were measured to be within ±10% of the true value.

Before the X-ray analyses, the aerosol particles had been shadowed with Pt/Pd alloy at an angle of 27° (=arctan 0.5) to the film surface. For the individual particles where elements with $Z \geqslant 11$ had been detected, we evaluated their volumes, by assuming a spherical-cap shape (Okada, 1983). When the particle was surrounded by satellite droplets on the film, the volume of the droplets were added as described in Gras and Ayers (1979). From the volume of the particle, the pre-impaction dry spherical radius (r) was computed. As a result, the composition and size data have been obtained for about 100 aerosol particles with $0.1\ \mu m < r \leqslant 1.0\ \mu m$ in each of our samples (Table 1).

Since the measured X-rays were not from the entire particle, we comment on possible elemental heterogeneities within particles. In the atmosphere, particles are wet. After collection, the particles dry on the carbon film, and might leave distinct crystalline phases due to the solubility differences. Though this effect is not important in the measurements of the major constituents, some researchers claim the importance of this effect in the measurements of the minor constituents (Pósfai et al., 1995). Accordingly, we focus on the major constituents of our particles, i.e., Na, Cl and S.

2.3. *Backward trajectories*

For the individual samples, isentropic backward trajectories were computed, with the twice-daily wind data at standard pressure levels that were produced by the Japan Meteorological Agency (the JMA Global Analysis Data). We ignored the sedimentation of aerosol particles. The falling speed of a particle with 2 g cm^{-3} density and 1 μm radius is only 0.03 cm s^{-1} (Kasten, 1968). Thus the sedimentation would be negligible with respect to the vertical transports due to synoptic-scale disturbance and cumulus convection, which are too complicated to be included in the analyses. Also, meteorological observations at high latitudes of the Southern Hemisphere are sparse. Consequently, the trajectory shows a general flow pattern rather than the exact path of a specific air

parcel. Since such transport assessments have to be based on trajectories above the boundary layer (Savoie et al., 1992b), our calculations started at the height of 750 hPa over Syowa Station.

Fig. 1 illustrates the five-day backward trajectories (solid lines in the lower panel). The trajectories had been over Antarctica or the surrounding ocean. Thus our samples are unlikely to suffer from anthropogenic pollution.

3. Results and discussion

3.1. Overview

Most of the particles in our samples contain Na in $>10\%$ of the total mass or S in $>90\%$ (Table 1). The former is sea salt, which also contains Mg, S, Cl, K and Ca. The latter is dominated by sulfur species, i.e., sulfuric acid, methanesulfonic acid or ammonium sulfate. There are also particles of earth-surface origin (hereafter, mineral particles), which are defined to contain Al or Si in $>10\%$ of the total mass ($Na+Mg+Al+Si+S+Cl+K+Ca=100\%$). Mineral particles are found especially in the samples obtained in the austral summer (Table 1). This is because the surface around Syowa Station is not covered with snow in that season. To focus on marine aerosols, the mineral particles are excluded from the following discussion.

For reference, in Fig. 2, we illustrate the time series of the mass concentrations of Na^+ (solid line) and non-sea-salt SO_4^{2-} (dotted line). They were measured with ion-chromatography in the filter samples obtained at Syowa Station during the same period as our samples (Koga, 1997). On the upper vertical axis of Fig. 2, we indicate the times of our aerosol samplings.

The Na^+ concentration has several peaks in the austral autumn and winter. These peaks correspond to the enhancements of sea-salt production, which are attributable to enhanced storm activity during those seasons (Ito, 1985). On the other hand, the concentration of non-sea-salt SO_4^{2-} exhibits an annual cycle with a maximum in the summer and a minimum in the winter. This pattern is likely to reflect the cycle of the emission and the subsequent photo-chemical oxidation of marine organosulfur species such as dimethyl sulfide, which are the most plausible source of sulfur in the Antarctic atmosphere (Andreae, 1986). Similar long-term observations of bulk chemistry of coastal Antarctic aerosol were made at Georg von Neumayer Station (70°S, 8°W) and Mawson Station (68°S, 63°E) by Wagenbach et al. (1988), Legrand et al. (1998) and Savoie et al. (1992a). Their results are in qualitative agreement with the result of Koga (1997).

The panels of Fig. 3 show the relative weight ratios of Na, S and Cl for the individual aerosol particles in our samples. Squares stand for particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. Circles stand for particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. Dotted lines connect the ratios of seawater and Na_2SO_4. The

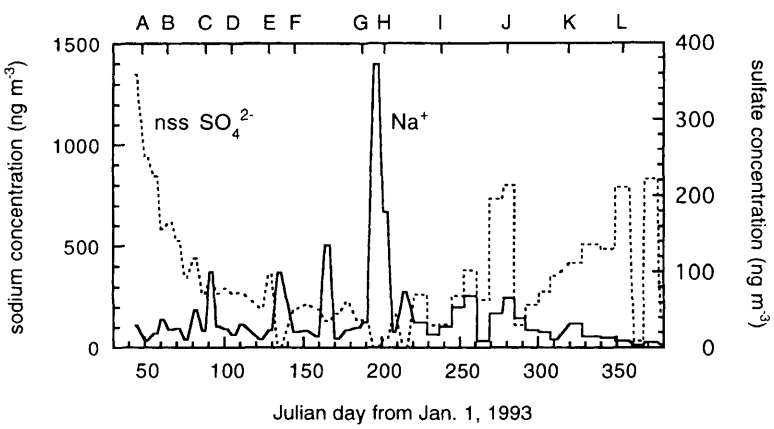

Fig. 2. Mass concentrations of Na^+ (solid line) and non-sea-salt SO_4^{2-} (dotted line) at Syowa Station from February to December 1993. The upper vertical axis indicates the times of our aerosol samplings (A–L).

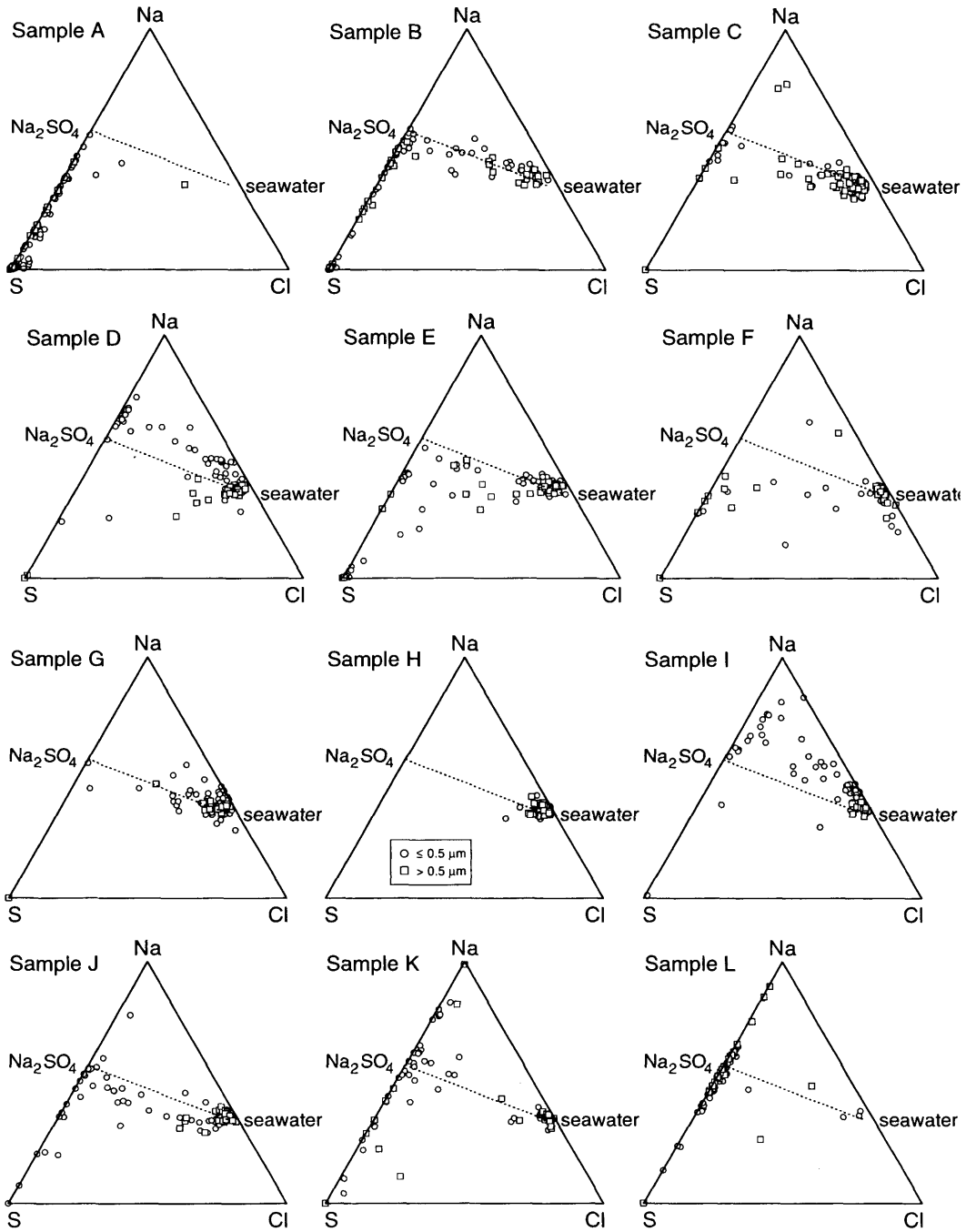

Fig. 3. Relative weight ratios of Na, S and Cl. Squares denote particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. Circles denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. Dotted lines connect the ratios of seawater and Na_2SO_4.

seawater data have been taken from Berg and Winchester (1978).

Seasonal variations of individual-particle characteristics are evident in Fig. 3. They are in accordance with the seasonal variations of bulk chemistry in Fig. 2. The summer samples (A, B and L) exhibit pronounced mixtures of sea salt and sulfur species. The particles on the line between seawater and Na_2SO_4 are sea-salt particles modified by SO_4^{2-}. Those below the line between seawater and Na_2SO_4 are modified sea-salt particles which are likely to have coagulated also with ammonium sulfates. Those on the line between Na_2SO_4 and S are sea-salt particles which have been entirely modified and have accumulated excess sulfur. Several sea-salt particles exist above the line between seawater and Na_2SO_4. The modification of them is partly attributable to NO_3^-. On the other hand, the winter samples (G and H) are dominated by genuine sea-salt particles. In particular, the weight ratios of particles in the sample H are all close to the seawater value. The sample H was obtained when the Na^+ concentration was enhanced (Fig. 2). A storm should have brought a large amount of fresh sea-salt particles and have caused the enhancement. The characteristics of the autumn samples (C, D, E and F) and the spring samples (I, J and K) are intermediate between those of the summer and winter samples. Similar seasonalities have been observed in the individual-particle analyses of Parungo et al. (1981) at the South Pole.

3.2. *Internal and external mixtures of sea salt and sulfur species*

The internal and external mixtures of sea salt and sulfur species are studied. The top and middle panels of Fig. 4 show the number fractions of the particles containing S in 30–60% (open areas), 60–90% (hatched areas), and >90% (filled areas) of the total mass (Na+Mg+S+Cl+K+Ca= 100%). The top panel is for particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. The middle panel is for particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. The bottom panel of Fig. 4 shows the median of the weight ratio S/(Na+Mg+S+Cl+K+Ca). Filled circles denote particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. Open circles denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. We note that the median is a robust estimator of the central value of a distribution, as compared

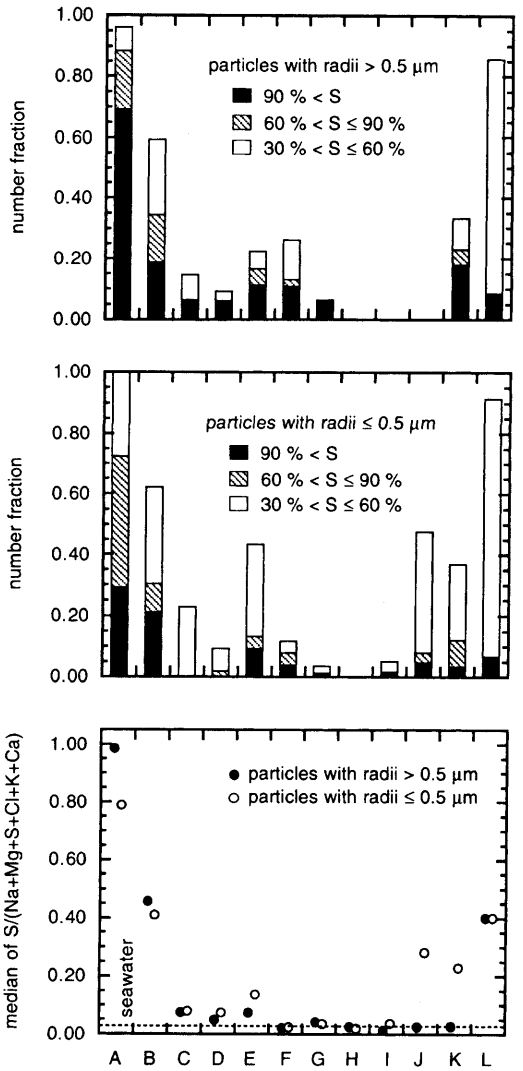

Fig. 4. Summary of sulfur abundances. Top and middle panels show the number fractions of particles with $0.3 < S/(Na+Mg+S+Cl+K+Ca) \leqslant 0.6$ (open areas), particles with $0.6 < S/(Na+Mg+S+Cl+K+Ca) \leqslant 0.9$ (hatched areas), and particles with $0.9 < S/(Na+Mg+S+Cl+K+Ca)$ (filled areas). The results for particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$ are in the top panel. Those for particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$ are in the middle panel. Bottom panel shows the median of S/(Na+Mg+S+Cl+K+Ca). Filled circles denote particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. Open circles denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. A dotted line indicates the seawater value.

with the average, especially when the scatter of the data is large.

The presence of seasonality is evident in both the size ranges of Fig. 4. The fraction of S-dominant particles and the median of S/(Na + Mg + S + Cl + K + Ca) are high in the austral summer. The fractions of S-dominant particles in our summer samples are greater than those observed over the remote ocean (Mouri et al., 1995), especially for particles with >0.5 μm radii. The summertime concentration of Na^+ at Syowa Station is low by a factor of >10 with respect to ocean regions, while the concentration of non-sea-salt SO_4^{2-} does not exhibit such a large difference (compare our Fig. 2 with Table 1 of Savoie et al. 1992a). Many coarse sea-salt particles should have fallen off during the transport over sea ice from open water to the sampling site. On the other hand, S-dominant particles could have grown in size via mutual coagulation or condensation of sulfuric-acid vapor during the transport.

We also observe in Fig. 4 that there are many particles containing S in 30–90%. These are sea-salt particles that have accumulated non-sea-salt sulfur. Thus a large amount of non-sea-salt sulfur is internally mixed with sea salt. Despite their relatively low concentration, sea-salt particles are still an important sink of sulfur in the coastal Antarctic atmosphere.

Though the X-ray spectra do not reveal the molecular forms of sulfur within the individual particles, their morphologies provide some information. Several of the S-dominant particles have satellite droplets, i.e., the signature of sulfuric or methanesulfonic acid (Frank and Lodge, 1967; Koga et al., 1991). Thus the sulfur is not completely neutralized into the form of ammonium sulfate. In fact, the molar ratio of NH_4^+ to non-sea-salt SO_4^{2-} and methanesulfonate at Georg von Neumayer Station does not exceed 40% (Legrand et al., 1998). Since the number of the S-dominant particles is not always significant (Table 1), the fraction of the particles with evident satellite droplets varies greatly among our samples (0–100%). Thus we cannot find any seasonalities.

3.3. *Modification of sea-salt particles*

The modification of sea-salt particles is studied with the weight ratio Cl/Na. Here particles containing Na in >10% of the total mass are regarded as sea-salt particles (Table 1). The upper panel of Fig. 5 is the histogram of the number fractions of sea-salt particles with $Cl/Na \leqslant 1$. These particles have been fairly modified, since the seawater ratio of Cl/Na is 1.80 (Berg and Winchester, 1978). The lower panel of Fig. 5 shows the median of Cl/Na. In both the panels, filled symbols denote particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$, and open symbols denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$.

The observed degree of modification exhibits a seasonal variation. The number fraction of modified sea-salt particles is high and the median of Cl/Na is low in the austral summer. This seasonal variation is likely to reflect the annual cycle of the concentration of acidic materials in the Antarctic atmosphere (Fig. 2). We also find that the particles with $\leqslant 0.5$ μm radii are modified more significantly

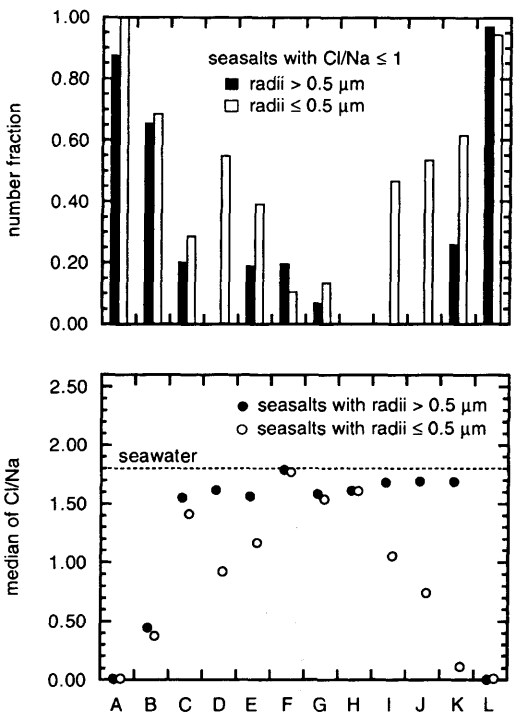

Fig. 5. Summary of Cl/Na. Upper panel shows the number fraction of particles with $Cl/Na \leqslant 1$. Filled areas denote particles with $0.5 < r \leqslant 1.0\ \mu m$. Open areas denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. Lower panel shows the median of Cl/Na. Filled circles denote particles with $0.5\ \mu m < r \leqslant 1.0\ \mu m$. Open circles denote particles with $0.1\ \mu m < r \leqslant 0.5\ \mu m$. A dotted line indicates the seawater value.

than the particles with >0.5 μm radii. Even when particles with >0.5 μm radii are not modified, particles with $\leqslant 0.5$ μm radii are not necessarily unmodified (e.g., samples D, I and J). The plausible explanation is: (1) smaller particles have longer residence time in the atmosphere so that they have more chance to react with acidic materials; and (2) smaller particles have larger surface-to-volume ratios.

The number fractions of modified sea-salt particles in our summertime samples are greater than those observed over the remote ocean (Mouri and Okada, 1993; Mouri et al., 1995). Sea-salt particles over Syowa Station are transported from open-water regions. Hence, as compared with samples taken over the ocean, our present samples contain large fractions of aged sea-salt particles, which should have been more modified than newly born sea-salt particles.

From the distribution of data points in the Na–S–Cl diagrams (Fig. 3), we infer the type of the acid material that has caused the modification. In the late-summer and autumn samples (A–F), most of the data points lie around the line between seawater and Na_2SO_4 or around the line between Na_2SO_4 and S. The Cl^- ions have been replaced by SO_4^{2-} alone. On the other hand, in the spring and early-summer samples (I, K and L), many of the data points lie well above the line between seawater and Na_2SO_4. The Cl^- ions are likely to have been replaced by both NO_3^- and SO_4^{2-}. This idea is supported by a difference in the annual cycle between the concentrations of sulfuric and nitric acids. The SO_4^{2-} concentration has a maximum in mid-summer while the NO_3^- concentration has a maximum in late spring, although SO_4^{2-} is always much more abundant than NO_3^- (Wagenbach et al. 1988, 1998; Savoie et al. 1992a). Here we note that the origin of nitric acid in the Antarctic atmosphere is still uncertain.

4. Summary

With X-ray spectrometry, we have studied the elemental composition of individual aerosol particles, which had been collected almost monthly during 1993 at Syowa Station. The aerosol is dominated by sea salt and sulfur species. They are internally mixed with each other in most cases. Small amounts of mineral particles are also present.

We have found seasonal variations of the individual-particle characteristics, in accordance with the bulk-chemistry data. In the austral summer, the production of marine organosulfer is enhanced, and hence the dominant aerosol component is sulfur. Through the reaction with SO_4^{2-}, the sea salt has lost most of the chlorine. In the austral autumn and winter, the dominant component is sea salt. The composition of the sea salt is close to that of seawater. This is because severe storms have brought large amounts of fresh sea-salt particles. In the austral spring, sulfur is again predominant. However, the chlorine loss of sea salt is sometimes due to NO_3^- in addition to SO_4^{2-}. This is probably because the NO_3^- concentration is relatively enhanced in spring.

5. Acknowledgment

This study was made as a part of the research campaign Antarctic Atmospheric Chemistry. We thank the members of the 34th Japanese Antarctic Research Expedition for assistance during our aerosol collections. The program to compute the backward trajectories was initially developed by S. Takahashi and P.-M. Wu. The comments of the referees were very useful in revising the manuscript. Thanks are also due to K. Miura for discussions.

REFERENCES

Andreae, M. O. 1986. The ocean as a source of atmospheric sulfur compounds. In: *The rôle of air-sea exchange in geochemical cycling* (ed. P. Buat-Ménard). D. Reidel, Hingham, 331–362.

Artaxo, P., Rabello, M. L. C., Maenhaut, W. and Van Grieken, R. 1992. Trace elements and individual particle analysis of atmospheric aerosols from the Antarctic peninsula. *Tellus* **44B**, 318–334.

Berg, W. W. Jr. and Winchester, J. W. 1978. Aerosol chemistry of the marine atmosphere. In: *Chemical oceanography*, vol. 7, 2nd edition (ed. J. P. Riley and R. Chester). Academic Press, London, 173–231.

Cadle, R. D., Fischer, W. H., Frank, E. R. and Lodge, J. P. Jr. 1968. Particles in the Antarctic atmosphere. *J. Atmos. Sci.* **25**, 100–103.

Chameides, W. L. and Stelson, A. W. 1992. Aqueous-

phase chemical processes in deliquescent sea-salt aerosols: a mechanism that couples the atmospheric cycles of S and sea salt. *J. Geophys. Res.* **97**, 20565–20580.

Cliff, G. and Lorimer, G. W. 1975. The quantitative analysis of thin specimens. *J. Microscopy* **103**, 203–207.

Frank, E. R. and Lodge, J. P. Jr. 1967. Morphological identification of airborne particles with the electron microscope. *J. Microscopie* **6**, 449–456.

Gras, J. L. and Ayers, G. P. 1979. On sizing impacted sulfuric acid aerosol particles. *J. Appl. Meteor.* **18**, 634–638.

Harvey, M. J., Fisher, G. W., Lechner, I. S., Isaac, P., Flower, N. E. and Dick, A. L. 1991. Summertime aerosol measurements in the Ross Sea region of Antarctica. *Atmos. Environ.* **25A**, 569–580.

Ito, T. 1985. Study of background aerosols in the Antarctic troposphere. *J. Atmos. Chem.* **3**, 69–91.

Japan Meteorological Agency. 1994. *Antarctic Meteorological Data* **34**.

Kasten, F. 1968. Falling speed of aerosol particles. *J. Appl. Meteor.* **7**, 944–947.

Keene, W. C., Pszenny, A. A. P., Jacob, D. J., Duce, R. A., Galloway, J. N., Schultz-Tokos, J. J., Sievering, H. and Boatman, J. F. 1990. The geochemical cycling of reactive chlorine through the marine troposphere. *Global Biogeochem. Cycles* **4**, 407–430.

Koga, S. 1997. The formation of HNO_3 via the reaction of CH_3SCH_3 with NO_3 (in Japanese). *Proc. Meteor. Soc. Japan* **72**, 275.

Koga, S., Tanaka, H., Yamato, M., Yamanouchi, T., Nishio, F. and Iwasaka, Y. 1991. Methanesulfonic acid and non-sea-salt sulfate over both hemispheric oceans. *J. Meteor. Soc. Japan* **69**, 1–14.

Legrand, M. R. and Delmas, R. J. 1988. Formation of HCl in the Antarctic atmosphere. *J. Geophys. Res.* **93**, 7153–7168.

Legrand, M., Ducroz, F., Wagenbach, D., Mulvaney, R. and Hall, J. 1998. Ammonium in coastal Antarctic aerosol and snow: role of polar ocean and penguin emissions. *J. Geophys. Res.* **103**, 11043–11056.

Mouri, H. and Okada, K. 1993. Shattering and modification of sea-salt particles in the marine atmosphere. *Geophys. Res. Lett.* **20**, 49–52.

Mouri, H., Okada, K. and Takahashi, S. 1995. Giant sulfur-dominant particles in remote marine boundary layer. *Geophys. Res. Lett.* **22**, 595–598.

Okada, K. 1983. Nature of individual hygroscopic particles in the urban atmosphere. *J. Meteor. Soc. Japan* **61**, 727–736.

Parungo, F., Ackerman, E., Caldwell, W. and Weickmann, H. K. 1979. Individual particle analysis of Antarctic aerosols. *Tellus* **31**, 521–529.

Parungo, F., Bodhaine, B. and Bortniak, J. 1981. Seasonal variation in Antarctic aerosol. *J. Aerosol Sci.* **12**, 491–504.

Pósfai, M., Anderson, J. R., Buseck, P. R. and Sievering, H. 1995. Compositional variations of sea-salt-mode aerosol particles from the North Atlantic. *J. Geophys. Res.* **100**, 23063–23074.

Savoie, D. L., Prospero, J. M., Larsen, R. J. and Saltzman, E. S. 1992a. Nitrogen and sulfur species in aerosols at Mawson, Antarctica, and their relationship to natural radionuclides. *J. Atmos. Chem.* **14**, 181–204.

Savoie, D. L., Prospero, J. M., Oltmans, S. J., Graustein, W. C., Turekian, K. K., Merrill, J. T. and Levy, H. II 1992b. Sources of nitrate and ozone in the marine boundary layer of the tropical North Atlantic. *J. Geophys. Res.* **97**, 11575–11589.

Saxena, V. K., Curtin, T. B. and Parungo, F. P. 1985. Aerosol formation by wave action over Ross Sea, Antarctica. *J. Rech. Atmos.* **19**, 213–224.

Wagenbach, D., Görlach, U., Moser, K. and Münnich, K. O. 1988. Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. *Tellus* **40B**, 426–436.

Wagenbach, D., Legrand, M., Fischer, H., Pichlmayer, F. and Wolff, E. W. 1998. Atmospheric near-surface nitrate at coastal Antarctic sites. *J. Geophys. Res.* **103**, 11007–11020.

Wolff, E. W., Legrand, M. R. and Wagenbach, D. 1998. Coastal Antarctic aerosol and snowfall chemistry. *J. Geophys. Res.* **103**, 10927–10934.