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Tests for Individual Sulfate–Containing Particles in Urban Atmosphere in Beijing①

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ABSTRACT

Thin film methods and *X* ray energy dispersive technique were applied to analyze sulfate–containing particles in Beijing in order to examine their features and sources. Atmospheric aerosol particles were collected on electron microscope meshes according to two size ranges: coarse particles ($r > 05\mu m$) and fine particles ($0.5\mu m > r > 0.1\mu m$) by using a two–stage impactor. It was found that more than seventy percent of the fine particles and about twenty percent of the coarse particles were sulfate–containing particles. These particles were formed mainly through heterogeneous nucleation. The element composition analyses revealed that the atmospheric aerosol particles in Beijing were dominated by crustal particles and construction dust.

Key words: Individual sulfate–containing particles, Thin film method, Morphological analysis, *X* ray energy dispersive analysis

I. INTRODUCTION

Sulfate–containing particles are an important part of the atmospheric aerosol (Junge and Manson, 1961; Appel, 1978; Okada, 1985). They are believed to be formed either through gas–to–particle conversion processes, homogeneous nucleation, or through the oxidation in the aqueous phase of aerosol particles, heterogeneous nucleation. Sulfates in atmospheric aerosol are usually examined by applying various methods to a bulk sample in which the identity of individual particles is lost and the results may not give all the information required to assess their environmental effects. Knowledge of the size distribution, chemical composition and generation mechanisms of individual sulfate–containing particles is essential to clarify their origination and transformation processes in the atmosphere.

A thin film method for chemical analysis of individual particles has been developed by Bigg et al.(1974). For sulfate–containing particles, they used barium chloride film and the particles could be identified by the appearance of Liesegang rings, which were composed of insoluble barium sulfate. This method was improved and perfected by following works(Ayers, 1977, 1978; Ono et al., 1981) and was used successfully to detect sulfate particles in ambient

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atmosphere (Mamane et al., 1978; Ono et al., 1983).

Recent studies showed that atmospheric aerosol particles originated from the East Asian continent were found over the North Pacific Ocean(Iwasaka et al., 1988; Yamato and Tanaka, 1994). However, few convincing evidences of such transport have been obtained so far. A main reason is that the knowledge of individual particles in the atmosphere of the East Asian continent is still very poor and it is hard to compare the particles found over the North Pacific Ocean with the particles emitted from the East Asia continent. The purpose of this paper is to report the features of sulfate–containing particles collected in Beijing, the capital of China, and give a general concept of such particles in urban atmosphere in the northern China. The thin film tests including morphological analyses and chemical tests were carried out in September 1994 and the particles were examined by using the transmission electron microscope and X ray dispersive analyzer of the Electron Microscope Laboratory of Peking University.

II. METHOD

Atmospheric aerosol particles were collected on the top of Physics Building of Peking University, which is about 15 m high above the ground, in the morning on September 25 and 26, 1994, when the weather was clear, the temperature was about 18oC, the wind direction was NNE, the wind speed was 2–4 ms–1, the relative humidity was about 35 percentage and the visibility was about 15 km(there was a light haze). The aerosol particles were impacted onto electron microscope meshes by using a two–stage impactor in order to fractionate them into two size ranges: coarse particles ($r > 0.5\mu$m) and fine particles ($0.5\mu m \geqslant r > 0.1\mu$m). The sampling time for each sample was 12 min and the air was drawn by an electric pump at a rate of 1.2 liters per minute.

The meshes were prepared with a formvar membrane and strengthened with thin films of vacuum–evaporated carbon. Some of them were then coated with the thin films of barium chloride, the chemical reagent for sulfate radicals, through vacuum deposition. The thickness *of the reagent film was 3–5 nm. After sampling, the specimen of containing barium chloride* films and particles were exposed to octanol vapor for 18 hours at room temperature to promote the reactions of sulfate with the chemical reagent. Then they were analyzed and photographed by the transmission electron microscope. Sulfate–containing particles could be identified by the appearance of Liesegang rings on the films. The specimen which did not contain chemical reagent was applied for morphological analyses to examine the morphologies of the particles by using the same electron microscope. Pure sulfuric acid particles could be identified by the distinctive morphology: a central disc surrounded by one or more rings of smaller droplets on carbon films(Waller et al., 1963; Frank and Lodge, 1967). Details of the experimental procedures were described in Ono et al. (1981).

In order to specify the elemental composition of the collected particles, X ray energy dispersive analyses were carried out for some particles.

III. RESULTS AND DISCUSSION

The morphological analyses of the particles on carbon film indicated clearly that the collected particles could be classified mainly into three types according to their morphologies. Examples of coarse and fine particles were shown in Fig.1. Type I particles had irregular shapes and Type II particles had cubic crystal shapes. Frank et al.(1972) suggested that particles showing crystal cube were sea salt particles. But Type II particles found in the present tests were impossible to be sea salt particles because the synoptic meteorological system was

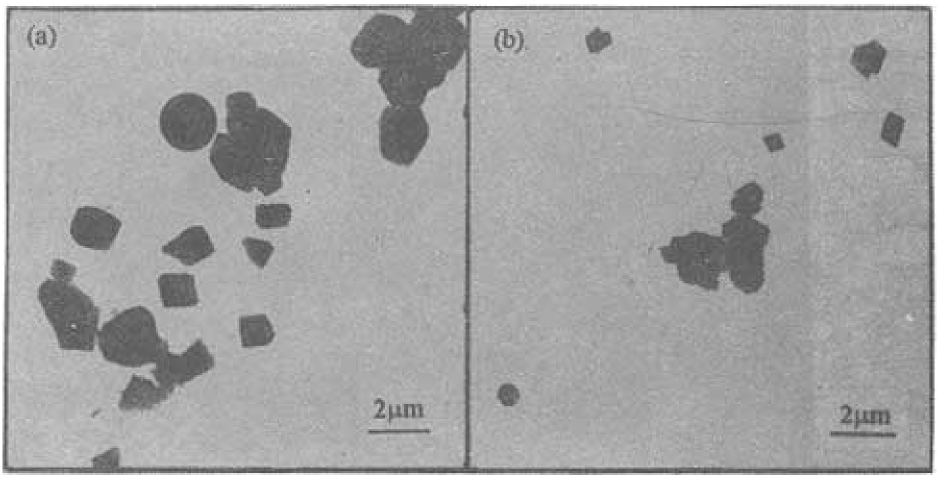

Fig. 1. Morphologies of coarse(a) and fine(b) particles on carbon film.

not suitable for particles to arrive in Beijing from sea during the two sampling days. The third type particle, referred to as Type III particle, in the figure was a disc particle found in coarse particles. The concentration of such particles was relatively small. Previous studies suggested that such particles were sodium sulfate(Frank and Lodge, 1967) or ammonium sulfate (Okada, 1985). The elemental composition of such particles indicated that they were not pure sulfate particles. This will be discussed later.

Fig.2 shows the typical appearance of the coarse and fine particles on barium chloride films after the exposure to octanol vapor. Obviously, there were many coarse and fine sulfate–containing particles. It is not strange because sulfate particles have been well found in urban atmosphere by many investigators (Kadowaki, 1977; Brosset, 1978; Stevens et al., 1978; Yang and Wang, 1994). The reaction spots on the film were counted and it was found that the percentage of sulfate–containing particles in fine particles, which was > 70, was much larger than that in coarse particles, which was about 20. Such features may be due to the distribution of the particles. The particle distributions on the two stage meshes of the present observation clearly showed that the number concentration of fine particles was much larger than that of coarse particles. Whitby and Sverdrup(1980) also suggested that atmospheric aerosol particles in a typical urban model aerosol accumulated mainly in the range from 0.05 to 1.0μm of diameter according to the surface distribution. As will be discussed, the sulfate–containing particles were mainly formed through heterogeneous nucleations on the surface of the primary particles. Therefore, fine particles were more effective to form sulfate–containing particles than coarse particles. Further, the life time of fine particles in the atmosphere is longer than that of coarse particles. The conversion reactions from sulfur dioxide to sulfate on the surface of fine particles were more efficient than that on the surface of coarse particles.

Another interesting feature of the sulfate–containing particles shown in Fig.2 is that there were clear residuals on either fine particles and coarse particles after the reactions. Generally, there are two main routes of sulfate particle formation in the atmosphere. One is homogeneous nucleation and the other is heterogeneous nucleation. Particles formed by homogeneous nucleation ought to be in the submicrometer size range and are pure sulfuric acid or sulfate particles. However, pure sulfuric acid particles, the particles showing a central disc surrounded by one or more rings of small droplets, were not found through morphological analyses, and the barium chloride film analyses indicated that there were few pure sulfate

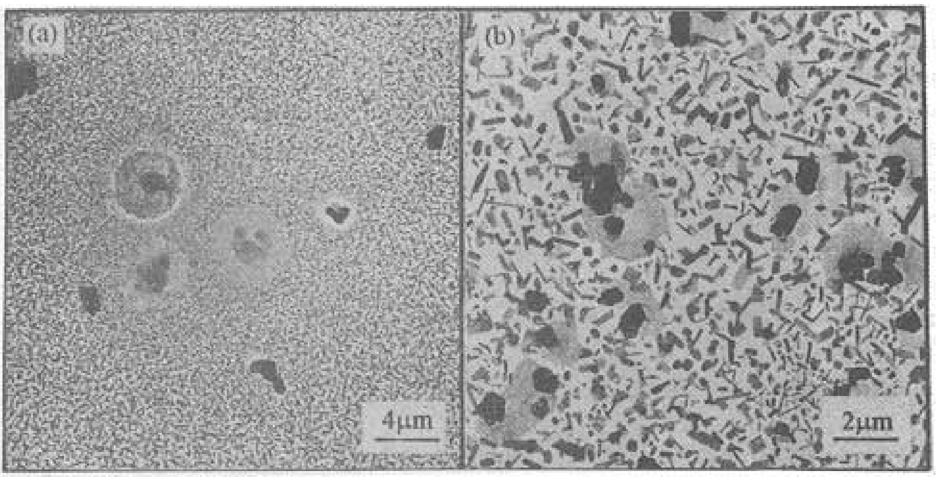

Fig. 2. Electron micrograph of coarse(a) and fine(b) particles on the barium chloride thin film.

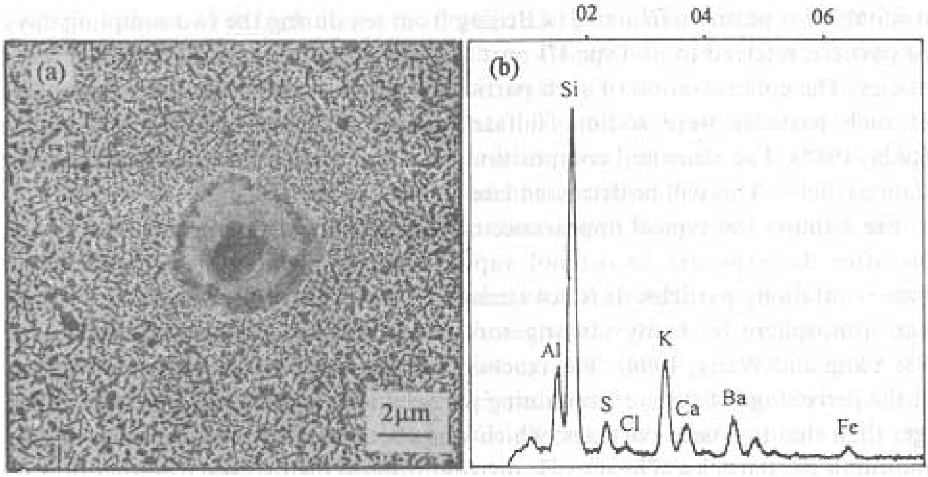

Fig. 3. A Type I sulfate–containing particle on barium chloride film (a)and its X ray spectrum (b).

particles, on which there were no residuals after the reaction. These results suggested that sulfate–containing particles formed through homogeneous nucleation were not the main part of sulfate in Beijing. A possible reason is that Beijing is a dry(average relative humidity is about 35%) and serious polluted area. During the two days of the tests, there was a light haze and the concentration of primary aerosol particles was very high. Before the ambience became suitable for homogeneous conversion to form sulfate, the oxidation of S(IV) to sulfate *probably occurred on the surface of the primary particles. Previous studies also showed the* oxidation rate of sulfur dioxide in polluted urban atmosphere was larger than that in clean air by 100 factors (Roberts and Friedlander, 1975). Furthermore, even though there were pure sulfate particles formed through homogeneous nucleation, they easily coagulated with the primary particles and their life time must be very short. Thus, homogeneous nucleation for the formation of sulfate particles in Beijing was probably unimportant compared with heterogeneous nucleation. The mechanisms of S(IV) to sulfate on the aqueous surface of particles have been well described by McArdle and Hoffmann (1983), Martin(1984) and Hoffmann (1986). But the fraction of the two nucleation quantities is much difficult to be determined.

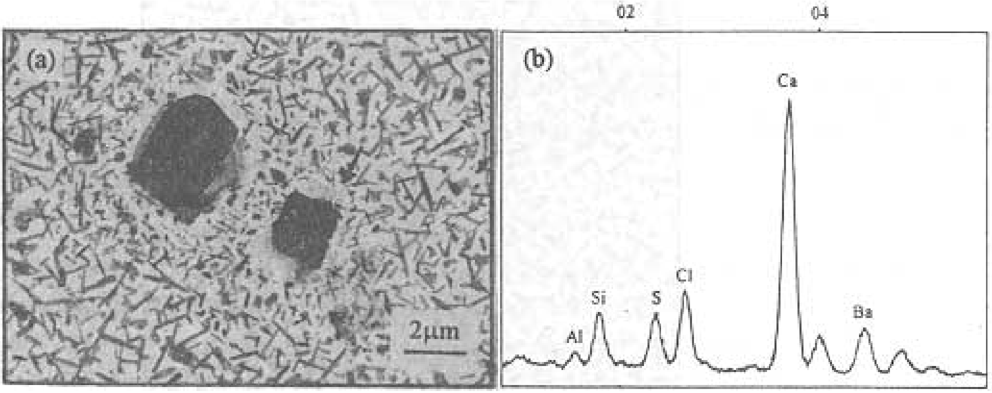

Fig. 4. Type II sulfate–containing particles on barium chloride film (a) and the *X* ray spectrum of one of them (marked by an arrow) (b).

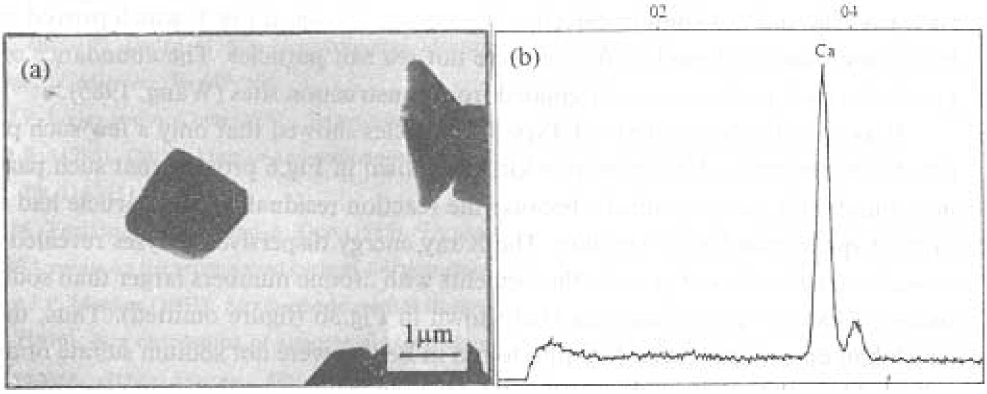

Fig. 5. A Type II particle on carbon film (a) and its X ray spectrum (b).

X–ray energy dispersive analyses were carried out to specify the composition of the particles. Fig.3 shows one of the Type I sulfate–containing particle reacting with the barium chloride film and its X ray dispersive spectrum. It should be noted that light elements with atomic number less than sodium were unable to be detected by the X ray analyzer we used. The spectrum shows the existence of Al, Si, S, Cl, K, Ca, Ba and Fe. The peaks of Cu were omitted here because the electron microscope mesh was made of copper. Considering the reaction reagent was barium chloride, Al, Si, S, K, Ca and Fe were the major elements found in the particle. These elements are crustal elements except S, suggesting that such particles were crustal dust particles.

The element composition of Type II particles was much different from that of Type I particles. An example of the Type II particles reacting with barium chloride film and the X ray spectrum of one particle are shown in Fig.4. The chemical reagent was barium chloride. Therefore, the particle contained Al, Si, S and Ca. To surprise us was that the particle was abundant in Ca. Since the reagent film contained barium chloride and the *X* ray dispersive analysis was not effective enough for the detection of sodium, it was unclear whether such particles contained sodium chloride although the spectrum showed the existence of chlorine.

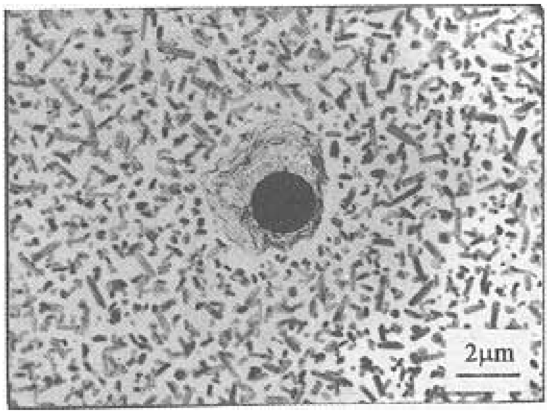

Fig. 6. A sulfate–containing particle of Type III on barium chloride film.

But the spectrum of Type II particles on carbon films (without any reagent) revealed that such particles did not contain chlorine. A case was shown in Fig.5, which proved that the cubic crystal particles found in Beijing were not sea salt particles. The abundance of Ca is the proof that such particles were originated from construction sites (Wang, 1985).

Barium chloride film tests of Type III particles showed that only a few such particles reacted with the films. A reaction particle was shown in Fig.6 proving that such particles were not abundant in sulfate radicals because the reaction residuals of the particle had almost the same shape as that before reaction. The X ray energy dispersive analyses revealed that some of such particles did not contain the elements with atomic numbers larger than sodium except sulfur or had the composition as that shown in Fig.3b (figure omitted). Thus, the particles which had disc shapes on carbon film found in Beijing were not sodium sulfate or ammonium sulfate. More than that, such particles did not evaporate under the strong electron microscope beam, suggesting that they were not hygroscopic particles. The original chemical composition and source of such particles are still unclear.

The results presented here were obtained in Beijing when the air was relatively dry and there was a light haze. Results during other weather events, such as fog, rain or dust storms, are probably much different. They will be discussed in other papers.

IV. CONCLUSION

Sampling and analyses of individual particles were performed to investigate the features of individual sulfate–containing particles in urban atmosphere in Beijing. Morphological analyses showed that the particles in this area could be classified mainly into three types: irregular shapes, cubic crystals and disc shapes. Chemical tests of these particles showed that more than 70 percent of the fine particles and about 20 percent of the coarse particles were sulfate–containing particles. These sulfate–containing particles were formed mainly through heterogeneous nucleation.

X ray energy dispersive analyses were carried out to determine the elemental composition of the aerosol particles. It was found that particles of cubic crystals were abundant in calcium, proving that they were originated from construction sites. Particles having irregular shapes

were crustal dust particles because they were mainly composed of crustal elements. But the original composition and sources of disc particles were still unknown.

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