# Mixture state and size of Asian dust particles collected at southwestern Japan in spring 2000

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[1] Atmospheric particles were collected at Kumamoto ($32°48'$N, $130°45'$E), a coastal city in southwestern Japan, during three dust storm events in spring 2000. The elemental composition and size of individual dust particles and their mixture state with sea salt, sulfate, and nitrate were analyzed using electron microscopes and an energy dispersive X-ray spectrometer. About $60 \sim 85\%$ of dust particles were internally mixed with sea salt. Weather records indicated these particles were most probably formed by the collisions and coagulations of dust particles and sea-salt particles. The relative weight ratios of mineral components to sea salt in individual particles showed that the mixtures of particles were dominated by mineral, by sea salt, or by both. Size distributions of the particles segregated by the mixture levels of mineral and sea salt in the three dust storm events were similar and all distributions showed a diameter range of $1 \sim 8$ μm with maximum mode around 3 μm. Out of $1 \sim 8$ μm, dust particles were rarely detected. The combination of dust particles with sea salt caused an increase in size of the dust particles. Therefore the decrease of particle concentrations in the range of diameter >3 μm suggests the critical diameter for dust particle dispersion was possibly around 3 μm and a dust particle might be removed rapidly if it became larger than this scale in the marine atmosphere. Detection of sulfate and nitrate revealed that 91% or more dust particles contained sulfate and 27% or less contained nitrate. The comparisons of the relative weight ratios of sodium, sulfur, and chlorine in mixture particles and in sea-salt particles confirmed previous results that mineral materials could enhance particulate sulfate and nitrate formation and restrain chlorine depletion from the sea-salt components in mixture particles. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; *KEYWORDS:* Asian dust, composition, size

## 1. Introduction

[2] Asian dust particles are frequently dispersed to eastern China, Korea peninsula, Japan, the northern central Pacific and sometimes even to North America [*Duce et al.*, 1980; *Uematsu et al.*, 1983; *Iwasaka et al.*, 1988; *Husar et al.*, 2001]. It is estimated that the annual input of mineral dust into the North Pacific from the Asian continent is about 480 Tg, which is more than half of the global annual deposition of mineral into the ocean [*Duce et al.*, 1991]. Studies have suggested that Asian dust can not only change the geochemical mass cycles in East Asia and the North Pacific areas but also have an influence on climate change [*Gao et al.*, 1992; *Levin et al.*, 1996; *Sokolik and Toon*, 1996; *Tegen et al.*, 1996]. Recently, *Bishop et al.* [2002] observed that Asian dust did stimulate plankton growth in seawater and confirmed the importance of dust input for the primarily production of plankton in the ocean [*Gao et al.*, 2001; *Martin et al.*, 1989; *Fung et al.*, 2000]. Thus understanding the physical and chemical properties of Asian dust particles during their long-range transport is also important for marine ecosystem studies.

[3] As dust particles disperse in the atmosphere, they uptake gaseous species and coagulate with other particles. At the same time, surface reactions can change the chemical composition of the particles and may lead to losses of volatile products. These processes sometimes make the particles much different from their original morphology

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**Table 1.** Summary of Sampling Time and Surface Weather Conditions at the Sampling Site When Particle Collection was Held

| Dust Event | Sampling Time,[a] JST | | Relative Humidity, % | Visibility, km | Wind | |
|---|---|---|---|---|---|---|
| | Date | Period | | | Direction | Speed, m s$^{-1}$ |
| K-1 | 8 April 2000 | 15:15–16:30 | 35 | ~10 | NW | ~2 |
| K-2 | 12 April 2000 | 15:30–16:30 | 33 | ~15 | W | ~8 |
| K-3 | 27 April 2000 | 10:30–11:30 | 40 | ~8 | W | ~2 |

[a]Japanese standard time (JST) is GMT + 9 hours.

and composition. It has been confirmed by single particle analysis that dust particles observed around Japan are frequently mixed with sea salt, sulfate and nitrate [*Okada et al.*, 1990; *Fan et al.*, 1996; *Zhou et al.*, 1996; *Niimura et al.*, 1998; *Yamato and Tanaka*, 1994]. However, similar characteristics were rarely detected at and near dust source areas [*Okada and Kai*, 1995; *Trochkine et al.*, 2003; *Zhang and Iwasaka*, 1999] and even at coastal areas of China [*D. Zhang et al.*, 2003]. This suggests the modifications of dust particles mainly occur in the marine atmosphere between China and Japan. On the other hand, size distributions of Asian dust particles observed by *Chun et al.* [2001], *Murayama et al.* [2001], *Trochkine et al.* [2002], *Tratt et al.* [2001], and *Husar et al.* [2001] in Korea, Japan, and North America showed similar distribution patterns and modes. If the modifications of dust particles in the marine atmosphere are significant, following interesting questions newly appear. What are the reasons for the consistence of the distribution modes along the transport routes? Is the influence of the modifications on particle sizes minute, or are there other reasons?

[4] In addition, the formations of particulate sulfate and nitrate on sea-salt particles usually result in chlorine loss in the particles [*Eriksson*, 1959; *McInnes et al.*, 1994]. Although the enhancement of sulfate and nitrate formations by dust particles in marine atmosphere have been confirmed by observations and postulated numerical studies [*Nishikawa et al.*, 1991; *Dentener et al.*, 1996; *Zhang and Carmichael*, 1999], there are few further detailed observational data to assess how dust particles influence the reactions related to sulfate, nitrate and sea salt.

[5] In spring 2000 we collected dust particles at Kumamoto, a coastal city in southwestern Japan, during three dust storm events. Contents of mineral, sea salt, sulfate, and nitrate in individual particles and their sizes were investigated. On the basis of the obtained data, the mixture state of dust particles with sea salt, size distributions of the particles segregated by the mixture levels of mineral and sea salt, sulfate and nitrate formations on the particles, and the changes of sea-salt components due to the formations are described and discussed in this paper. The purposes of this study are to (1) provide more precise information of dust particles after they leave the Asian continent, (2) investigate the variation of dust particles relevant to sea salt, sulfate and nitrate, and (3) get insight into the evolution of dust particles and their influences on mass cycles in the marine atmosphere.

[6] In this study, a scanning electron microscope attached with an energy dispersive X-ray spectrometer was applied to analyze the morphologies, sizes and elemental compositions of individual particles. With reagents on sampling films, a tra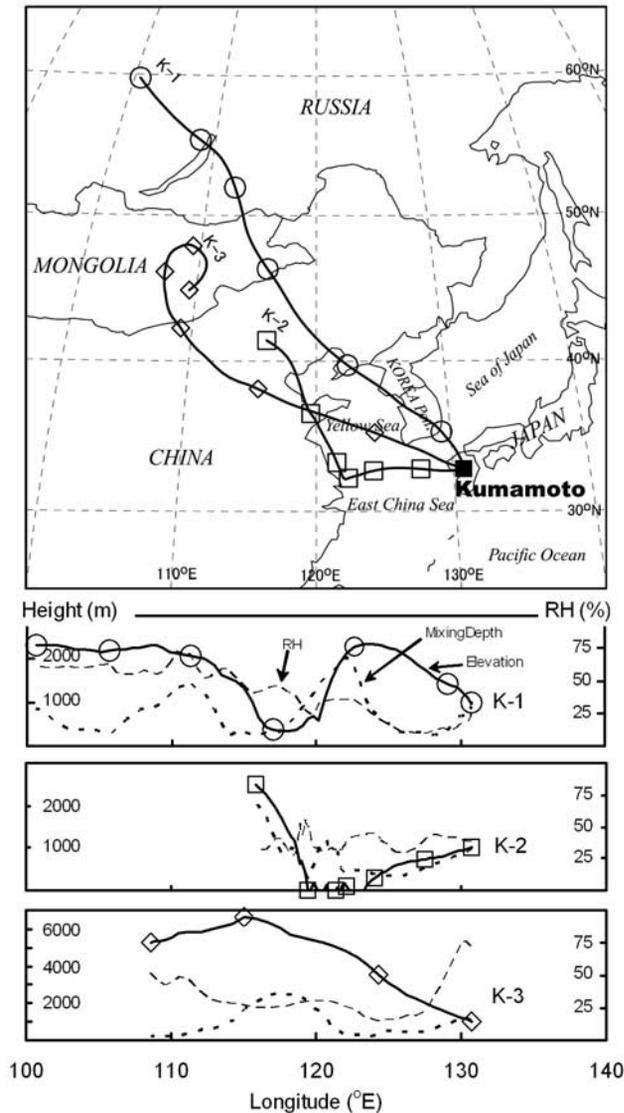nsmission electron microscope was applied to identify the presence of sulfate and nitrate in individual particles. Compared to bulk sample analysis by which only the average information of total collected particulate matter is available, single particle analysis allows the exact characteristics of each particle to be obtained and such data are more precise in elucidating what has occurred on the particles.

## 2. Experiment and Backward Trajectory Calculation

[7] Dust particles were collected during three dust storm events at Kumamoto (named as K-1, K-2, and K-3) in spring 2000. Sampling time and weather conditions are listed in Table 1. Figure 1 shows the geographic position of the sampling site and the isentropic backward trajectories of the observed dust events. The sampling site was on the roof of a 25-m high building (about 32 m asl) on the campus of Prefectural University of Kumamoto (32°48′N, 130°45′E) in the urban area of Kumamoto. Around the campus are residences, streets and shopping areas. The distance from ocean (the Ariake sea) in the upstream area (west) is about 18 km. The areas between the city and the ocean are agriculture fields, which were covered mainly by wheat grass at the sampling time. There were no considerable local sources of mineral particles in these areas. Thus the mineral particles collected during the three events can represent the dust particles arriving at the site through long-range transport.

[8] Particles were collected onto electron microscope Pt grids (3 mm diameter) and formvar film-covered copper meshes (Maxtaform H7) using a single-stage cascade impactor. Before particle collection, the film on the meshes was coated with nitron and barium chloride which were the reagents for the detection of nitrate and sulfate in individual particles. Details of the reagent coating are given by *Qian et al.* [1991], except that both reagents were pre-coated before particle collection. The jet of the impactor is circular and its diameter is 1 mm. The flow rate of inlet air was 5 L min$^{-1}$. Assuming particle density is 2.3 g cm$^{-3}$, the 50% cutoff aerodynamic diameter of the impactor is about 0.25 μm and the collection efficiency for particles larger than 0.6 μm is 1.0. The collection time for each grid and mesh was 2 minutes. After collection, each grid was put in a plastic capsule, which, in turn, was sealed in plastic bags together with paper-packaged silica gel. After the particle collection of one event, all plastic bags sealing sample capsules were put into a box with packaged silica gel and the box was preserved cooling in a refrigerator in laboratory until subsequent analysis.

[9] Particles on Pt grids were investigated and photographed using the scanning electron microscope (SEM; Hitachi S-3000N) of the Solar Terrestrial Environment

0.001 mass fraction or approximately $10^{-16}$ g by weight. However, the accuracy and precision associated with the analysis are highly dependent on particle shape, size, composition and operating conditions. The SEM-EDX was operated at 20 keV accelerating voltage and about 80 $\mu$A filament current. The X-ray spectrum of a particle was generated from a square covering the particle and was integrated for 50 live seconds with the probe current around 0.3nA. The atom number fractions and weight fractions of different elements in individual particles were calculated using ZAF (Z: element atom number; A: X-ray absorption; F: X-ray fluorescence) matrix correction. To avoid underestimating the content of sodium (Na), low energy correction was not applied in the ratio calculation, which lead to the ratios of carbon and oxygen being unreasonably large and the ratios of Na being somewhat overestimated. If the SEM-EDX system did not identify the existence of an element in a particle automatically, we regard the particle did not contain the element.

[10] In terms of elemental composition, dust particles were defined as particles containing silicon (Si) together with/without other mineral elements, such as aluminum (Al) and iron (Fe), based on the results of *Okada and Kai* [1995] and *Nishikawa et al.* [2000]. Sea-salt particles were those being abundant in Na and chlorine (Cl) and containing minor sulfur (S) and/or magnesium (Mg) [*Eriksson*, 1959; *Posfai et al.*, 1996]. Our previous identification of fresh sea-salt particles using the same instruments under the same operating conditions revealed that Si appeared in a few sea-salt particles and its relative weight ratios among total detected elements were usually less than 0.2%. In this study, if Si was detected and its relative weight ratio was smaller than 0.2% in a sea-salt particle as defined above, the particle was still regarded as a sea-salt particle.

[11] Before analyzing particles collected on meshes covered with reagent-coated films, the meshes were exposed to octanol vapor in a small chamber at room temperature for 18 hours to promote the reactions of sulfate and/or nitrate with the reagents. And then particles on the films were viewed and photographed using the Hitachi H-9 transmission electron microscope (TEM) of the Hydrospheric-Atmospheric Research Center of Nagoya University. From the TEM images, particles containing sulfate on their surface could be identified by the appearance of Liesegang rings of barium sulfate, which was the product of the reaction of sulfate with barium chloride, and particles containing nitrate by the appearance of bundles of needle-like crystals of nitron nitrate, which was the product of the reaction of nitrate with nitron. Particles containing both sulfate and nitrate could be identified by the simultaneous appearance of barium-sulfate rings and nitron-nitrate bundles around the particles. If there were not the distinctive reaction products around a particle, we regard the particle did not contain sulfate or nitrate on their surface. According to the laboratory study of *Qian et al.* [1991], the detection limits of the reagent films for sulfate and nitrate contained in individual particles are $10^{-17}$ g and $10^{-14}$ g, respectively.

[12] Isentropic backward trajectories of the three observed dust storm events were calculated on-line using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model with the $1° \times 1°$ latitude-longitude grid, FNL meteorological database [*Draxler and Hess*, 1997] at



**Figure 1.** Isentropic backward trajectories and relevant information along the trajectories of the three dust events. The top panel illustrates the horizontal movements of the air parcels. The bottom three panels illustrate the elevations (marked solid lines), relative humidity (thin dashed lines) of the air parcels and the surface mixing layer depths (dot lines) along the trajectories of the three events, respectively. Circles, squares, and diamonds on the trajectories mark K-1, K-2 and K-3, respectively, and they indicate the 12-hour interval.

Laboratory of Nagoya University, and the photographs were used later for the observation of particle morphology and size. After a photograph was taken, the elemental composition of every particle in the photograph was determined using the energy dispersive X-ray (EDX) spectrometer (Horiba EMAX-500) attached to the SEM. This SEM-EDX is able to quantitatively measure the relative weight and atom ratios of elements with atom number 6 (carbon) and greater except nitrogen in a single particle of about 0.1 $\mu$m. The energy resolution of the EDX detector is 10eV and its lowest detection limit of a trace element is about

NOAA Air Resources Laboratory's web server. Details of the model and the database can be found at http://www.arl. noaa.gov/ready/hysplit4.html. The trajectories started at the altitude of 1000 m above the sampling site and from the sampling time.

## 3. Results and Discussion

[13] The backward trajectories (Figure 1) indicate that the three dust events were originated from North (K-2, K-3) and Mongolia or Northeast (K-1) China. K-2 and K-3 events left the continent from North and East China and crossed over the Yellow Sea (K-3) or the East China Sea (K-2), and K-1 event left from Northeast China and passed over the Korea peninsula before they arrived at southwestern Japan. The elevations of air parcels along the trajectories of K-1 and K-2 events indicate the movements of the air parcels arriving at the sampling site should not be straight downward or upward over the ocean, while the parcels probably experienced up and down movement there. The depths of surface mixing layer along the trajectories over the ocean were between about 300 m to 2000 m. The elevations of the air parcels of K-1 and K-2 events were sometime (about 8 hours in K-1 event and 38 hours in K-2 event) lower than the surface mixing layer top. These characteristics of the trajectories suggest the particles collected in the two events had probably moved upward and downward in the marine boundary layer. The air parcel of K-3 event kept downward movement in the marine atmosphere before arriving at the sampling site. Thus the particles collected in this event might have a shorter history in the marine boundary layer than those in the other two. It should be noted the altitude of the start points of the trajectories was 1000 m over the observational site.

### 3.1. Dust Particles Mixed With Sea Salt

[14] Figure 2 shows an example of an electron micropho- tograph of particles on Pt grids and examples of X-ray spectra of particles marked in the microphotograph. It was found that particles containing elements with atom number 11 or larger mainly had three types according to their major elemental components. One type of particles, such as Particle A in Figure 2, was mainly composed of crustal elements and no Na was detected in them. Hereafter, such particles are named as "pure dust particles". The second type of particles, such as Particle B, was mainly composed of crustal elements and sea-salt elements (Na and Cl). Such particles were the mixture of mineral and sea salt, i.e., they were dust particles internally mixed with sea salt. Hereafter such type particles are named as "mixture particles". The third type of particles, such as Particle C, was mainly com- posed of Na and Cl and such particles were sea-salt particles.

[15] Figure 3 shows the number fractions of Na-contain- ing dust particles and Non-Na dust particles in detected dust particles of the three events. The fractions of Na-containing dust particles were 71.9 ∼ 85.1% (mean 79.9%). Analysis of the mineral particles collected in the free troposphere over the desert areas in Northwest China and dust particles collected during three dust-storm events at a coastal site of China by the instruments of this study indicated that the ratios of crustal Na-containing dust particles to total detected dust particles were about 10% or less [Iwasaka et al., 2003; D. Zhang et al., 2003]. If the upper threshold of
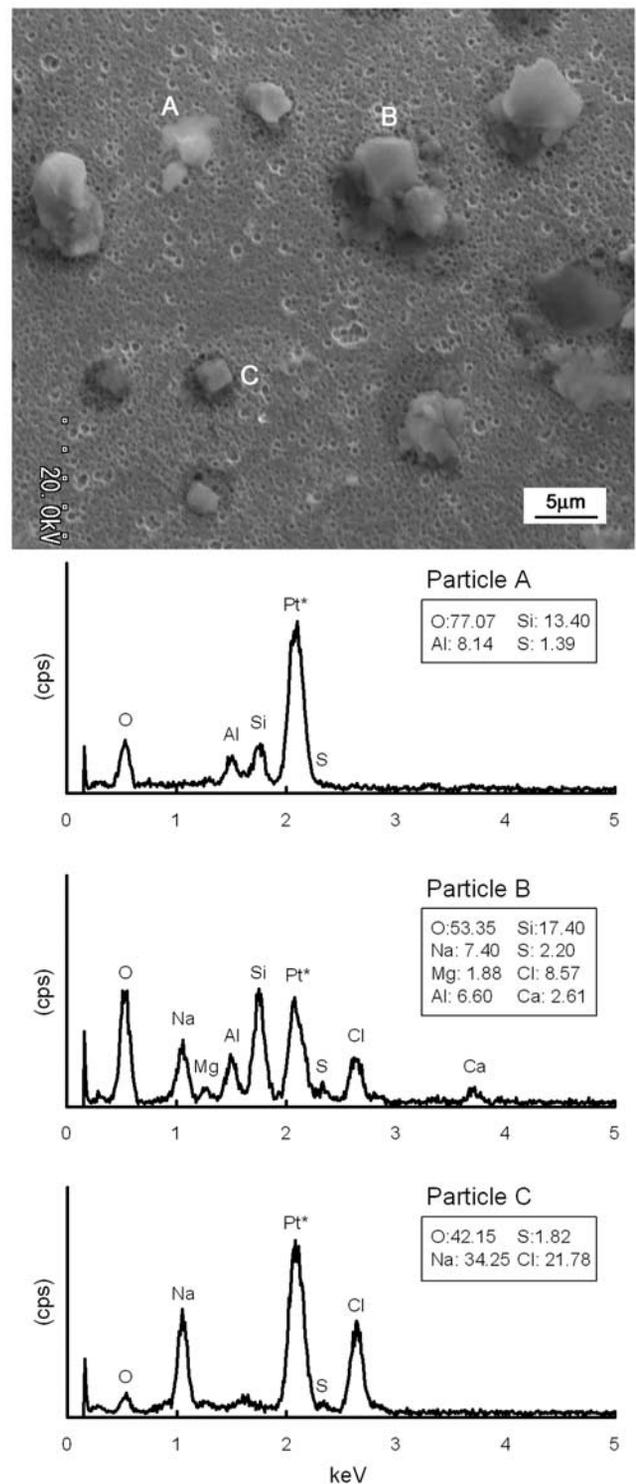


**Figure 2.** An electron photomicrograph (SEM) showing collected particles on a Pt grid of K-1 event and the EDX spectra of the three particles marked by A, B and C in the photograph. Pt marked by stars in the spectra was caused by the grid. Data in the frames in each spectrum are the raw data of relative weight ratios of detected elements in the particles. Notice O in each particle was largely over- estimated and Na was somewhat overestimated.
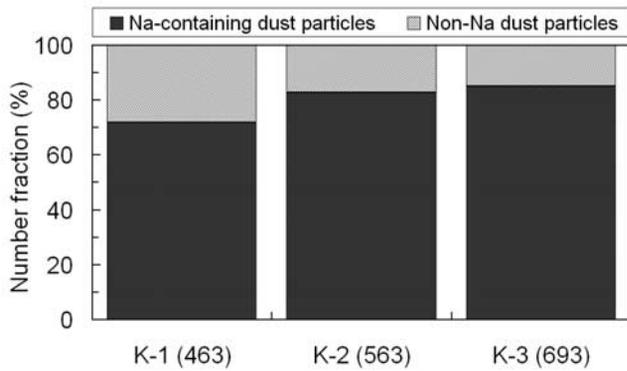
**Figure 3.** Number fractions of Na-containing particles and non-Na particles in detected dust particles of the three dust events. Total numbers of dust particles detected in each dust event are listed in the parentheses.

the percentage ratios of crustal Na-containing dust particles to total dust particles at Kumamoto was also 10%, the fractions of mixture dust particles should be about 60 ~ 85%. As a consequence, the fractions of pure dust particles should be about 15 ~ 40%. The fractions of mixture particles were much larger than that observed at a coastal site of China, where the fractions were much less than 10% [*D. Zhang et al.*, 2003], which supports the hypothesis that dust particles can be modified greatly by sea salt during their dispersion from China to Japan in the marine atmosphere [*Fan et al.*, 1996; *Zhou et al.*, 1996].

[16] *Niimura et al.* [1998] suggested two mechanisms to interpret the formation of mixture particles observed in the marine atmosphere. One is that dust particles and sea-salt particles are enclosed into cloud droplets through cloud processing. If the droplets evaporate due to ambient changes, the evaporation residues are mixture particles.

The other one is that mixture particles are produced by direct collisions and coagulations of dust particles with sea-salt particles in the marine atmosphere. They also suggested that the former mechanism should be more efficient than the later one. However, the weather records of the present studies show the oceanic areas where the collected particles of K-1, K-2 and K-3 passed were occupied by high-pressure systems or were in transitions from low pressures to high pressures. There were no clouds at the places where the air parcels passed along the transport path ways shown in Figure 1. Figure 4 illustrates the examples of cloud images and surface weather charts. Kumamoto areas had high pressure, the wind was weak and the sky was clear except dust during sampling periods (Table 1). Moreover, the trajectory calculation reveals that the relative humidity of the air parcels of the three events were between 10% and 50% when they were moving in the marine atmosphere, except that of K-3 which increased rapidly from 40% to 75% when approaching the sampling site (Figure 1). If the histories of the dust particles in marine atmosphere were consistent with that shown by the trajectories in Figure 1, the collected particles should not have experiences in cloud or fog. That means the mixture particles were not formed through cloud processes. As a result, they were more likely formed through direct collisions and coagulations of fresh dust particles and sea-salt particles. If this is true, the present results suggest that the direct collisions and coagulations in the marine atmosphere may also efficiently produce mixture particles of mineral dust and sea salt. Consequently, the influence of sea salt on dust particles is probably essential and cannot be neglected in the investigation of dust particles in marine atmosphere even when there is no cloud or fog.

### 3.2. Size Distributions Segregated by the Mixture Levels of Mineral and Sea Salt

[17] Sizes of dust particles were estimated from their SEM images. The diameter of a particle was defined by
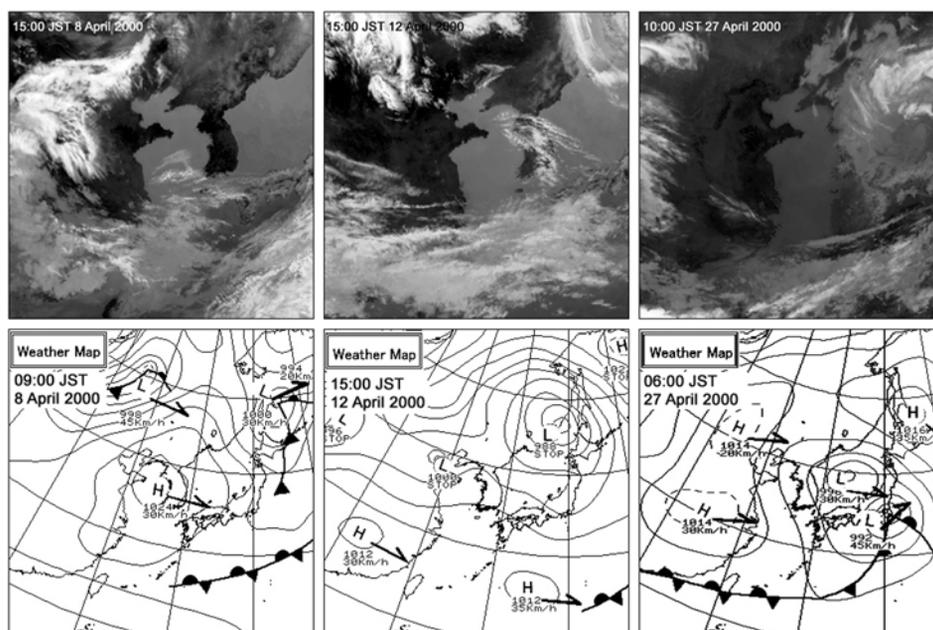


**Figure 4.** Satellite images and surface weather charts for the three dust events.
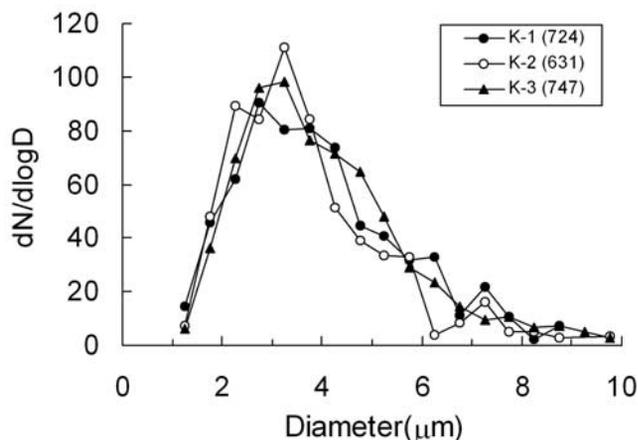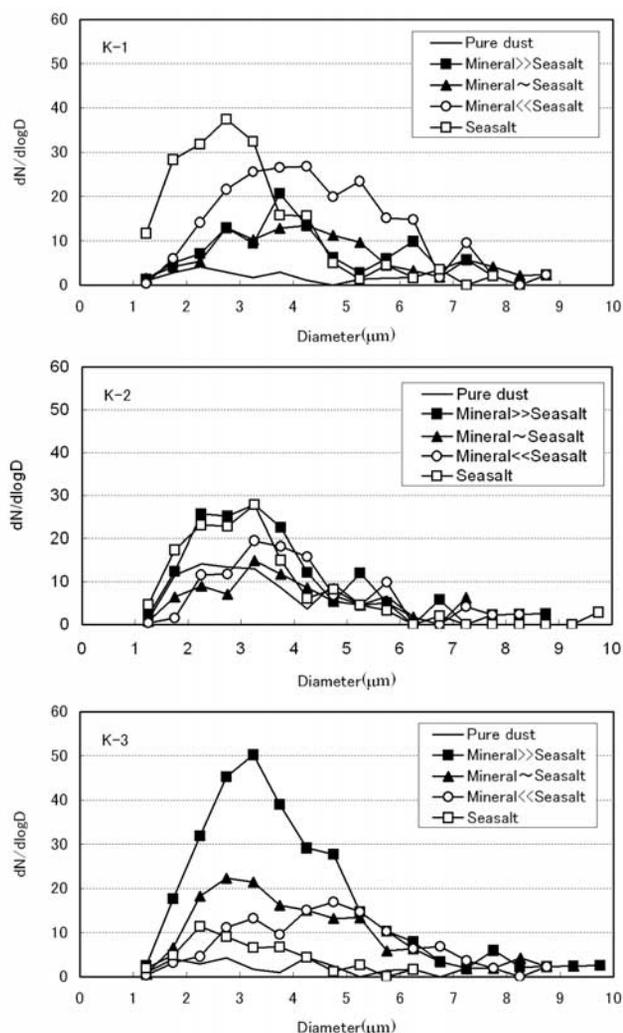
**Figure 5.** Number-size distributions of total particles including pure dust, mixture, and sea-salt ones detected in each event. Total numbers of detected particles in each event are listed in the parentheses. In the calculation of the distributions the total number of each event was normalized to 100.

the mean of its longest dimension and the orthogonal width. Although the particles were dehydrated in preservation and analyzed under vacuum, large changes in size were not expected since the particles analyzed here were mainly composed of mineral and sea salt. According to *McInnes et al.* [1997], diameters of solid particles, such as sea-salt particles, on electron microscope microphotographs are approximately the same as their aerodynamic diameters. Figure 5 shows the size distributions of total particles including pure dust, mixture and sea-salt ones detected in each event. Other particles were not included in the distributions since the dust and sea-salt particles together occupied about 95%, 90% and 95% of detected particles of the three events in the range of diameter >1 μm, respectively. Figure 5 shows that all the three events had their distribution modes around 3 μm. The particles were mainly in the range of 1.0 ~ 8.0 μm. Out of this range, dust particles were rarely detected. These are similar to our recent results of dust particles at a coastal site of Qingdao in China [*D. Zhang et al.*, 2003] and the distributions are approximately consistent with those of dust particles recorded at Korea, Japan and the North America [*Chun et al.*, 2001; *Husar et al.*, 2001; *Murayama et al.*, 2001; *Tratt et al.*, 2001; *Trochkine et al.*, 2002]. However, the contributions of mixture particles to the distributions here were larger than pure dust particles (Figure 3), while at Qingdao the majorities were the so-called pure dust particles.

[18] These size distributions in conjunction with the composition information suggest that most of the dust particles arriving in Japan had interacted with sea salt leading to an increase in particle size, and in consequence, additional dust particles were removed by gravitational settling. Thus the distribution consistency of dust storm particles at different sites suggests that the combination of dust particles with sea salt did not change the particle size very much or the combination changed the sizes considerably but in that sense the particles should be removed rapidly when they became larger than 3 μm.

[19] To investigate the conjunctions of distributions with mixture levels, the size distributions in Figure 5 were segregated according to the mixture levels of mineral components and sea salt. The results are shown in Figure 6. The distributions of mixture particles dominated by sea salt (Mineral ≪ Seasalt), by both sea salt and mineral (Mineral ~ Seasalt) and by mineral (Mineral ≫ Seasalt) had similar patterns in the size range of 1.0 ~ 8.0 μm. The peak size ranges (3.0 ~ 5.0 μm) of Mineral ≪ Seasalt and Mineral ~ Seasalt particles were similar to that of Mineral ≫ Seasalt particles in K-1 event. In the other two events, the peak size ranges of Mineral ≫ Seasalt (2.0 ~



**Figure 6.** Number-size distributions of particles segregated by mixture levels of mineral and sea salt. The particles are the same ones as in Figure 5. In the calculation of the distributions, the total number of each event was normalized to 100. The mixture levels of a particle is defined by $r$ [=Mineral/(Mineral + Seasalt)], where "Mineral" is the sum of weight ratios of Al, Si and Fe, and "Seasalt" is the sum of weight ratios of Na and Cl of the particle. Pure dust particles, Mineral ≫ Seasalt particles, Mineral ~ Seasalt particles, Mineral ≪ Seasalt particles and Seasalt particles are particles of $r = 1$, $1 > r \geq 0.65$, $0.65 > r \geq 0.35$, $0.35 > r > 0$, and $r = 0$, respectively.

4.0 μm) shifted a little to smaller ranges compared with the peak size ranges of Mineral ≪ Seasalt particles (3.0 ∼ 5.0 μm). It was confirmed that the combination with sea salt could significantly increase the sizes of original dust particles (see pictures of Asian dust particles collected at Japan before and after dialysis treatment in the works of *Niimura et al.* [1994, 1998]). Since the particles of Mineral ≪ Seasalt were mainly composed of sea salt, the original dust particles must be much smaller than the mixture particles. Similar combinations occurring to larger dust particles should have also caused the growth of the particles although the increase in size might not be as significant as small dust particles. Therefore the decrease of dust particles in the range larger than 3 μm can only be interpreted by a hypothesis that particles would be removed rapidly when they became larger than this scale. Otherwise the distributions of Mineral ≪ Seasalt particles, compared to those of Mineral ≫ Seasalt particles, should have apparently shifted to larger ranges.

[20] A potential significance of this hypothesis is that it can provide a plausible interpretation for why the distribution modes of dust storm particles observed at Korea, Japan and North America during Asian dust are approximately consistent and at 3 ∼ 5 μm. If combinations with sea salt increase the size of dust particles when the particles disperse in the marine atmosphere, the peak range of dust particles observed at downstream areas should not be conserved by the original dust particles emitted in the source areas. They should be the results of growth of smaller particles and removal of larger particles. Limited published data indicated that the peak range of mass-particle size distributions of Al was larger than 8 μm (dust events in 1990) or larger than 16 μm (dust events in 2001) at dust source areas in West and northwest China, was around 5 μm to 8 μm at Beijing areas (dust events in 1990), and was around 4 μm at Japan (dust events in 1987) [*X. Y. Zhang et al.*, 1993, 2003; *Kanamori et al.*, 1991], suggesting the rapid removal of original large dust particles along the transport path ways during their dispersion. This is further confirmed by a recent case study of *Mori et al.* [2003], who after comparing the particles collected at a Chinese site and a Japanese site during one dust storm event, reported that the particle diameter with maximum mass concentrations of crustal elements at the Japanese site was smaller than that at the Chinese site.

### 3.3. Sulfate and Nitrate Formations

[21] The reagent film tests revealed that a lot of particles contained sulfate or nitrate and some contained both. Figure 7 shows the examples of particles on reagent films, which were photographed by the TEM. The number fractions of reaction spots that had obvious electron-dense cores after reaction among total electron-dense particles were estimated from TEM images. The results are listed in Table 2. 70 ∼ 75% of electron-dense particles contained sulfate, 2 ∼ 6% contained nitrate, and 17 ∼ 25% contained both sulfate and nitrate.

[22] The above results were about the electron-dense particles, and were not the accurate fractions for dust particles. It is known from the elemental analysis that more than 90% of electron-dense particles were pure dust particles, sea-salt particles or their mixture. Given that there were no other particles except pure dust particles, mixture particles and sea-salt particles in electron-dense ones, and



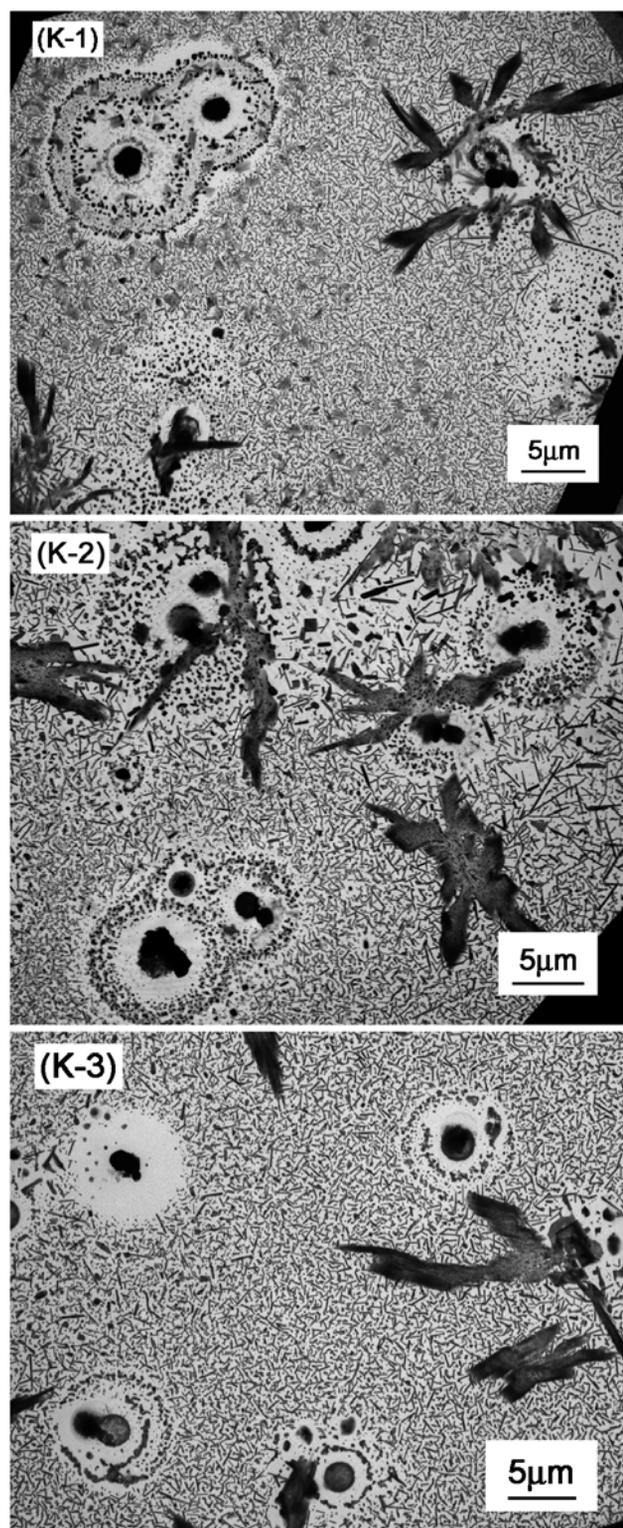**Figure 7.** Electron microphotographs (TEM) of particles of the three events on reagent films.

all sea salt-containing particles contained sulfate and no sea salt contained nitrate, the number fractions of sulfate- and nitrate-containing dust particles (including pure dust particles and mixture particles) were calculated. The results are also listed in Table 2. 91 ∼ 96% (mean 93%) dust particles

**Table 2.** Number Fractions of Sulfate-, Nitrate- and Sulfate-and-Nitrate-Containing Particles in Electron-Dense Particles Detected by Reagent Film Analysis, Number Fractions of Sea-Salt Particles and Dust Particles Detected by Element Analysis, and the Number Fractions Of Sulfate- and Nitrate-Containing Ones in Dust Particles Which Are Estimated With the Assumption That All Sea-Salt Particles Contained and None Contained Nitrate[a]

| Dust Event | Reagent Film Analysis | | | | Element Analysis | | | In Dust Particles | |
|---|---|---|---|---|---|---|---|---|---|
| | Sulfate | Nitrate | Sulfate and Nitrate | $N$p | Sea Salt | Dust | $N$p | Sulfate | Nitrate |
| K-1 | 70 | 2 | 25 | 429 | 38 | 61 | 761 | >91 | <27 |
| K-2 | 75 | 2 | 22 | 569 | 25 | 70 | 751 | >96 | <24 |
| K-3 | 75 | 6 | 17 | 719 | 9 | 87 | 798 | >91 | <23 |
| Average | | | | | | | | 93 | 25 |

[a]$N$p is the number of total accounted particles in the analysis for each event. Fractions are in percents.

contained sulfate, and 23 ∼ 27% (mean 25%) contained nitrate. The given conditions made the fractions of sulfate-containing dust particles being a little underestimated and the fractions of nitrate-containing particles being somewhat overestimated. Thus it was estimated that 91% or more dust particles were sulfate-containing ones and 27% or less were nitrate-containing ones. The fractions, particularly those of sulfate-containing dust particles, were much larger than what we observed at Qingdao [*D. Zhang et al.*, 2003], which supports that the enhancement of particulate sulfate and nitrate formation by dust particles mainly occur in the marine atmosphere [*Fan et al.*, 1996; *Zhou et al.*, 1996; *Uematsu et al.*, 2002].

[23] The number fractions of sulfate-containing particles were much larger than those of nitrate-containing ones. This is consistent with the results reported by *Yamamoto and Tanaka* [1994], who applied single particle analysis to identify the presence of sulfate and nitrate in particles in free marine troposphere near Japan. In marine atmosphere, the mass concentrations of both particulate sulfate and nitrate substantially increase in the size range larger than 1 μm during dust storm episodes and sulfate increase is several times larger than nitrate increase in the marine atmosphere [*Kanamori et al.*, 1991; *Li-Jones and Prospero*, 1998], suggesting the formation of sulfate on dust particles is more efficient than that of nitrate. $SO_2$ emission is much larger than $NO_x$ emission in East Asia and the ambient concentration of $SO_2$ is expected to be larger than $NO_x$ [*Akimoto and Narita*, 1994], which can lead to the formation of more sulfate than nitrate if dust plumes mix with the emissions in this region. Another possible reason for the difference of sulfate and nitrate in the dust particles might be the different volatilities of sulfuric acid and nitric acid. Sulfuric acid is less volatile than nitric acid. Besides gaseous phase, sulfate produced from gas phase oxidation of sulfur dioxide followed by nucleation can exist in the form of sulfuric acid or ammoniated sulfate particles in the range smaller than 1 μm (fine mode) [*Andreae et al.*, 1999]. However, nitrate hardly exists in that range. Besides heterogeneous conversions on dust particle surface, sulfate can also appear on the particles by the uptake of pre-existing sulfate and sulfuric particles, while the major routes of nitrate formation on dust particles are surface heterogeneous conversions and uptake of nitric acid gas [*Zhang et al.*, 1994; *Zhang and Carmichael*, 1999; *Phadnis and Carmichael*, 2000]. Even after it has formed on dust particles, nitrate has a strong tendency to escape back into gas phase if the particles absorb sulfuric acid gases or particles while sulfate is hardly

transferred back to gas phase. We did find a large number of particles containing only S in the range smaller than 1 μm. They did not have electron-dense cores and their morphologies were similar to neutralized sulfate particles. Thus it is reasonable to anticipate that part of the particulate sulfate in the coarse mode was produced originally in fine mode and transferred into coarse mode due to the adsorption by dust particles, through which more sulfate-containing particles were produced.

### 3.4. Sea Salt in Mixture Particles

[24] The variations of mixture particles were investigated on the basis of their sea-salt content. Figure 8 shows the relative weight ratios of Na, S and Cl (Na:S:Cl) in dust particles which contained at least two of Na, S and Cl. A few dust particles contained only one of the three elements and they were not included in Figure 8 because we did not think most of such particles contained sea salt. For reference, the average positions (stars) and ranges (hexagons) of fresh sea-salt particles which were detected by the SEM-EDX under the same conditions and the lines along which Na:S:Cl was changed by postulated processes are also shown in Figure 8. The hexagons and lines divide the triangles into four regions (A, B, C and D). If particles appear in those regions due to the change of their relative Na, S and Cl contents, the modification processes can be sketched (see Figure 8 caption). In this investigation, crustal contributions of Na, S and Cl were not considered. We were unable to identify strictly the crustal contributions due to the significant contributions of sea salt and the potential modifications of sea-salt content in mixture particles. The differences of Na:S:Cl of the particles from that of sea salt were regarded as the results of S deposition onto the particle surfaces and Cl depletion from sea salt in the particles. An estimation of dust particles collected at a coastal site of China during three dust storm events indicated that the number fractions of dust particles containing crustal Na, S and/or Cl were much less than 10% in total dust particles [*D. Zhang et al.*, 2003]. In the present events, about 60 ∼ 85% of dust particles were mixed with sea salt. Thus the discrepancies due to the ignorance of crustal Na, S and Cl contributions in the investigation of Na:S:Cl relative changes in sea-salt components of these particles should be much smaller than 8.5%.

[25] The number fractions in different regions of the triangles in Figure 8, i.e., the fractions of particles whose relative Na, S, and Cl contents were changed by presumable processes, are summarized in Table 3. In K-1 and K-2
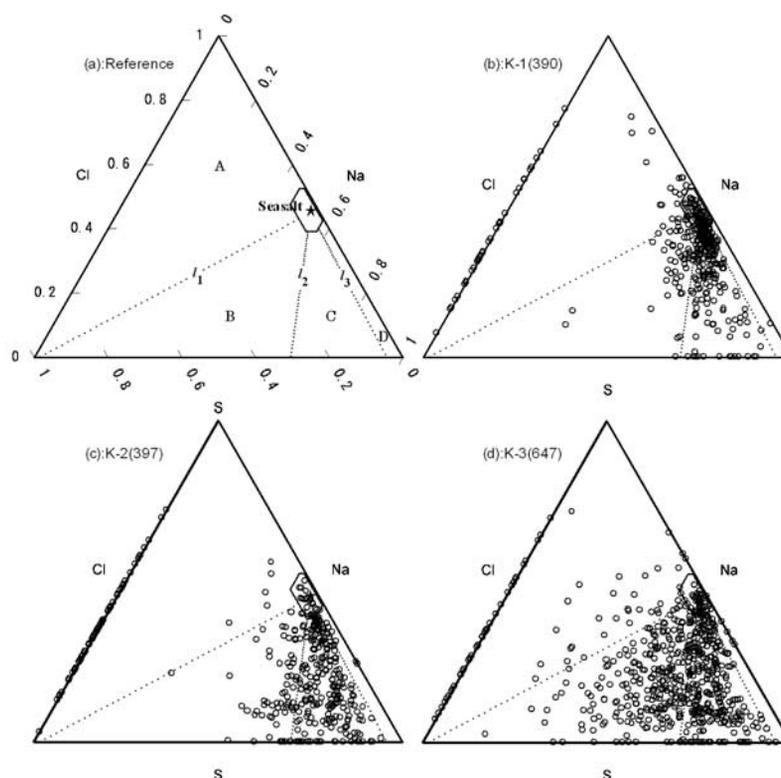
**Figure 8.** The weight ratios of Na:S:Cl of dust particles in which at least two of Na, S and Cl were detected. Figure 8a is the reference plot for Figures 8b, 8c, and 8d, which are for K-1, K-2 and K-3, respectively. The stars show the position of mean Na:S:Cl of fresh sea-salt particles which were collected near the surface of the Sea of Japan when only natural sea-salt particles were expected. The hexagons circling the star show the range of fresh sea-salt particles. The relative weight ratio ranges of Na, S, and Cl for the hexagons are $0.456 \leq r_{Na} \leq 0.569$, $0.003 \leq r_S \leq 0.065$, and $0.395 \leq r_{Cl} \leq 0.529$ ($r_{Na} + r_S + r_{Cl} = 1$), respectively. If a particle appears in the hexagon, the sea-salt component in it is regarded as unmodified. $l_1$ is the line along which Na/Cl is constant as in fresh sea salt, $l_2$ is the line along which Na:S:Cl is changed only by the postulated reaction of $H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl(g)$ [*Eriksson*, 1959], and $l_3$ is the line along which Cl depletion is independent from sulfur deposition. $l_1$, $l_2$ and $l_3$ separate the remained areas of triangles besides the hexagons into four regions denoted as A, B, C and D in each triangle. S in all particles was presumably in the form of sulfate. Particles in region A were those which contained extra Cl besides that from seawater even assuming no Cl depletion occurred. Particles in region B were those which contain extra S besides Cl replacement. Particles in region C were those in which the amount of S could not compensate Cl losses and there should be other processes leading to Cl losses. Particles in region D were those in which Cl losses were identified but S content did not increase. Numbers in the parentheses are the particle numbers of K-1, K-2 and K-3 events in Figures 8b, 8c, and 8d, respectively.

events, S deposition on less than 22% particles was sufficient to compensate Cl losses (region B) and processes irrelevant to S deposition caused Cl losses in more than 70% particles (region C). In K-3 event, Cl losses in nearly half of the particles could be compensated by S deposition and the deposition on many particles occurred without Cl loss. From Figure 8, it can be seen that many more particles in K-2 and K-3 events were close to Cl = 0 line than in K-1 event, suggesting modifications of sea-salt contents in dust particles of K-2 and K-3 events were much more severe than that of K-1 event. The trajectories in Figure 1 indicate that (1) the air parcels of K-2 and K-3 events left the continent from North China and the northern part of East China; (2) the air parcel of K-1 event left the continent from the south part of Northeast China, and it passed Korea

peninsula before arriving at the sampling site; and (3) the air parcels of K-1 and K-3 events took about 24 hours to arrive at the sampling site after leaving the continent, but the air parcel of K-2 event took more than 48 hours to cross the ocean area between China and Japan. East China and North China are the major regions of anthropogenic emissions, and the emissions in Northeast China are much weaker than in North China and East China [*Akimoto and Narita*, 1994]. Although it is not conclusive because no similar data sets for comparisons, (1) and (2) are the possible reasons for the different levels of sea-salt modifications in the three events. However, the reasons why there were many particles containing extra S besides Cl replacement are unknown. These results indicate that variations of dust particles due to interaction with sea salt in the marine atmosphere are not

**Table 3.** Number Fractions of Na-S-Cl-Containing Dust Particles in Different Regions in Figure 8[a]

| Dust Event (Particles Detected) | Region A (Extra Cl Besides Sea Salt) | Region B (Extra S Besides Cl Replacement) | Region C (Cl Replaced Not Only by S) | Region D (Cl Loss With No S Increase) |
|---|---|---|---|---|
| K-1 (260) | 7.3 | 20.0 | 70.4 | 2.3 |
| K-2 (277) | 1.8 | 22.0 | 74.4 | 1.8 |
| K-3 (524) | 5.7 | 45.8 | 47.9 | 0.6 |

[a]Fractions are in percents.

identical. Transport path ways, history in continental and marine atmosphere, and weather conditions seem all closely relate to the modifications of dust particles during their transport.

[26] The number fractions of nitrate-containing dust particles were less than 27% (sum of nitrate-containing and nitrate-plus-sulfate-containing particles in Table 2), which was much smaller than that of dust particles in region C in each event (Table 3). This suggests that not all particles in region C contained nitrate even all nitrate-containing particles were presumably in region C. Since S deposition could not composite Cl losses in the particles of region C, there must have been other processes leading to Cl losses besides reactions related to S deposition and nitrate formation. *Zhang et al.* [1999] found similar results in heavily polluted atmosphere in Hong Kong and they suggested organic ions might be a reason of Cl depletion in sea salt. Unfortunately, we do not have data to further identify this issue.

[27] Another result from Figure 8 is that S and Cl appeared in some Na-free dust particles. The absence of Na indicates that S and Cl in the particles were not caused by sea salt. The appearance of Cl in most the dust particles was attributed to the deposition of HCl, details of which were described and discussed by *Zhang and Iwasaka* [2001].

[28] In order to investigate the influences of mineral components on sea salt in mixture particles and the modification of sea-salt particles by Cl-replaced reactions associated with S chemistry in dust storm events, the ratios of Na:S:Cl in detected sea-salt particles in the three dust events were investigated and compared to the sea-salt components in mixture particles. Table 4 lists the number fractions of the sea-salt particles in regions A, B, C and D as shown in Figure 8a. The modification of sea-salt particles was different from that of sea salt in the mixture particles. In K-1 and K-2 events, the number fractions of sea-salt particles were much smaller than those of mixture particles in region A and region B, respectively, while the number fractions of sea-salt particles were much larger than those of mixture particles in region C. In K-3 event, this nature was not significant but consistent with K-1 and K-2 events. This

indicates S/Cl ratios in mixture particles were larger than that in sea-salt particles.

[29] If the sea salt in mixture particles and sea-salt particles had same history in the marine atmosphere, S deposition onto mixture particles must not have lead to Cl losses as efficient as onto sea-salt particles, or processes irrelevant to S deposition had caused significant Cl losses from the mixture particles. In other words, the Cl depletion due to S deposition from mixture particles was weaker than that from sea-salt particles. Since mineral particles are highly alkaline and they can act as an effective sink of acidic materials such as sulfuric acid and nitric acid [*Larssen and Carmichael*, 2000; *Wang et al.*, 2002], it is possible for S to deposit onto mixture particle without leading to Cl losses from the sea-salt component in the particles. Therefore Cl depletion from sea salt in mixture particles was likely restrained by the mineral components. This means dust particles appearing in the marine atmosphere will not only change the mass transformation associated with gaseous species such as $SO_2$ and $NO_x$, but also modify the S- and Cl-chemistry associated with sea salt through the enhancement of sulfate formation and the restraint of Cl depletion.

## 4. Conclusions

[30] Asian dust particles were collected at Kumamoto, a coastal city in southwestern Japan, during three dust storm events in spring 2000. The elemental compositions and sizes of individual dust particles and their mixture state with sulfate, nitrate and sea salt were investigated. The following conclusions are arrived at. (1) Collisions and coagulations with sea-salt particles might be efficient path ways to change Asian dust particles into the mixture of mineral and sea salt in the marine atmosphere. (2) During their dispersion, dust particles grew due to the combination with sea salt. It seems that the critical diameter for dust particle dispersion was around 3 μm and a particle would be rapidly removed if it became larger than this scale. (3) Dust particles enhanced the formation of particulate sulfate and nitrate. Accumulation of sulfate on dust particles was much more efficient than that of nitrate. (4) Mineral components

**Table 4.** Number Fractions of Sea-Salt Particles in Different Regions as Shown in Figure 8a[a]

| Dust event (particles detected) | Region A (Extra Cl besides sea salt) | Region B (Extra S besides Cl-replacement) | Region C (Cl replaced not only by S) | Region D (Cl loss with no S increase) |
|---|---|---|---|---|
| K-1 (179) | 1.1 | 7.3 | 89.4 | 2.2 |
| K-2 (131) | 0.0 | 4.6 | 94.7 | 0.8 |
| K-3 (52) | 9.6 | 32.7 | 57.7 | 0.0 |

[a]Fractions are in percents.

in mixture particles restrained Cl depletion from the sea-salt component in the particles.

[31]  In addition to the above conclusions, our results also suggest some other topics. One is that there were other potential processes leading to Cl losses from sea-salt components in many mixture particles besides S deposition and nitrate formation. Another is that the variations of dust particles associated with sulfate, nitrate and sea salt were not identical but very complicated in different dust events. More case data and the analyses of candidates having the potential ability to replace Cl in sea salt are necessary to clarify these issues.

[32]  The results reported here are on dust particles that had no experiences in cloud. It is known that dust particles enclosed in central parts of low pressure systems in East Asia usually interact with clouds after they leave the continent. Those dust particles may have very different physical and chemical properties.

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