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Mixture of sulfate and nitrate in coastal atmospheric aerosols: individual particle studies in Qingdao (36°04'N, 120°21'E), China

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Abstract

Atmospheric aerosol particles were collected at Qingdao (36°04'N, 120°21'E) in October 1996 in order to investigate the characteristics of aerosols in coastal areas of China. Morphologies and element compositions of individual particles were analyzed using a transmission electron microscope and an energy dispersive X-ray spectrometer. Particulate sulfate and nitrate were detected with nitron and barium chloride films pre-coated on the collecting grids. The collected particles were classified into two modes according to their diameter: fine mode ($D_p < 1.0 \mu\text{m}$) and coarse mode ($D_p \geq 1.0 \mu\text{m}$). It was found that spherical particles dominated the fine mode in all urban and marine samples. Analyses of morphology and composition suggested that these particles were droplets containing ammonium sulfate. Diameters of the droplets were mainly in the range of 0.04–0.11 μm . Sulfuric acid or partially neutralized sulfate particles were not found in any samples. These results suggested that sulfuric acid was neutralized by ammonia rapidly in the gas- or aqueous-phase after it was formed through homogeneous or heterogeneous reactions, and the droplets were formed through gas-phase nucleation followed by condensation, aqueous-phase chemistry and coalescence. Particles internally mixed with sulfate and nitrate were detected in both coarse and fine modes. Element analysis indicated that most of them contained mineral elements, suggesting that the soil particles were more suitable for the internal mixture of sulfate and nitrate than other kinds of particles. In terms of number frequency, sulfate-containing particles dominated the fine mode and nitrate-containing particles dominated the coarse mode. Some particulate nitrate was attributed to the formation of soot particles. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coastal aerosols; Sulfate; Nitrate; Droplets; Individual particles

1. Introduction

Energy consumption increased rapidly in China with the rapid growth of economic activities in recent decades. Consequently, the increasing contribution of atmospheric loads of sulfur dioxide and nitrogen oxides, and

as a result, the loads of sulfate and nitrate, from this area to global climate change are anticipated. Air pollutants from natural and anthropogenic sources in China have been discussed in numerous publications and it was found that their strength of emission was growing rapidly (Zhao and Sun, 1986; Huebert et al., 1988; Kato and Akimoto, 1992; Akimoto and Narita, 1994; Zhang and Iwasaka, 1999). Some of the pollutants, such as dust particles, could be transported eastward by westerlies and cross Japan to arrive at the western Pacific regions (Iwasaka et al., 1988; Zhou et al., 1992; Parungo et al., 1994). Radiative effects of atmospheric aerosol particles

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in East Asia also have attracted much interest recently (Zhou et al., 1994; Parungo, 1997).

The comparison of dust particles collected in China and Japan indicated that not only sea salt but also sulfate and nitrate have deposited on the particles during their transport from China to Japan (Okada et al., 1990; Wu and Okada, 1994; Zhou et al., 1996; Zhang and Iwasaka, 1998). Dust particles collected over the Japan Sea were covered by crystals after dehydration and most of them were larger than $2\ \mu\text{m}$ (Zhang and Iwasaka, 1998). These results suggested that particle morphology and composition changed considerably during their transport. In order to investigate the modification of particle size and composition, aerosol particles in the inter-region of the transport from continent to ocean, e.g. coastal areas of China, should be paid more attention to. Some characteristics of aerosols in these areas were obtained through the analysis of long-term integrated samples. The main water-soluble components in aerosols collected in Qingdao areas were NH_4^+ , Ca^{2+} , Na^+ , SO_4^{2-} , NO_3^- and Cl^- (Li et al., 1995). Na^+ , Cl^- and part of SO_4^{2-} were mainly from sea salt and others were due to human activities. Particularly, a considerable amount of sulfur was emitted from coal burning in urban areas of Qingdao. Zhuang et al. (1999) analyzed the size distribution of particulate sulfate, nitrate and ammonium of aerosol particles col-

lected in Hong Kong. They reported that sulfate and ammonium were the dominant species in particles of diameter $< 1.8\ \mu\text{m}$ and nitrate was mainly in particles with a diameter of about $3.95\ \mu\text{m}$. These results were obtained by integrated samples and particle sizes were specified by the cut-off diameters of impactors. Therefore, the results were average characteristics of aerosols during sampling periods and particle diameters were estimated aerodynamic diameters.

In the consideration of the formation of particulate sulfate and nitrate, size distributions and radiative forcing of particles and their impacts on environment, knowledge of individual particles is essential. For the analysis of individual particles in coastal areas of China, we collected aerosol particles at five Qingdao areas, which are located in the coast of the Yellow Sea of China (Fig. 1), in October 1996. Particulate sulfate and nitrate in individual particles together with particle morphology, element composition and size were investigated. Particle size was determined through their images on the collecting grids. Therefore, it is the geometric size of a particle. The main purposes of this study are to characterize the aerosols in morphological and chemical ways, gain insight into the formation and source of particulate sulfate and nitrate, and contribute to the determination of the impacts that these aerosols might have on the local and remote areas.

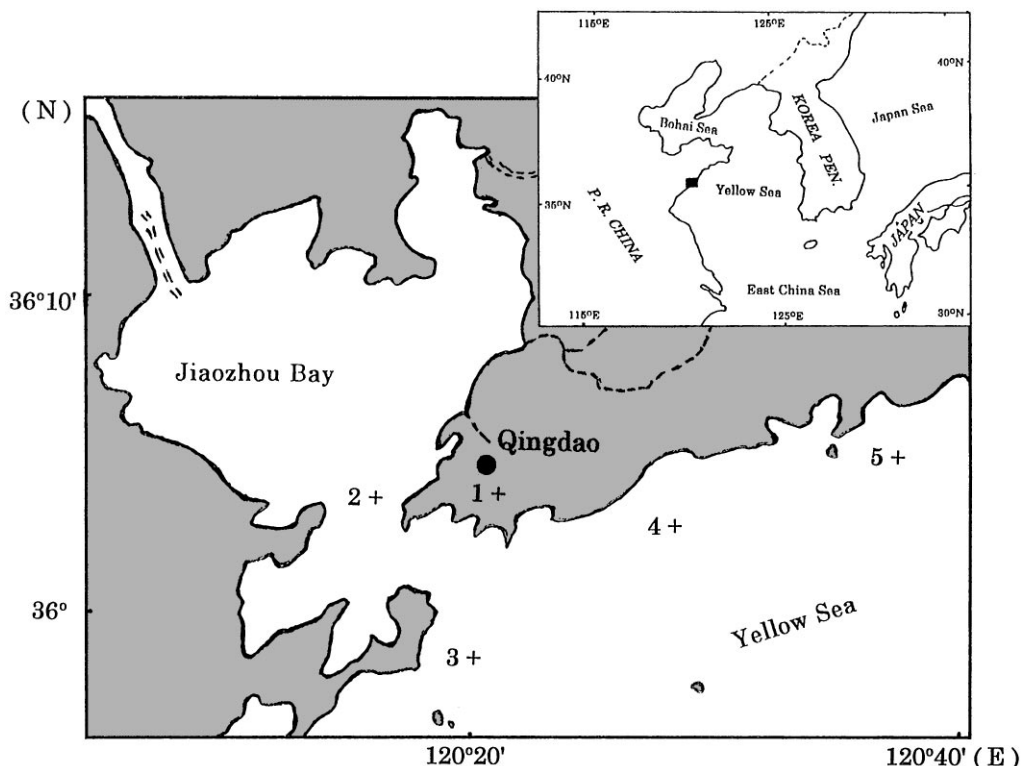


Fig. 1. Location of sampling sites.

2. Methods of observation and analysis

Atmospheric aerosol particles were collected on standard 3 mm electron microscope grids. Three groups of samples were collected. The first group, urban samples, was collected on the roof of a 20-m high building located on a small mountain in an urban area of Qingdao on October 9 (Site 1 in Fig. 1). The second and third groups, marine samples, were collected on the stack of a small ship when it was moving from Sites 2 to 3 and from Sites 4 to 5 on October 10, respectively (Fig. 1). The collecting grids were covered with Formvar film sprayed by carbon (hereafter called carbon film). In order to detect sulfate and nitrate in individual particles, some grids were coated with multiple films of nitron and barium chloride by vacuum deposition before sampling (hereafter called multiple film).

Two single-stage impactors were applied for sampling. The 50% cut-off aerodynamic diameters were 0.3 (first stage) and 0.05 μm (second stage), respectively, when the pump rate was 4.5 l min^{-1} . Air flow passed through first stage impactor firstly and then the second stage impactor. The inlet air was dried by a diffusion dryer, which could dry the air below 30% relative humidity for normal atmospheric conditions. The sampling time for every grid was 5–10 min, depending on visibility. After sampling, every grid was kept in a dry sealed plastic capsule and was brought to the laboratory for subsequent analyses. During analyses, particles were classified into two size modes: fine mode ($D_p < 1.0 \mu\text{m}$) and coarse mode ($D_p \geq 1.0 \mu\text{m}$), according to their real images on grids. As will be described in the Discussion, the diameter of a particle was determined by an empirical formula based on the method suggested by Ayers (1978), if the particle was round on film. If a particle's shape was irregular, its size was regarded as its maximum scale. It is noted that particles in fine mode were generally collected on the second stage grids and particles in coarse mode on the first stage grids.

Particles on carbon film were applied to observe particle morphologies and size distribution. Sulfuric acid and partially neutralized sulfate particles, if existed, could be identified on the basis of their distinctive morphology: a central spherical cap surrounded by one or more rings

of small satellite droplets. These satellite particles were formed by the splash of liquid droplets against a substrate during impaction (Frank and Lodge, 1967; Bigg et al., 1970). Ammonium sulfate or mostly neutralized sulfate particles existed as moist solids or aqueous droplets, and appeared as spherical caps with no impaction satellite rings (Bigg, 1980; Ferek et al., 1983). Before the analyses of particles collected on grids coated with multiple film, the grids were exposed to octanol vapor for 18 h at room temperature to promote the reactions of sulfate and/or nitrate with the multiple film. Then sulfate-containing particles could be identified by the appearance of Liesegang rings of barium sulfate, the product of the reaction of sulfate with barium chloride. Nitrate-containing particles could be identified by the appearance of bundles of needle-like crystals of nitron nitrate, 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. According to the laboratory work of Qian et al. (1991), the detection limits of multiple film for sulfate and nitrate contained in individual particles were 10^{-17} and 10^{-14} g, respectively.

Particles and reaction spots were viewed and photographed using the transmission electron microscope (JEOL-200CX) of the Electron Microscope Laboratory of Peking University. After photograph, elemental composition of some particles was detected using an energy dispersive X-ray spectrometer attached to the same electron microscope. The spectrometer we used was unable to detect the elements with atom number smaller than 11 (sodium). The counting time for every particle was 180 s. It is noted that the elemental composition and morphology of particles, along with their mixture with sulfate and nitrate, were sufficient to classify particles in this study and provided enough information to identify their possible sources.

3. Results

Sampling date, time, and weather during the observational periods are summarized in Table 1. From 8 to 10 October, the center of a high-pressure system (maximum

Table 1
Summary of sampling time and weather

Observation site	Sampling time (BST ^a)		Temp. (°C)	Pressure (hPa)	RH (%)	Wind		Visibility (km)
	Date	Period				Direction	Speed (ms^{-1})	
1	9 October, 1996	10:30–11:30	21	1018	68	N	1.5	2
2–3	10 October, 1996	9:40–12:15	22	1018	72	SW	2.8	6
4–5	10 October, 1996	14:30–16:30	23	1018	68	S	1.1	15

^aBeijing standard time (8 h prior to GMT).

pressure: 1026 hPa), followed by another similar system, passed through Qingdao areas and the weather was fine (Sakai, 1996). And the wind was very weak. No rain and other small-scale meteorological phenomena, such as fog or regional convection, were reported. Therefore, aerosol particles collected during this period were formed in local areas or emitted from local sources.

3.1. Particles on carbon film

A few particles were collected on the first stage grids although a great number of particles were collected on the second stage grids in the urban samples (Site 1). But almost no particles were found in the first stage samples in marine samples (Sites 2–5). Fig. 2a and b show electron microscope pictures of particles on carbon film collected in urban areas. In the samples on second stage grids, there were several kinds of particles in view of morphology. The major particles were those showing a patch circled by a ring, such as Particle A. Another kind of considerable particles were chains or fragments of small particles, such as Particle B. There were a few of spherical electron-condensed particles, such as Particle C. Besides were irregular electron-condensed ones. Fig. 3 shows the pictures of particles on the second stage grids of Sites 2–5. In both areas, particles like Particle A in Fig. 2b were predominant and other particles, particularly chain or fragment particles, were less than in urban areas relatively. No sulfuric acid particles or partially neutralized sulfate particles, showing spherical caps surrounded by one or more rings of smaller droplets, were found in either urban or marine samples.

Samples were kept in dry capsules and investigated in high vacuum conditions of the transmission electron microscope, which should have led to the dehydration of collected particles. Particles, like Particle A, were weakly electron-condensed. Therefore, the central patches and surrounding circles were supposed to be the residua of aerosol particles after dehydration and such particles originally were small droplets in the air. Fortunately, the residua, to a great extent, retained the chemical characteristics of original particles. Analyses of chemical elements indicated that only sulfur existed in such particles (Fig. 2c). Many investigations have suggested that particles like Particle B were soot particles and produced by biomass burning and/or traffic combustion (Weiss et al., 1992; Parungo et al., 1994; Colbeck et al., 1997). Fig. 2 also shows that there were aqueous layers on some soot particles, suggesting that they absorbed water vapor as condensation nuclei or coalesced with droplets or other water-borne particles. Spherical particles like Particle C usually emitted no detectable X-rays and also were attributed to biomass burning or traffic combustion (Parungo et al., 1994; Zhang, 1996).

In order to evaluate the dominance of different kinds of particles, number frequencies were estimated from

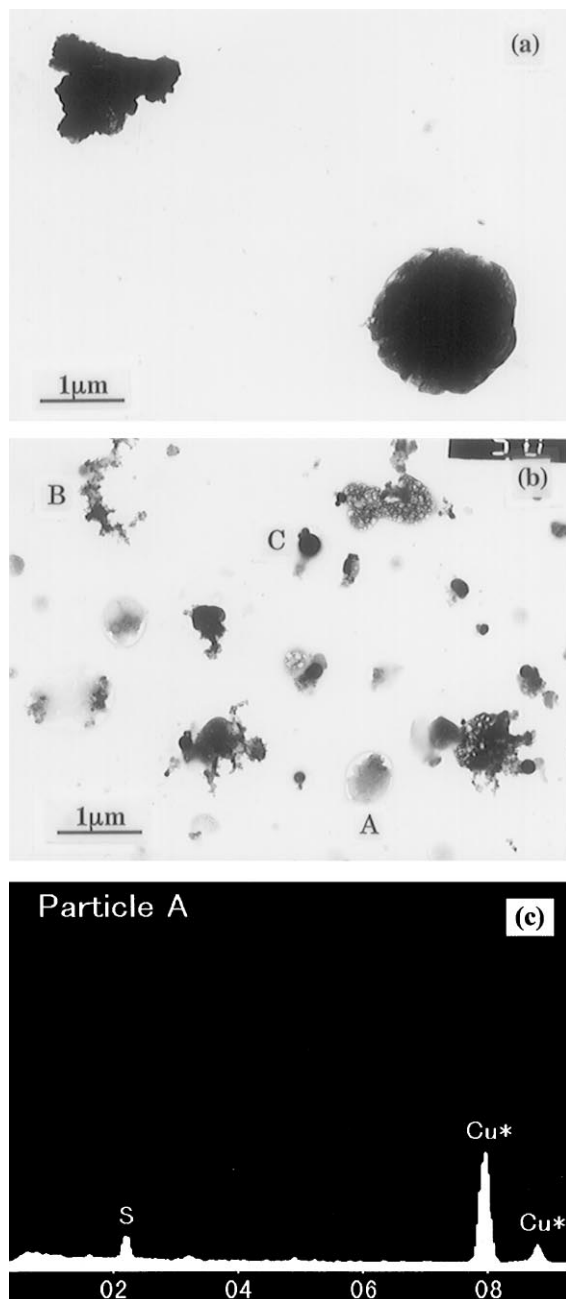


Fig. 2. Electron micrographs of aerosol particles collected on carbon film at Site 1 [(a) first stage samples; (b) second stage samples], with the X-ray spectrum of Particle A [(c)]. Cu* in the spectra, also in the following figures, is caused by the electron microscope and sampling grids.

randomly taken pictures. The results were listed in Table 2. More than half of particles were droplets in either urban and marine air and the frequency of droplets in urban area, 57.6%, was smaller than those in marine air due to the large frequency of soot particles.

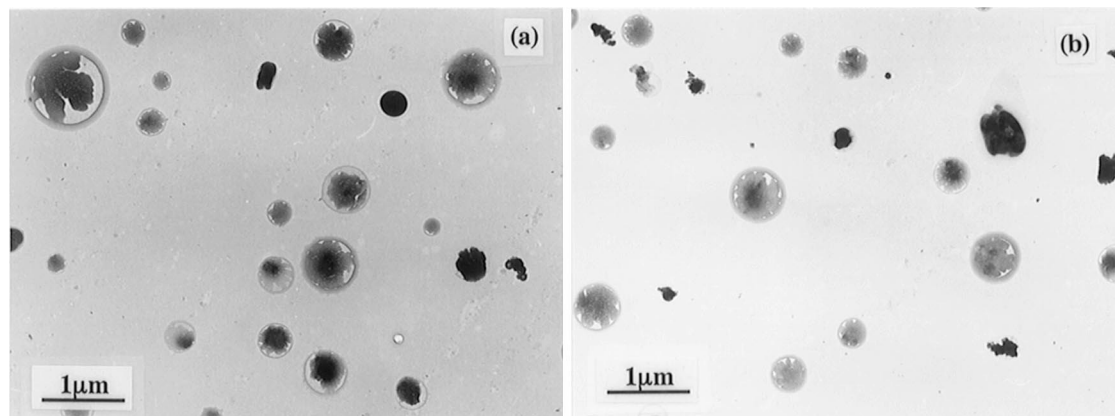


Fig. 3. Electron micrographs of aerosol particles of second stage samples on carbon film: (a) particles collected at Sites 2 and 3; (b) particles collected at Sites 4 and 5.

Table 2
Frequencies of different particles of fine mode on carbon-coated grids

	Droplet	Soot	Spherical particles	Others	Counted particles
Site 1	57.6	32.9	4.3	5.2	255
Sites 2 and 3	86.2	4.6	3.4	5.8	238
Sites 4 and 5	80.8	7.5	1.0	10.7	199

In addition, a number of cubic crystals were found in both coarse and fine modes (Fig. 4a). X-ray analysis revealed that some of them contained only calcium in the elements heavier than sodium (Fig. 4b). Previous investigations suggested such particles were composed of CaO and/or Ca(OH)₂ and emitted from construction sites in urban areas where lime was well applied (Huebert et al.,

1988; Zhang et al., 1995; Malderen et al., 1996; Zhang and Iwasaka, 1999). Besides, some cubic particles contained mainly chlorine and they were sea salt particles undoubtedly.

3.2. Particles on multiple film

Test results of sulfate-containing particles (SPs), nitrate-containing particles (NPs) and sulfate-nitrate internally mixed particles (SNPs) on multiple film are summarized in Table 3. SPs were well detected in fine mode in all samples but merely a few were detected in coarse mode in urban samples. NPs were detected mainly in coarse mode in urban samples. Fig. 5a, b and c show the reaction spots of particles of second stage samples of the three group samples, respectively. Examples of reaction spots of first stage samples of urban atmosphere were shown in Fig. 5d. Liesegang rings indicated that the

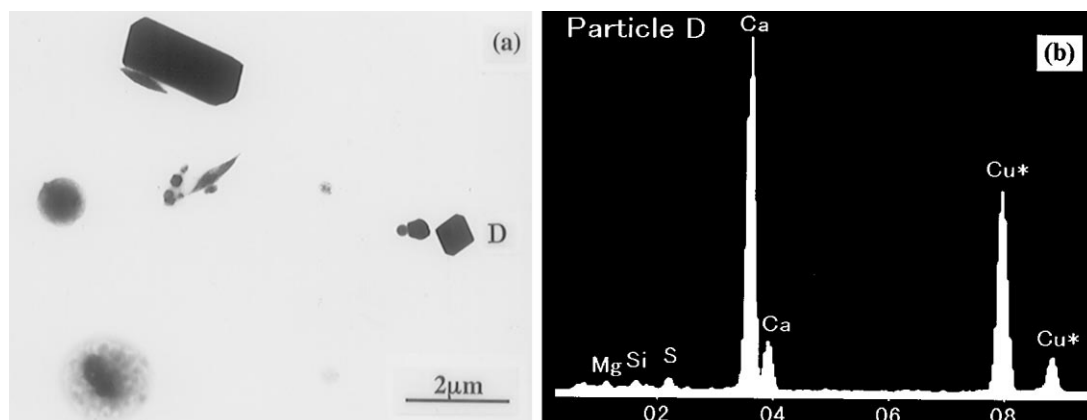


Fig. 4. Electron micrograph of aerosol particles of second stage samples collected on carbon film at Sites 2 and 3, with the X-ray spectrum of Particle D.

Table 3
Detection summary of sulfate and nitrate in different modes^a

	SP		NP		SNP	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Site 1	●	○	○	●	○	○
Sites 2 and 3	●	×	○	○	○	○
Sites 4 and 5	●	×	○	○	○	○

^a ● A great number were found. ○ A few were found. × No one was found.

particles were SPs and bundles indicated that the particles were NPs. SNPs were found in both coarse and fine modes of all samples. Their reaction spots indicated that ring products in coarse mode were ambiguous compared to needle products but those in fine mode were much clearer (Fig. 6a and b). This result possibly suggested that nitrate, other than sulfate, was predominant in the mixture of sulfate and nitrate in coarse SNPs but was not in fine ones. Table 4 illustrates the number frequencies of SPs, NPs, SNPs and other kinds of particles. NPs were much more than SPs in coarse mode but conversely in fine mode. SNPs were comparatively much less in either coarse or fine modes.

Analysis of chemical elements indicated that the detectable elements in most SPs in fine mode were sulfur, chlorine and barium (Fig. 5e). Because chlorine and barium peaks in the spectra were caused by the barium-chloride reagent for the detection of sulfate, sulfur was the only detectable element in these particles. This feature was similar to those like Particle A in Fig. 2b. Comparisons of electron microscope pictures on carbon film (Fig. 2b, 3a and b) and multiple film (Fig. 5a–c) and of the frequencies of droplet particles (Table 2) and SPs (Table 4) suggested particles like Particle A were sulfate-containing droplets. Since, no satellite structures were detected, these particles were fully neutralized. The most possible candidate of the neutralizer was ammonia emitted from the local areas because no elements heavier than sodium except sulfur were detected in those particles and ammonia was the only common alkaline gas in the atmosphere. Particles with similar morphology were observed in Japan and the North Pacific areas and suggested to be ammonium sulfate particles (Qian et al., 1992; Yamato and Tanaka, 1994). Recent observation also indicated that the mode diameters of sulfate and ammonium in Hong Kong were always in the range smaller than 1.0 μm (Zhuang et al., 1999). Therefore, the residua of the sulfate-containing droplets after dehydration should be ammonium sulfate.

X-ray spectra of NPs indicated that some of the particles contained mineral elements (Fig. 5f) and some contained no detectable elements (Particle G in Fig. 5d). The presence of mineral elements indicated that the particles

were soil particles emitted from the ground initially. Nitrate was formed on their surface due to the absorption of nitric acid and/or NO_x , or the particles collected other NPs. For the particles without detectable elements like Particle G, the methods we applied in this study, unfortunately, could not identify whether they were pure nitrate particles or organic nitrate-containing particles with no elements heavier than sodium although a lot of soot particles were detected on carbon film (Fig. 2b and 3). X-ray spectra of SNPs indicated that most of SNPs contained mineral elements as shown in Fig. 6c and d, suggesting that soil particles were more easier to become SNPs than droplet and soot particles.

3.3. Size distribution of ammonium sulfate droplets

Number-size distributions of ammonium sulfate droplets in the three group samples were estimated from their morphologies on carbon film. Because of the loss of water on particle surface, it is impossible to obtain exact particle size by the method suggested by Ayers (1978). Fortunately, the residua of particles still retained the morphology images of spherical caps created on impact. Based on the results about $(\text{NH}_4)_2\text{SO}_4$ particles obtained through laboratory experiments by Qian (1992), an empirical relationship between the diameter (d_c) and height (h) of the spherical caps of particles on carbon films was set up and it was

$$h = \begin{cases} 0.674d_c^3 - 1.625d_c^2 + 1.4344d_c, & d_c \geq 0.5 \mu\text{m}, \\ 0.2889d_c, & d_c < 0.5 \mu\text{m}, \end{cases}$$

where d_c were read directly from electron microscope pictures. Then the volumes of particles and, in turn, their geometric diameters in the air were calculated. The estimated distributions of the three group samples were shown in Fig. 7. They were log diameter-number fraction distributions. It should be noted that the vertical axis was not the usual $dN/d \log D_p$ but $dN_{\text{count}}/d \log D_p$ with N_{count} being the number of counted particles from electron microscope pictures. The distributions were tentative ones because the numbers of counted particles (also shown in Fig. 7) were not adequate to obtain complete size distributions and particles smaller than 0.05 μm should have been underestimated due to the small collecting efficiency of the impactors. As shown in Fig. 7, the droplets were mainly in the range from 0.04 to 0.11 μm and size distributions of droplets collected at different sites were similar and approximately mono-modal.

4. Discussion

4.1. Formation of ammonium sulfate droplets

Ammonium sulfate droplets (Particle A in Fig. 2b) dominated fine mode aerosols in Qingdao areas. The

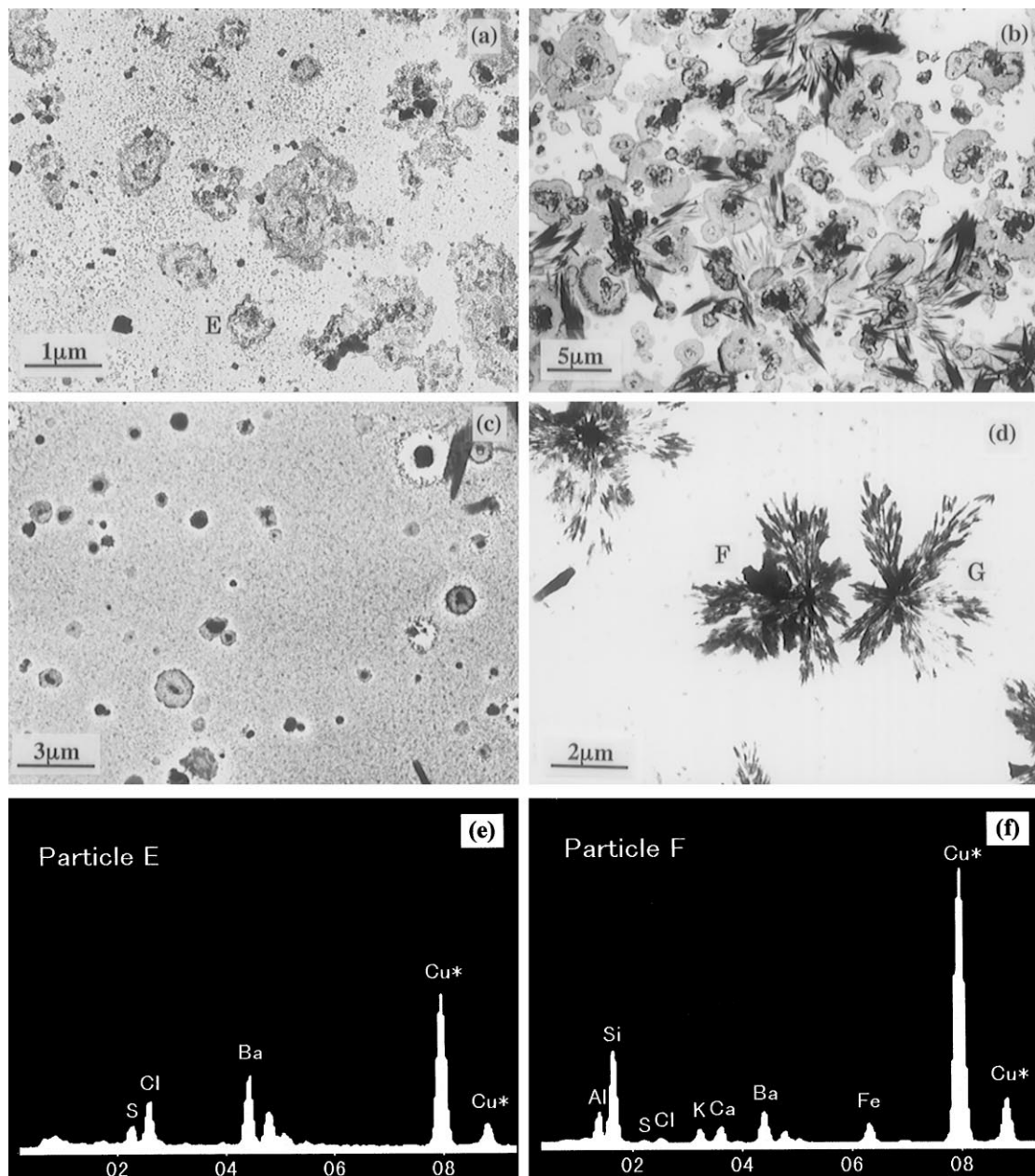


Fig. 5. Reaction spots of aerosol particles on multiple film and X-ray spectra: (a) second stage samples at Site 1; (b) second stage samples at Sites 2 and 3; (c) second stage samples at Sites 4 and 5; (d) first stage samples at Site 1; (e) X-ray spectrum of Particle E; (f) X-ray spectrum of Particle F.

presence of ammonium sulfate in droplets should be attributed either to water condensation on pre-existing ammonium sulfate particles or absorption of sulfur dioxide and ammonia on existing droplets. Because droplets were probably not formed through homogeneous nucleation in the absence of condensation nuclei (Hobbs, 1993), one possible interpretation is that the droplets found in

this study were formed initially through heterogeneous nucleation on ammonium sulfate particles or on sulfuric acid particles which were neutralized by ammonia later.

Qingdao is a coastal city with Jiaozhou Bay to its west and the Yellow Sea to its east (Fig. 1). SO_2 was always emitted from anthropogenic sources, such as industries in urban areas (Li et al., 1995). The natural source of SO_2

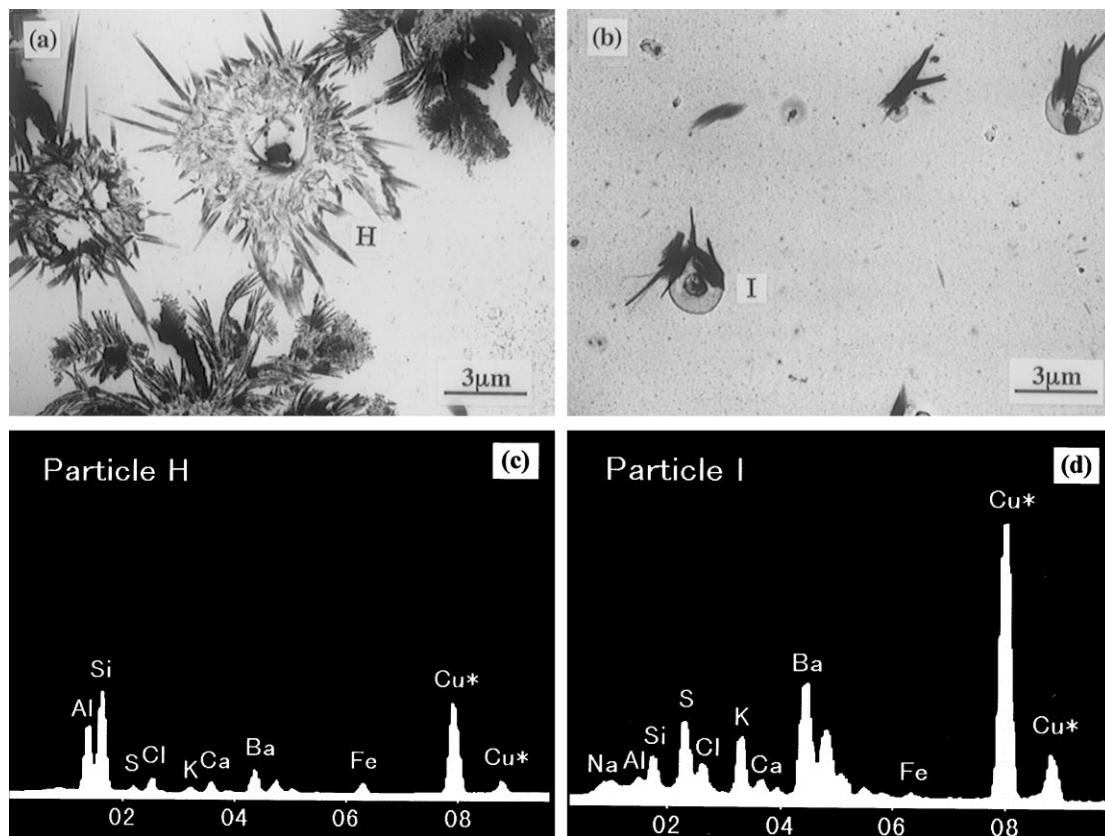


Fig. 6. Reaction spots of aerosol particles on multiple film and X-ray spectra: (a) first stage samples at Site 1; (b) second stage samples at Sites 4 and 5; (c) X-ray spectrum of Particle H; (d) X-ray spectrum of Particle I.

Table 4
Frequencies of different particles detected by multiple films

	SP	NP	SNP	Others	Counted particles
Coarse mode of Site 1	1.3	69.3	4.0	25.4	75
Fine mode of Site 1	91.4	2.4	2.8	3.4	255
Fine mode of Sites 2 and 3	95.7	3.5	0.6	0.2	680
Fine mode of Sites 4 and 5	84.4	6.6	8.8	0.2	635

was the oxidation of DMS, which was emitted from seawater (Hu et al., 1997). Due to human activities, a large amount of ammonia was emitted from urban areas. The average concentration of ammonia in Qingdao areas was about 7.6 ppb in summer (Li et al., 1995). Consequently, sulfuric acid formed by the oxidation of SO_2 would be neutralized either in gas phase or on particle surface and what the droplets contained should be ammonium sulfate.

Tentative number distributions of the droplets indicated that the droplets were mainly in the range from 0.04 to 0.11 μm . Such small particles were generally formed through gas-to-particle conversion (Seinfeld and Pandis, 1998). Number-size distributions were mostly measured by optical particle counters which determine particle sizes by particles' optical properties and the results were sensitive to particle morphology and composition. Particle sizes obtained in this study were the

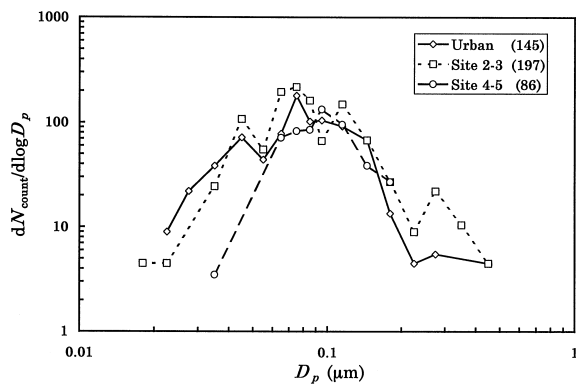


Fig. 7. Tentative size distributions of ammonium sulfate droplets collected at different sites. Numbers of counted particles for different site samples are listed in parentheses.

geometric diameters estimated from their images on the collecting grids, which could be easily applied to evaluate other properties of the particles. The estimated distribution should indicate the main characteristics of number size distributions of the ammonium sulfate droplets in the range larger than $0.05 \mu\text{m}$ although the distributions were not complete ones and more particles should be counted. With a numerical model including detailed mechanisms of nucleation, condensation and coalescence, Zhao et al. (1998) simulated the formation of new particles and the evolution of their size distributions in the marine boundary layer. In the model, new particles were formed through nucleation including sulfuric acid gas, followed by condensation and coalescence. Their results indicated that newly formed particles were mainly in the range of $0.01\text{--}0.13 \mu\text{m}$ in view of number concentration. As discussed previously, sulfuric acid was neutralized by ammonia in Qingdao areas. But the neutralization was not expected to considerably impact the sizes of particles formed through condensation and coalescence.

4.2. Mixture of sulfate and nitrate

It was found that few particles containing nitrate appeared in the droplets. Similar results were well observed in other coastal areas, such as in the United States (Hidy et al., 1975; Appel et al., 1978), Japan (Okada, 1985; Wu and Ono, 1988) and Hong Kong (Zhuang et al., 1999). Bassett and Seinfeld (1983) reported that, in the presence of liquid drops of ammonium sulfate, gaseous HNO_3 could condense on the particles to form ammonium nitrate before the $\text{NH}_3\text{--HNO}_3$ partial pressure product was exceeded. However, the formation was very sensitive to the concentrations of HNO_3 and NH_3 , the size distribution and chemical composition of particles, relative humidity and temperature. Based on the volatility of

sulfate and nitrate, a theoretical model explanation for the different distribution of sulfate and nitrate in fine particles was performed by Bassett and Seinfeld (1984). Sulfate, being essentially non-volatile, has a size distribution controlled by gas-phase diffusion and will tend to accumulate in small particles. On the contrary, nitrate, being more volatile than sulfate, will tend to evaporate from smaller particles and deposit on large particles where surface curvature effects on vapor pressure are minimal. Bassett and Seinfeld's simulation suggested that NH_4NO_3 , if formed in ammonium sulfate drops, would be mainly in the particles larger than $0.1 \mu\text{m}$. But the droplets observed in Qingdao areas were in the range of $0.04\text{--}0.11 \mu\text{m}$ (Fig. 7).

The internal mixture of sulfate and nitrate were detected mainly on the surface of soil particles (Fig. 6a and b). In moist surface of soil particles, heterogeneous formation of sulfate and nitrate is effective (Warneck, 1988; Seinfeld and Pandis, 1998). S(IV) could be oxidized by oxygen with the presence of catalysts of iron and manganese to form S(VI) (Hegg and Hobbs, 1978), and by ozone and hydrogen peroxide (Penkett, 1972; Hoffmann and Edwards, 1975). Nitrate could be formed through heterogeneous reactions including nitrogen oxides on the surface of soil particles besides the absorption of nitric acid (Mamane and Gottlieb, 1989; Zhang et al., 1994). The average concentrations of gaseous sulfuric dioxide, nitrogen dioxide, nitric acid and ozone in Qingdao areas in summer were about 2.9, 2.0, 0.2 and 50.9 ppb , respectively (Li et al., 1995). Although we did not measure the concentration of hydrogen peroxide in the present observation, several ppb could be anticipated since concentrations of such level were observed in coastal areas of Los Angeles, US (Sakugawa and Kaplan, 1989) and Nagoya, Japan (Watanabe and Tanaka, 1995). Therefore, sulfate and nitrate would be formed on soil particles. Because of their large capacity of absorbing acidic materials, alkalinity soil particles would suppress the possibility that sulfuric acid molecules acquired cations from nitrate and the depletion of nitrate due to the absorption of acidic materials. As a result, sulfate and nitrate were preferably formed on the surface of soil particles. The phenomenon which nitrate was predominant in the mixture of sulfate and nitrate in coarse SNPs was possibly due to the different volatilities of sulfuric acid and nitric acid. Sulfuric acid condenses according to available surface area, which maximizes in the fine mode, and does not re-evaporate, whereas nitrate has a vapor phase available to nitric acid. Thus, nitrate can sublime into whatever size of particles has the greatest alkalinity. Often it is either mineral particles or sea salt (both $> 1 \mu\text{m}$) that have the greatest alkalinity and therefore the nitrate goes to those particles.

Pure ammonium nitrate particles seemed impossible to be formed through gas-to-particle conversion in Qingdao areas. If ammonium nitrate is presented in pure

aerosol phase, the equilibrium mass concentration of NH_3 plus HNO_3 in gas phase at 20°C temperature and 64% relative humidity is about $11.0 \mu\text{g m}^{-3}$ and increases rapidly with temperature increase (Stelson et al., 1979). But in Qingdao areas, the average concentrations of NH_3 and HNO_3 were 5.3 and $0.33 \mu\text{g m}^{-3}$ in summer time and their sum was merely $5.63 \mu\text{g m}^{-3}$ (Li et al., 1995), much smaller than the level for the equilibrium of the existence of pure ammonium nitrate particles.

5. Conclusions

Characteristics of individual aerosol particles collected at Qingdao, a coastal city of China, were investigated. Morphologies of particles were obtained from their electron-microscopic images on carbon film. Sulfate and nitrate were detected using nitron-barium chloride film and elements were detected using an X-ray spectrometer.

Sulfate mainly existed as ammonium sulfate in droplets and these droplets dominated fine mode of particles either in the urban and marine air. They were mainly in the range of $0.04\text{--}0.11 \mu\text{m}$ and formed through heterogeneous nucleation on ammonium sulfate particles followed by condensation, aqueous-phase chemistry and coalescence. Nitrate was formed mainly on soil particles and soot particles in coarse mode and few nitrate-containing particles existed in fine mode. Compared to soot particles and droplets, soil particles were more suitable to form internally mixed particles by sulfate–nitrate due to their large capacity of bearing acidic materials. In the mixture on coarse mode particles, nitrate, rather than sulfate, was predominant. But on the particles in fine mode, it was not.

The predominant aerosol particles and their composition in Qingdao areas were determined through individual particle analysis in this study. There might be large uncertainties in the size distributions estimated from particle morphology, and the empirical formula should be evaluated further. However, if the results could be calibrated by those measured through optical particle counters and size segregated impactors, they would be much more valuable not only for the study of morphology and composition modification of aerosols, but also for climate models in which aerosol radiative forcing is included.

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