Size change of Asian dust particles caused by sea salt interaction: Measurements in southwestern Japan

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[1] Water dialysis was applied to remove water-soluble components in the individual Asian dust particles collected in southwestern Japan. Size and composition of the particles before and after the dialysis were compared. It was found that the post-dialysis number-size distributions of mineral-sea salt mixture particles shifted toward smaller ranges compared to their pre-dialysis distributions and the more sea salt the particles contained the larger the shift of their distribution was, while the dialysis did not cause apparent changes in size or morphology of particles in which sea salt was not identified. Estimation from total detected dust particles revealed that mixing with sea salt had caused their size distributions to shift to larger ranges approximately by $0.4 \sim 0.8$ μm. Hence, the interaction of dust particles and sea salt is likely an important process in size and composition changes of dust particles during their long range transport, consequently affecting mass transformation and radiation transfer in the atmosphere as well as the sedimental flux of mineral dust to sea surface. 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. Citation: Zhang, D., and Y. Iwasaka (2004), Size change of Asian dust particles caused by sea salt interaction: Measurements in southwestern Japan, Geophys. Res. Lett., 31, L15102, doi:10.1029/2004GL020087.

1. Introduction

[2] Mineral dust is an important atmospheric aerosol due to its potential influences on biogeochemical systems and climate forcing [IPCC, 2001]. After being lifted into the atmosphere, dust particles usually interact with gases and other aerosol particles besides gravitational settling. Particularly in the marine atmosphere, they may rapidly become mixtures of mineral, sea salt, sulfate and/or nitrate [Fan et al., 1996; Zhou et al., 1996; Niimura et al., 1998; Zhang et al., 2003]. All of these processes can cause the changes of particle size and composition, which are essential data for evaluating the activities of dust particles in mass transformation and radiation transfer. A number of studies have suggested that the interaction of dust particles and sea salt in the marine atmosphere might significantly change the composition of the original particles [Andreae et al., 1986; Okada et al., 1990]. However, no quantitative data on dust particle modification caused by the interaction are available yet, and in consequence the significance of the interaction is poorly understood.

[3] In this study, we succeeded in extracting the water-insoluble parts enclosed in mineral-sea salt mixture particles that were formed in the marine atmosphere between China and Japan. Their size and composition were compared with the mixture particles to quantitatively investigate the influence of mixing with sea salt on dust particle size.

2. Methods

[4] Particles were collected in Kumamoto (32°48′N, 130°45′E) in southwestern Japan during three dust storm events on April 8, 12, and 27, 2000 (hereafter denoted as K-1, K-2 and K-3, respectively). Details of site information, particle collection and conservation, weather conditions and the analysis of individual particles by a SEM-EDX system were described by Zhang et al. [2003]. Through the analysis, morphology and elemental composition of individual particles including the relative weight and atom ratios of each detected element to total detected elements were obtained. We want to emphasize that the 50% cutoff aerodynamic diameter of the collection impactor was about 0.25 μm and for particles larger than 0.6 μm the collection efficiency was 100%. This ensured that possible sampling loss of dust and sea salt particles should be very small since they were usually larger than 1 μm. Further, most collected particles were photographed and we detected the elemental composition of every SEM 'visible' particle in all photographs. Sample reservation and SEM-EDX analysis should have resulted in the loss of volatile particles. Thus, the obtained results from the detected particles should be representative for non-volatile particles in the range of diameter larger than 0.6 μm. As in Zhang et al. [2003], dust particles were defined as those containing silicon (Si) together with/without other mineral elements, such as aluminum (Al) and iron (Fe). Sea salt particles were those abundant in sodium (Na) and chlorine (Cl) and containing minor sulfur (S) and/or magnesium (Mg). Mixture particles were dust particles in which both Na and Cl were detected besides minerals.

[5] In order to extract the water-insoluble parts in mixture particles, the particles were treated by water dialysis, which was an effective approach to remove water-soluble components in individual particles for single particle anal-
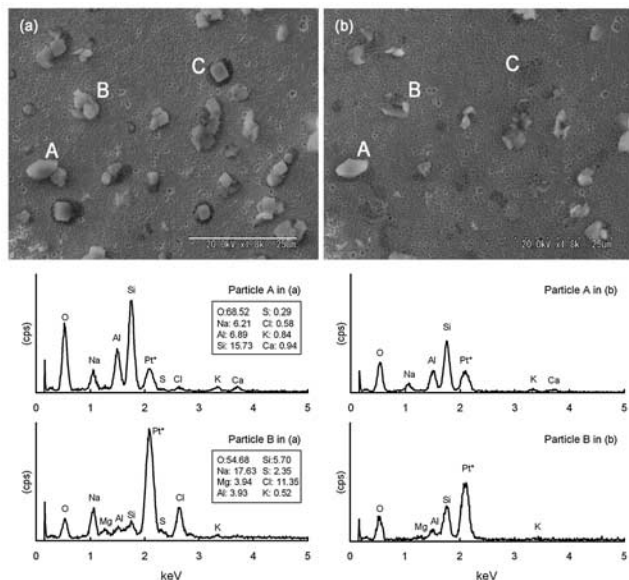
Figure 1. Electron microphotographs of particles before (a) and after (b) the water dialysis and X-ray spectra of particles marked in the photographs. The particles were collected on April 8, 2000. Data in frames are the raw data of relative weight ratios of detected elements in the particles. Notice that O in each particle was largely overestimated and Na was somewhat overestimated.

ysis [*Okada*, 1983; *Niimura et al.*, 1998]. The water dialysis we applied in this study was different from that in *Okada* [1983] and *Niimura et al.* [1994]. We put the sampled grids into distilled water to let water-soluble components in particles dissolve directly into the water. The difficulty in the dialysis was to avoid particle movement and loss on grids when the grids were put into and taken out from the water. After several rounds of tests, we confirmed the confidence of the dialysis performed as the following stepwise procedures: (1) fix sampled grids on a stainless steel mesh stand (Okenshoji Co. Ltd., $\phi 10$ cm); (2) put the stand in a stainless steel settlement dish (Okenshoji Co. Ltd.), which has a drain tap at its bottom; (3) input gradually distilled water into the dish and stop before water reaches the top of the stand; (4) cover the dish and leave it for one hour; (5) remove the cover of the dish and add distilled water with a syringe slowly into the dish until the grids were completely got into water; (6) cover the dish and leave it for another hour; (7) remove slowly the water in the dish from the drain tap; and (8) transfer the stand to a desiccator (RH < 30%) for dehydration. With (3) and (4), the possible influence of water surface stress on particles was minimized. These procedures were performed at room temperature. In this study, it was about 18°C. After these treatments, all areas containing particles analyzed before the dialysis on the grids were photographed again using the SEM. It was confirmed that in this study water-insoluble parts in most dust particles analyzed before the dialysis were successfully extracted. Some post-dialysis particles were analyzed using the EDX at the same operating conditions as pre-dialysis analysis except that weight ratios of carbon (C) and oxygen (O) were not estimated. Figure 1

shows examples of electron microscope photographs of particles on a Pt grid before and after the dialysis. X-ray spectra of marked particles are included to show the changes of element composition due to the dialysis.

3. Results and Discussion

[6] Dust particles were categorized according to their pre-dialysis mixture degrees of minerals and sea salt. Number fractions of particles at different mixture degrees were estimated to evaluate the contribution of mixture particles. The mixture degree of a dust particle was defined by r [= Mineral/(Mineral+Seasalt)], where "Mineral" was the sum of weight ratios of Al, Si and Fe, and "Seasalt" was the sum of weight ratios of Na and Cl. Particles with $r = 1$, $1 > r \geq 0.65$, $0.65 > r \geq 0.35$, and $0.35 > r > 0$ were named non-mixture, Mineral≫Seasalt, Mineral∼Seasalt, and Mineral≪Seasalt particles, respectively. So non-mixture particles were dust particles in which no sea salt was identified, Mineral≫Seasalt particles were those dominated by mineral components, Mineral∼Seasalt particles were those dominated by mineral components and sea salt together, and Mineral≪Seasalt particles were those dominated by sea salt. The number fractions of particles at different mixture degrees in the total analyzed particles before the dialysis are listed in Table 1. Dust particles occupied 61% (K-1), 70% (K-2) and 87% (K-3) of detected particles, in which those of mixture particles were 57%, 54% and 83%, respectively. This result indicates that size distributions of non-volatile particles in the range of diameter larger than 0.6 μm should closely depend on mixture particles.

[7] As shown in Figure 1, some particles after the dialysis did not show greatly different morphologies from before the dialysis (such as particle A), and some had apparent changes and became smaller (such as particle B). The elemental composition of particle C (its spectrum is not shown) indicated it was a sea salt particle. Most of such particles completely disappeared after the dialysis. Comparisons of the pre- and post-dialysis morphology and composition of dust particles revealed that particles not showing large differences were non-mixture particles or Mineral≫Seasalt particles and particles having apparent changes were usually Mineral∼Seasalt particles or Mineral≪Seasalt particles. As indicated later, residues of mixture particles, to a large extent, could represent the original dust particles enclosed in the mixture particles. Therefore, mixing with sea salt could cause significant changes of dust particle size and shape.

[8] Tentative number-size distributions of analyzed dust particles were investigated to assess the modifications of

Table 1. Number Fractions (%) of Different Particles in Detected Particles Before the Dialysis

	K-1	K-2	K-3
Non-mixture dust	3.8	15.5	4.5
Mineral ≫ seasalt	15.5	26.6	45.0
Mineral ∼ seasalt	14.2	12.3	22.5
Mineral ≪ seasalt	27.7	15.2	15.0
Seasalt	37.5	25.0	9.3
Others	1.3	5.4	3.7
No. of particles	**761**	**699**	**788**
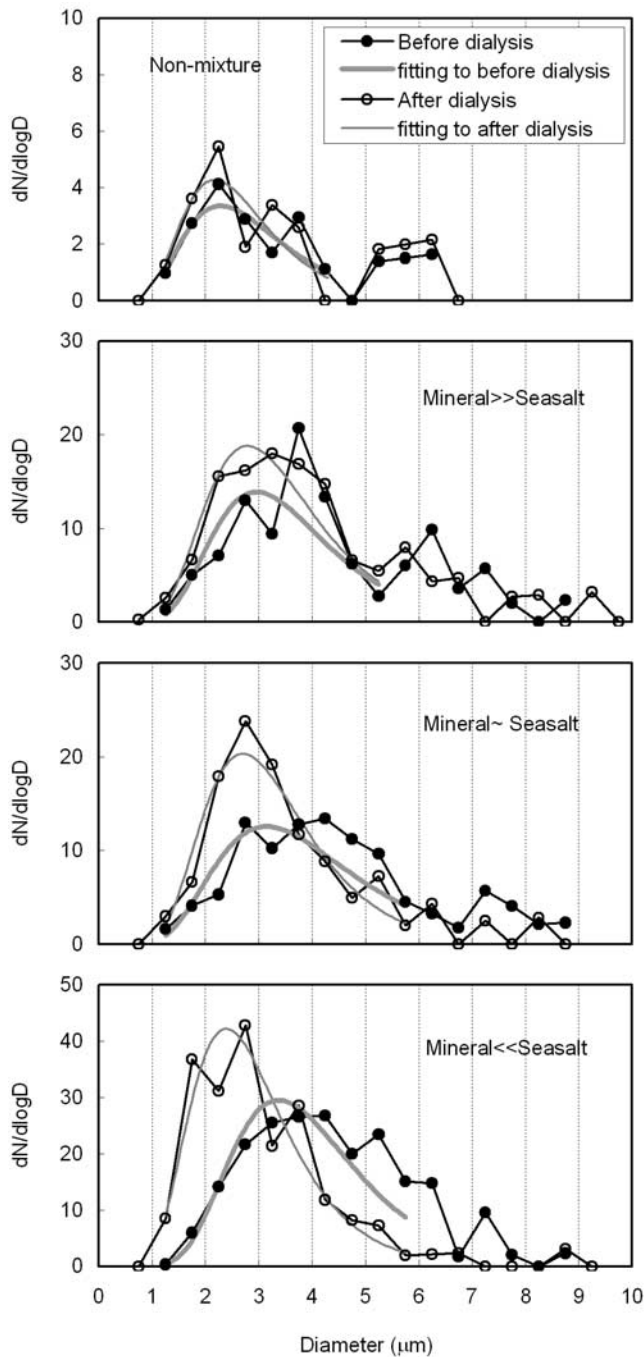
Figure 2. Tentative number-size distributions of dust particles at different mixture degrees before and after the water dialysis and their fitting curves in K-1 dust event. The pre-dialysis distributions were re-plotted from *Zhang et al.* [2003]. The detected particles for the post-dialysis distributions were 576 including identified residues of non-mixture and mixture dust particles. The number was normalized to 100 in the distribution calculation.

size distributions of dust particles due to the mixing with sea salt. The diameter of a particle was defined with the average of its longest dimension and the orthogonal width. According to *McInnes et al.* [1997], diameters of solid particles, such as sea salt particles, on electron microscope photographs are approximately the same as their aerody-

namic diameters. In addition, a few mixture particles separated into several small particles after the dialysis. In such cases, the small particles were sized individually while their mixture degrees before the dialysis were defined by their mother-particles. Figure 2 shows the distributions of dust particles of K-1 event at different mixture degrees before and after the dialysis. It is clear that size distributions of mixture particles shifted toward smaller ranges due to the dialysis. We applied lognormal functions [*Baron and Willeke*, 2001] (the distributions were presumably lognormal) to fit the distributions. The fitting curves for K-1 event are also shown in Figure 2 and the geometric mean diameters together with the relevant parameters of conducted fitting functions for all distributions of the three events are listed in Table 2. Peak sizes and distribution patterns of non-mixture particles before and after the dialysis in each event were almost the same and no systematic or large shifts could be confirmed. In contrast, the post-dialysis distributions of mixture particles shifted to smaller ranges compared to their pre-dialysis distributions in all three events. Moreover, the shifts became larger with the increase of sea salt content. The shifts of Mineral≫Seasalt particles were from 0.14 to 0.20 μm with an average of 0.17 μm, the shifts of Mineral~Seasalt particles were from 0.28 to 0.45 μm with an average of 0.38 μm, and the shifts of Mineral≪Seasalt particles were from 0.95 to 1.07 μm with an average of 1.0 μm. It should be noted that these results were conservative estimates because we applied same fitting ranges for the pre- and post-dialysis distributions of same particle groups (Table 2). If we use selected ranges, i.e., the most favorable size ranges for peaks in the distributions at different mixture degrees in each event, the results of mixture particles will be a little larger than those in Table 2.

[9] The consistency of peak sizes and patterns of post- and pre-dialysis distributions of non-mixture particles in the three dust events indicates that loss of water-soluble components in the particles did not cause apparent changes in

Table 2. Geometric Mean Diameters (d_g in μm) Together With the Geometric Standard Deviations (σ_g in μm) of the Lognormal Distributions Fitting to the Tentative Number-Size Distributions of Dust Particles at Different Mixture Degrees (Mi.De.) Before (Suffixed by *b*) and After (Suffixed by *a*) the Water Dialysis and Their Differences [$\Delta d_g (= d_{gb} - d_{ga})$] for the Three Dust Events. $d_1 \sim d_2$ are Fitting Ranges in μm.[a]

Mi.De.	Event	d_{gb} (σ_g)	d_{ga} (σ_g)	Δd	$d_1 \sim d_2$
Non-mixture	K-1	2.29 (1.50)	2.18 (1.45)	0.11	1.0~4.5
	K-2	2.55 (1.41)	2.54 (1.40)	0.01	1.0~5.0
	K-3	2.07 (1.40)	2.14 (1.42)	−0.07	1.0~3.5
Mineral ≫ seasalt	K-1	2.96 (1.43)	2.79 (1.45)	0.17	1.0~5.5
	K-2	2.65 (1.37)	2.45 (1.40)	0.20	1.0~5.0
	K-3	2.95 (1.41)	2.81 (1.41)	0.14	1.0~6.0
Mineral ~ seasalt	K-1	3.15 (1.50)	2.70 (1.43)	0.45	1.0~6.0
	K-2	2.79 (1.41)	2.39 (1.39)	0.40	1.0~5.0
	K-3	3.04 (1.41)	2.76 (1.41)	0.28	1.0~6.0
Mineral ≪ seasalt	K-1	3.38 (1.41)	2.39 (1.45)	0.99	1.0~6.0
	K-2	3.16 (1.34)	2.21 (1.40)	0.95	1.0~5.5
	K-3	3.61 (1.45)	2.54 (1.40)	1.07	1.0~6.5

[a]The distributions of particles before the dialysis for K-2 and K-3 events in *Zhang et al.* [2003] were applied. The accounted particles for the distributions of the two events after the dialysis were 419 and 562, respectively. The number of accounted particles in each event was normalized to 100 in distribution calculation.

Table 3. Similar to Table 2 but for Total Detected Dust Particles in Each Event

Event	d_{gb} (σ_{gb})[a]	d_{ga} (σ_{ga})[b]	$d_{gb} - d_{ga}$	N_b / N_a[c]
K-1	3.48 (1.51)	2.66 (1.48)	0.82	388/411
K-2	2.98 (1.46)	2.50 (1.43)	0.48	442/352
K-3	3.20 (1.47)	2.76 (1.41)	0.44	647/522

[a]Fitting range: $1.0 \sim 8.5$ in μm.
[b]Fitting range: $1.0 \sim 6.5$ in μm.
[c]Numbers of detected dust particles before (N_b) and after (N_a) the dialysis, which were normalized to 100 in distribution calculation.

particle size. Based on this result, we think that, to a large extent, the sizes of residue water-insoluble parts of mixture particles obtained after the dialysis can represent the sizes of original dust particles enclosed in the mixture particles, and the identified distribution shifts of the particles before and after dialysis were mainly caused by materials that mixed into the particles in the atmosphere. As shown in Figure 1, S in most mixture particles was much less than Na and Cl in mass [*Zhang et al.*, 2003]. That means the predominant components in the removed water-soluble materials should be sea salt and others such as non-sea salt sulfate should be much less important in mass compared to sea salt, suggesting the distribution shifts were caused mainly by sea salt. Therefore, mixing with sea salt did systematically lead to the growth of particles and dust particles became larger and larger as more and more sea salt mixed into them.

[10] It could be expected from the above results that the distributions of total dust particles would have been in smaller ranges if mixing with sea salt had not occurred. We estimated shifts of the distributions of total detected dust particles toward larger range due to the mixing in each event; the results are listed in Table 3. The shifts were about 0.82, 0.48 and 0.44 μm for K-1, K-2 and K-3 events, respectively. This means dust particles arriving at southwestern Japan were averagely enlarged by about $0.4 \sim 0.8$ μm due to the combination with sea salt after leaving the Asian continent. Moreover, although we had only three datasets of dust events, it was found that the shift was proportional to the number fractions of Mineral≪Seasalt particles in total particles (Tables 1 and 3), which further supports the idea that the size distributions of dust particles were closely related to their mixture with sea salt.

[11] In light of the above results, the interaction with sea salt is a significant process in size and composition changes of dust particles in the marine atmosphere. Since the size and composition of a particle are key factors in controlling its gravitational settling, the interaction will consequently influence the sedimental flux of mineral dust to sea surface, suggesting understanding the interaction is further important for mapping the input of minerals into the ocean. Sea salt usually concentrates in low levels near sea surface. Thus, the interaction should mainly occur in the marine boundary layer. It was suggested that collisions and coagulations of dust particles and sea salt-containing particles were important in the present three events [*Zhang et al.*, 2003]. But the mechanism of the interaction is far less clear and is still an urgent task of future studies. Nevertheless, the investigation of mixture state of dust and sea salt is essential in the evaluation of dust particles in cases when they have had interaction with sea salt.

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