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ANTHROPOGENIC CALCIUM PARTICLES OBSERVED IN BEIJING AND QINGDAO, CHINA

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Abstract. Analysis of individual particles collected at Beijing in northern China revealed that particles abundant in calcium (Ca) always constituted a large fraction of mineral particles in the urban atmosphere. The particles were characterized by cubic morphologies. The major mineral element in the particles was Ca and few or no other mineral elements were detected. A large number of the particles were in the range of diameter <1 μm, where common natural mineral particles were rarely detected. The contribution of the Ca particles to the volume of total mineral particles greatly exceeded that of other mineral particles during non-dust-storm periods and was comparable to that during dust-storm periods. Reagent film tests showed that particulate sulfate and nitrate formation on the Ca particles was similar to that on common mineral particles. These results indicate that a large portion of Ca in the atmospheric particulate matter in Beijing was from anthropogenic sources rather than from natural sources, and the anthropogenic Ca particles acted as a significant medium for the formation of sulfate and nitrate. Similar particles were also detected at Qingdao, a coastal city in northern China. Data of a dust storm event showed that Ca-abundant particles from East China arrived there and moved out of the continent, similarly to Asian dust storm particles, suggesting possible contributions of anthropogenic Ca even in Asian dust storm samples in the downstream areas. Therefore, Ca may not be a good indicator of Asian dust from natural sources. However, the Ca particles, due to their unique shapes and elemental compositions, may provide an indicator for the atmospheric dispersion of anthropogenic particulate matters in East Asia.

Keywords: anthropogenic Ca, dust storm, East Asia, mineral particles

1. Introduction

The output of mineral particles from the Asian continent has been attracting special attention because of its influences on geochemical mass cycles (Duce *et al.*, 1980; Iwasaka *et al.*, 1983, 1988; Uematsu *et al.*, 1983; Arimoto *et al.*, 1985), marine biology (Fung *et al.*, 2000; Bishop *et al.*, 2002), and climate change (Sokolik and Toon, 1996; Tegen *et al.*, 1996; Sokolik *et al.*, 2001). In order to evaluate these influences, information on particle composition, morphology and size distribution over time and space is required (Langner and Rodhe, 1991; Sokolik and Toon,

1999). Characteristics of dust particles were usually obtained through the analysis of integrated filter samples (Zhang *et al.*, 1993; Gao *et al.*, 1997; Kim and Park, 2001), and calcium was frequently utilized as an indicator and an essential index of Asian dust (Nishikawa *et al.*, 1991; Mori *et al.*, 1998). This was naturally acceptable since the main water-soluble mineral component in dust particles is calcium and the arrival of Asian dust certainly leads to the increase of Ca concentrations in the atmosphere.

Recent measurements of Asian dust have revealed that the ratio of water-soluble non-seasalt calcium to total calcium increased with the distance between dust storms and their source areas (Mori *et al.*, 2001). The ratio was about 0.05 at the source areas of northwestern China, while it was 0.83 at the Sea of Japan. If a significant amount of mineral Ca became water-soluble during dispersion from the continent to Japanese islands, similar levels of sulfate and nitrate should have been formed simultaneously. The fact is, however, that mole concentrations of calcium cations were much larger than those of sulfate and nitrate around the Japanese islands in many dust cases (Mori *et al.*, 2001). Therefore, it seemed that water-soluble calcium was added into dust plumes during the long-range dispersion of dust. This means there were probably other sources of calcium besides natural dust. However, bulk filter samples are unsuitable for differentiating particles and not good for investigating variations occurring on particles in the atmosphere because the results obtained with such samples are the average of total collected particulate matter during sampling periods. Consequently, such analyses cannot afford much insight into particle category and origins.

To supplement the information, single particle analysis using electron microscopes is an effective measure. This analysis gives information on the sizes of individual particles, their morphology and even composition, and thereby particle categories and sources can be identified accurately (Okada *et al.*, 1990; Yamato and Tanaka, 1994; McInnes *et al.*, 1997). Characteristics of individual Asian dust-storm particles have been reported in many publications. The composition of Asian dust particles is similar to that of surface soil at their source areas. After leaving the continent, the particles meet marine air and are modified rapidly (Okada *et al.*, 1990; Fan *et al.*, 1996; Zhou*et al.*, 1996; Zhang and Iwasaka, 2001). In a study of Ca-containing particles around the Japanese islands, Zhou *et al.* (1996) reported a considerable number of Ca-rich mineral particles that apparently had a different elemental composition from usual mineral particles in the samples collected over southwestern Japan when dust storms appeared. So far the sources of the particles have not been identified and there is no further information about their contribution to total particulate calcium in the atmosphere.

To investigate primarily the source and characteristics of calcium in atmospheric particles in East Asia, in this article we summarize the results of the analysis of individual mineral particles which were collected in the urban atmosphere of Beijing and Qingdao during non-dust-storm and dust-storm periods in the past several years, report the finding of possible anthropogenic origins of calcium besides natural

sources there, and discuss the potential importance of anthropogenic calcium in the Asian continent.

2. Particle Collection and Analysis

Particle collection at Beijing was conducted during 1994–1996. At Qingdao, the analyzed particles were collected in October 1996 and spring 2002. Figure 1 shows the location of the two cities. Site information, sampling periods, relevant weather conditions, and mesh films applied at the sites are listed in Table I.

At Beijing, particles were collected onto electron microscope copper meshes (Maxtaform H7) using two single-stage impactors. The jet diameter of the first impactor was 1 mm and that of the second one was 0.5 mm. The air pumping rate was 4.5 l min^{-1} and the airflow passed through the first impactor and then the second one. The 50% cut-off aerodynamic diameters of the impactors were 0.3 μm and 0.05 μm, respectively, if the density of particles was 2.3 g cm^{-3}. The collection time of each sample during non-dust-storm periods was 5–10 minutes and that during dust-storm periods was 1.5–2 min. The meshes were covered with carbon-sprayed Formvar film. In order to detect sulfate and nitrate in individual

Figure 1. Location of Beijing (39°58′N, 116°19′E) and Qingdao (30°06′N, 120°27′E).

TABLE I

Summary of sampling site and date, weather and visibility when particles were collected, and films applied for particle collection and analysis

Sampling site	Sampling date	Weather	Visibility (km)	Films*
Beijing	May 6, 1994	Haze	~8	C, M, N
(39°58′N, 116°19′E)	Sept. 25, 1994	Clear	~15	C, M
	Sept. 26, 1994	Clear	~10	C, M
	Sept. 27, 1994	Clear	~15	C, M
	Dec. 16, 1994	Clear	~20	C, M
	Dec. 17, 1994	Haze	~5	C, M
	Dec. 18, 1994	Clear	~10	C, M
	Mar. 11, 1995	Dust	~2	C, Nitron, M
	Apr. 5, 1995	Dust	~1.5	C, Nitron
	Apr. 6, 1995	Dust	~1	C, M
	Apr. 24, 1995	Dust	~5	C, Nitron, $BaCl_2$, M
	May 12, 1995	Cloud	~10	C, M, $NaB(C_6H_5)_4$
	May 7, 1996	Dust	~6	C, M
Qingdao	Oct. 9, 1996	Haze	~2	C, M, N
(30°06′N, 120°27′E)	Oct. 10, 1996	Clear	~15	C, M, N
	Feb. 19, 2002	Clear	~15	C, M, Pt**
	Mar. 20, 2002	Fog	~5	C, M, Pt
	Mar. 21, 2002	Dust	~4	C, M, Pt

*Film coating: C-Carbon, N-nitron, M-Multiple films of nitron and $BaCl_2$.
**Pt-platinum grid for SEM-EDX analysis.

particles, some meshes were coated with barium chloride and/or nitron by vacuum vapor deposition before particle collection. After particle collection, the meshes were preserved in grid cases and the cases were preserved in plastic bags together with paper-packaged silica gel. Morphologies of individual particles were viewed and photographed using the JEM-200CX transmission electron microscope of the Electron Microscopy Laboratory of Peking University. Elements with atom number 11 (Na) or larger in individual particles were detected using the energy dispersive X-ray spectrometer attached to the same electron microscope. Before analyzing the particles on meshes covered with reagent films, the meshes were exposed to octanol vapor in a chamber at room temperature for 18 hours to promote the reactions of sulfate and/or nitrate with the reagents. Sulfate and nitrate in individual particles were identified by the appearance of Liesegang rings which were the products of sulfate-barium chloride reactions, and needle-like bundles which were the products of nitrate-nitron reactions, respectively. According to the laboratory study of Qian *et al*. (1991), the detection limits of the reagent film for sulfate and nitrate contained in individual particles are 10^{-17} g and 10^{-14} g, respectively.

At Qingdao, the samples in October 1996 were collected and analyzed using the same equipment and instruments used in the collection and analysis of particles at Beijing. The samples in spring 2002 were collected and analyzed using different equipment. The impactor was a single-stage one. Its jet diameter was 1 mm and the flow rate of inlet air was 5 l min^{-1}. Assuming particle density is 2.3 g cm^{-3}, the 50% cutoff diameter of the impactor is about 0.25 μm. The collection time of each sample was 5 minutes in 1996 and 2 minutes in 2002. After collection, each grid was kept in a plastic capsule, which, in turn, was sealed in plastic bags together with paper-packaged silica gel. Besides copper meshes with and without reagent films, Pt grids were also utilized for particle collection. Particles on the grids were investigated and photographed using the Hitachi S-3000N scanning electron microscope of the Solar Terrestrial Environment Laboratory of Nagoya University for the observation of particle morphology and size. After particles were photographed, their elemental composition was determined using the Horiba EMAX-500 X-ray spectrometer attached to the SEM. The procedures for analyzing particles on meshes were the same as those for particles collected in Beijing, except that the electron microscope used was the Hitachi H-9 transmission electron microscope of the Hydrospheric-Atmospheric Research Center of Nagoya University.

In terms of elemental composition, the major components of mineral particles are silicon (Si), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), or iron (Fe). Particles in which mineral elements were not a major component and that did not show clear electron-opaque features will not be described and discussed in this study.

3. Results from Beijing Samples

3.1. Ca PARTICLES AND THEIR DISTRIBUTION

During non-dust-storm periods, mineral particles similar to surface soil were frequently detected. Such particles had irregular shapes and their diameters were usually larger than 1 μm. The major components of the particle were mineral elements such as Si, Al, Ca, Mg, and Fe. Besides such particles, another kind of mineral particle was frequently detected. These had cubic or polygonal shapes and their size range was from 0.1 μm to several micrometers. Ca was the overwhelming mineral element in the particles. Other mineral elements were much less evident or not detectable. The typical morphology and elemental composition of the particles are illustrated in Figure 2. For comparison, a typical soil particle and its elemental composition is also shown in the figure. Apparently, the cubic particles were different from soil particles. During dust-storm periods, particles similar to the cubic mineral particles were also frequently detected (Zhang and Iwasaka, 1999). They had the same morphology, size range and mineral composition as those of non-dust-storm periods. For convenience in the following description, cubic particles

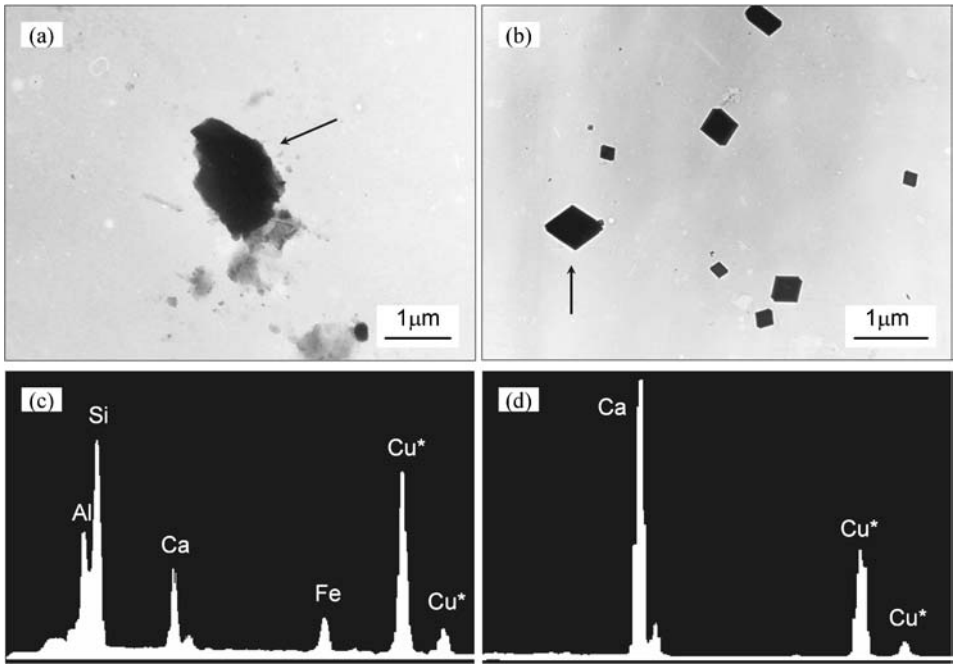

Figure 2. (a) and (b): Examples of electron microscope photographs of mineral particles collected at Beijing on carbon film during non-dust-storm periods; (c) and (d): X-ray spectra of the particles marked by arrows in (a) and (b), respectively. The particles were collected on May 12, 1995. Cu in the spectra was caused by the sampling mesh frames.

abundant in Ca like those in Figure 2b are described as "Ca particles" and other mineral particles like those in Figure 2a are described as "usual mineral particles".

The differences of particle morphology, size range and mineral composition between the Ca particles and usual mineral particles indicate that their sources were different. This was also supported by bulk sample analyses. The concentrations of calcium and aluminum in the particulate matter in the urban atmosphere in Beijing from 1991 to 1993 were not correlated with each other (R. Arimoto, New Mexico State University, Carlsbad, personal communication, 1997), suggesting that calcium had different sources from aluminum. If one supposes that aluminum was mainly from surface soil, there must be other sources of calcium besides surface soil in the urban atmosphere. The investigation of individual dust particles in the source areas in northwestern China revealed that most particles had irregular shapes and their compositions were similar to that of usual mineral particles (Okada and Kai, 1995; Fan *et al.*, 1996; Okada *et al.*, 2001; Okada and Kai, 2003). Although the major mineral element of a small number of natural dust particles was Ca, their shapes were irregular and different from the Ca particles and their size ranges were larger than the ranges of the Ca particles shown in Figure 2b (Iwasaka *et al.*, 2003; Okada *et al.*, 2003). Therefore, it is hard to attribute the Ca particles to natural sources.

Thus, they were more likely from anthropogenic sources. The candidate sources were construction sites, where lime mainly composed of CaO and $Ca(OH)_2$ was liberally applied in China. As far as we know, there was no other reasonably constant anthropogenic source apart from the construction activities. This is consistent with the integrated-sample measurements of He *et al.* (2001), who reported that the variations of Ca/Si were in fair agreement with construction activities in Beijing.

3.2. CONTRIBUTION OF Ca PARTICLES WITH RESPECT TO USUAL MINERAL PARTICLES

In order to investigate the significance of the Ca particles, we estimated the number percentages of the Ca particles and usual mineral particles to total mineral particles from randomly-taken electron photographs of the particles. Figure 3 shows the percentages in different size ranges during non-dust-storm periods and dust-storm periods. The diameter of a usual mineral particle was defined as the average of its maximum dimension and the orthographic width. The diameter of a Ca particle was defined as the average of its length and width. Although some Ca particles smaller than 0.1 μm could be seen on photographs, we did not account for them since there were a huge number of particles collected in that range and it was hard to determine if a particle was cubic or polygonal at such a small scale in many cases. Consequently, numbers of the particles around 0.1 μm or smaller will have been underestimated.

From the percentage distributions in Figure 3, several characteristics of the Ca particles were confirmed. In the range of diameter >1.0 μm, Ca particles were the majority of mineral particles while usual mineral particles were the minority during non-dust-storm periods. During dust-storm periods, the number percentages

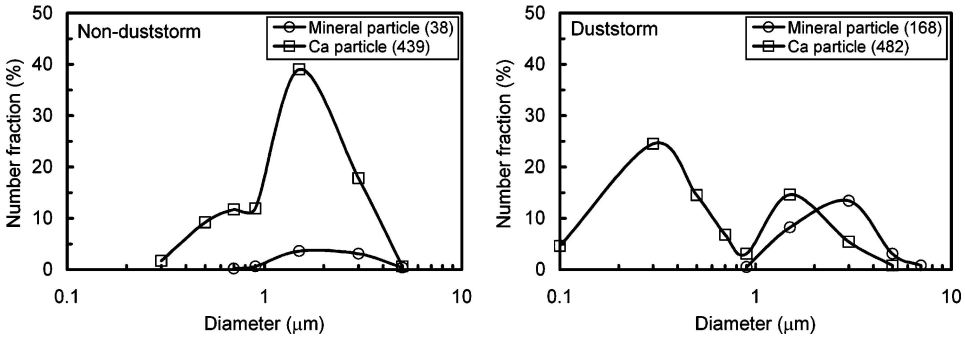

Figure 3. Number fractions of Ca particles and usual mineral particles in different diameter ranges at Beijing during non-dust-storm (Sept. 25–27, 1994 and Dec. 16–18, 1994) and dust-storm periods (Mar. 11, Apr. 5, 6, and 24, 1995). Total accounted mineral particles were 477 for non-dust storm periods, and 670 for dust-storm periods. The numbers of Ca particles and soil particles for different periods are listed in parentheses.

of the two kinds of mineral particles were comparable in this range. In the range of diameter <1.0 μm, there were always a large number of Ca particles while few usual mineral particles were detected. These results are consistent with the interpretation that Ca particles were from anthropogenic sources. No matter whether it was in non-dust-storm periods or dust-storm periods, Ca particles were constantly emitted from urban areas of Beijing. However, in dust-storm periods, a huge number of natural dust particles were input into the urban atmosphere, leading to the increase of the percentages of usual mineral particles in the range of diameter >1.0 μm. Therefore, it can also be confirmed from this result that the Ca particles had different sources from usual mineral particles. In summary, the Ca particles were always major mineral particles in the range of 1.0 μm $>$ diameter >0.1 μm while usual mineral particles were important only in the range of diameter $>1.0\mu$m during dust-storm periods, suggesting that particulate Ca in the urban atmosphere in Beijing was mainly from anthropogenic sources rather than natural ones.

Given that the volume of a particle is proportional to its cubic diameter and the relation between volume and diameter for the Ca particles were similar to that for usual mineral particles, the volume ratios of total Ca particles to total usual mineral particles in unit volume of mineral particles in the range of diameter larger than 1.0 μm were estimated based on the distributions in Figure 3. The ratios during dust-storm and non-dust-storm periods were 0.3 and 3.9, respectively. Therefore, the contribution of the Ca particles to total mineral particles was comparable to that of usual mineral particles during dust-storm periods and greatly exceeded that during non-dust-storm periods. Although the fractions of Ca particles might be different from case to case because the particles from local sources should be closely related to the instantaneous wind in the surface layer, the above results at least indicate that calcium from anthropogenic Ca particles made up a large fraction of total particulate calcium in the urban atmosphere in Beijing. In particular during non-dust-storm periods, the particulate calcium was dominated mainly by the Ca particles.

3.3. Influence of Ca particles on sulfate and nitrate formation

Although the morphologies, elemental compositions and size ranges of Ca particles and usual mineral particles were different, their properties mixing with sulfate and nitrate during non-dust-storm periods and dust-storm periods were similar. During non-dust-storm periods, many large Ca particles of diameter >1.0 μm contained sulfate and/or nitrate as shown in Figures 4a and b. This is similar to usual mineral particles (Figure 4c and d). In the range of diameter <1.0 μm, most Ca particles contained sulfate (Figure 5a). It is anticipated that the formation of particulate sulfate and nitrate on both Ca particles and usual mineral particles in the polluted urban atmosphere had similar mechanisms during non-dust-storm periods. Beijing areas were usually polluted by gases and particulate matter emitted from human activities (Huebert *et al.*, 1988; Xie *et al.*, 2000; He *et al.*, 2001), and both Ca particles and usual mineral particles were from local sources. The particles, after

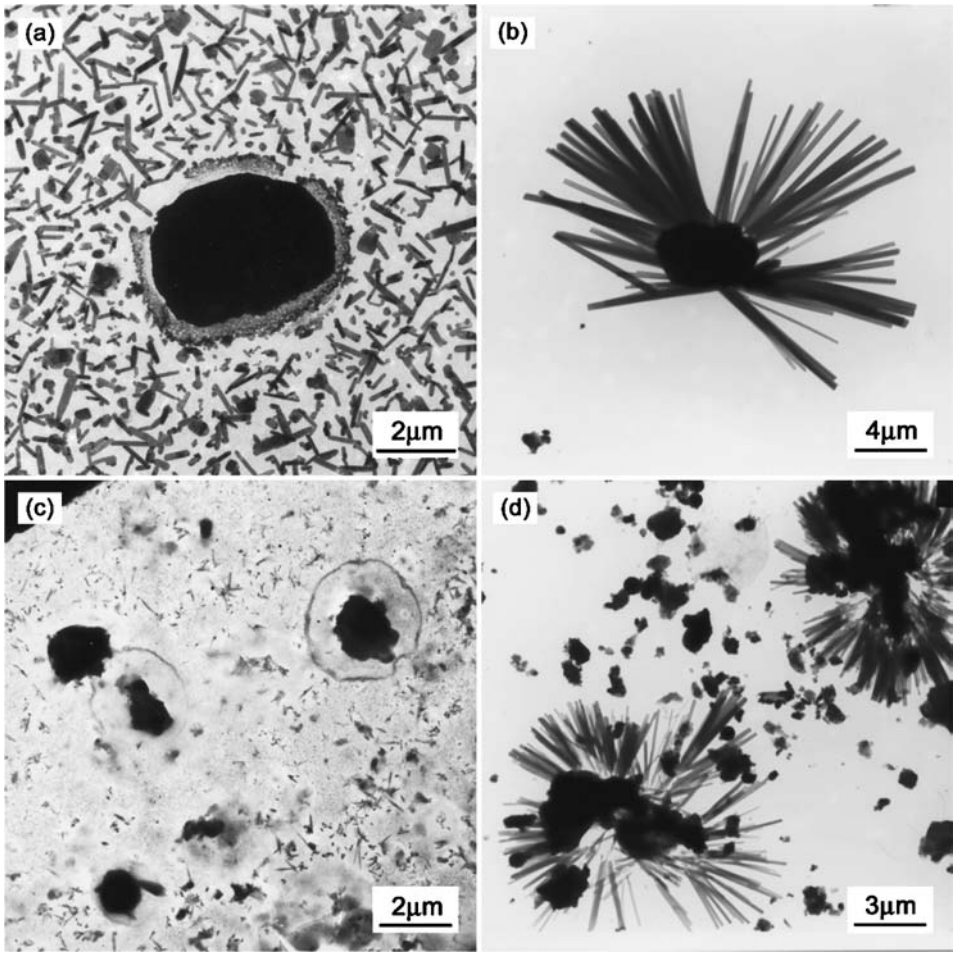

Figure 4. Electron microscope pictures of (a) Ca particles on barium chloride film, (b) Ca particles on nitron film, (c) usual mineral particles on multiple reagent film, and (d) usual mineral particles on nitron film. Particles in (a) and (b) were collected on September 26, 1994. Particles in (c) were collected on December 16, 1994, and Particles in (d) were collected on May 6, 1994.

emission into the air, were mixed with gaseous pollutants and as a result sulfate and nitrate appeared on their surface through adsorption, deposition or heterogeneous conversions.

During dust-storm periods, few Ca particles contained sulfate or nitrate. An example of reagent test results on small Ca particles on $BaCl_2$ film is shown in Figure 5b. These characteristics were also similar to those of dust particles (Zhang and Iwasaka, 1999). However, the reasons that Ca particles rarely contained sulfate and nitrate during dust-storm periods should be different from those of usual mineral particles since their sources were different. During dust-storm periods, most of the usual mineral particles should be dust particles, mainly from the source areas in

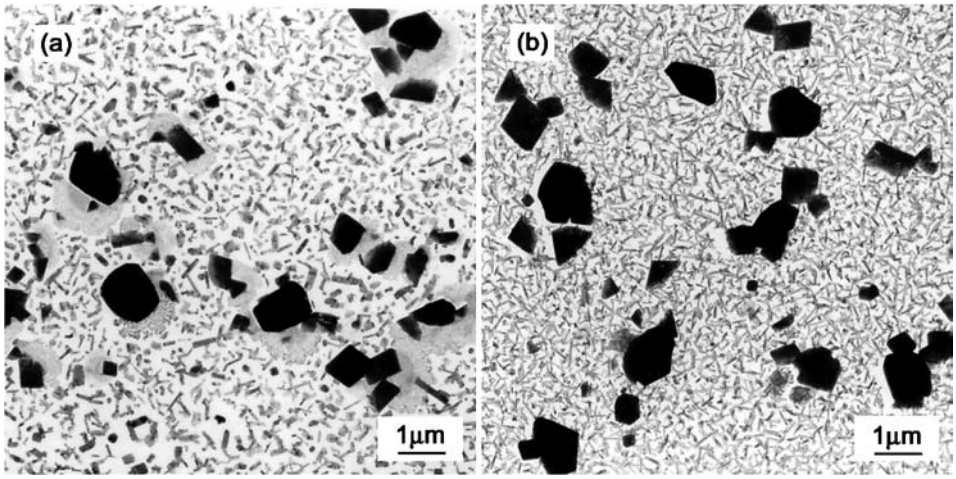

Figure 5. Electron microscope pictures of small Ca particles collected on barium chloride film during (a) non-dust storm periods, and (b) dust-storm periods. Particles in (a) were collected on December 16, 1994, and particles in (b) were collected on April 24, 1995.

northwestern China, while the Ca particles were from local sources. A possible explanation was that Ca particles collected in urban areas during dust-storm periods were 'young' particles and had not spent sufficient time in the urban atmosphere for the formation of sulfate and nitrate on their surface. Here, 'young' means that the time from the emission of the Ca particles to their capture was short. When dust storms appeared in Beijing, aged urban air was advected out of the city by the strong west wind. Air parcels in the urban atmosphere were those arriving through long-range transport and they were moving very fast. Therefore, Ca particles collected during dust-storm periods should be much younger than those collected during non-dust-storm periods. Dust particles rarely contained sulfate or nitrate at their source areas, and sulfate and nitrate were hardly formed on their surface during their transport from sources to Beijing since the air parcels enclosing the particles were very dry and no polluted sources that could considerably modify the particles during their transport were expected (Zhang and Iwasaka, 1999).

We estimated the number ratios of sulfate-containing Ca particles to total Ca particles from the test results of September 25–27, 1994, during non-dust-storm periods. It was found that about 70% Ca particles (total of 157 particles) in the range of diameter >1.0 μm and about 77% Ca particles (total of 305 particles) in the range of diameter <1.0 μm contained sulfate. Since Ca particles were the majority during non-dust-storm periods, the ratios indicate that Ca particles played the major roles in enhancing the formation of particulate sulfate and nitrate during non-dust-storm periods.

It was anticipated that the detected sulfate and nitrate on Ca particles and usual mineral particles were formed through heterogeneous reactions on the particles or

surface adsorption. Thus Ca particles could enhance the formation of particulate sulfate and nitrate as well as usual mineral particles in the range larger than 1 μm. If Ca particles had the same ability to promote sulfate and nitrate formation as usual mineral particles, particulate sulfate and nitrate formation on Ca particles were probably no less efficient than that on usual mineral particles. It should be noted that a great number of calcium particles contained sulfate during non-dust-storm periods in the range of diameter <1.0 μm, where usual mineral particles were rarely detected. Therefore, the enhancement of sulfate formation by Ca particles should exceed that by usual mineral particles during non-dust-storm periods. Smaller particles could provide a more effective surface for heterogeneous reactions, which could lead to more sulfate formed in that range. In the light of these results, Ca particles should be more important than usual mineral particles for sulfate and nitrate formation in the polluted urban atmosphere in cities like Beijing during non-dust-storm periods.

3.4. Observations in Qingdao and their implication

Besides Beijing, similar Ca particles were also frequently detected in Qingdao (36°04′N, 120°21′E), a coastal city in northern China (Figure 1). Figure 6 shows an example of Ca particles collected there during a non-dust-storm period. The particles had the same physical and chemical characteristics as those detected in Beijing, suggesting that there were similar anthropogenic Ca emissions in Qingdao. The analysis of integrated filter samples at Qingdao also revealed a significant contribution of Ca from local anthropogenic sources in some cases (Wang and Hu, 2001; Zhang *et al.*, 2001).

A recent observation at Qingdao (March 20, 2002: Table I), just before the arrival of a dust storm plume from western China, revealed that a large number of anthropogenic Ca particles dispersed to this area from East China, where several megacities such as Shanghai and Nanjing are located (Zhang *et al.*, 2003). The number ratio of Ca-containing mineral particles to total mineral particles in that case was about 0.83 in accounted for 209 mineral particles. The weight ratios of Ca to Mg + Al + Si + Ca + Fe in more than 20% of the Ca-containing particles were larger than 0.5, namely in those particles more than half of the mineral component by weight was Ca. The backward and forward isentropic trajectories of the air parcels carrying the particles indicated that the particles moved eastward out of the continent similarly to Asian dust-storm particles after they arrived at Qingdao from south (Zhang *et al.*, 2003). Therefore, anthropogenic Ca particles were not limited to Beijing and Qingdao, they were also being emitted from other cities in China and sometimes could disperse over a wide range.

These results suggest that the evaluation of the contributions of anthropogenic Ca to total Ca in particulate matter collected in the urban atmosphere in China is inevitable, although Ca is frequently utilized as the indicator of mineral dust in China. Since the anthropogenic Ca particles could disperse eastward from the

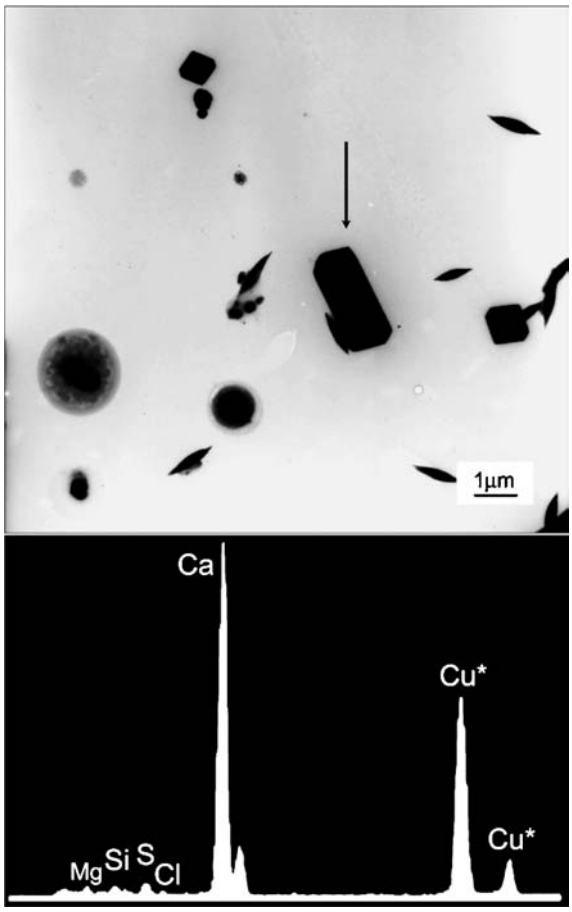

Figure 6. (a) Example of electron microscope photographs of Ca particles on carbon film collected at Qingdao during non-dust-storm periods (October 10, 1996), and (b) the X-ray spectra of the arrow-marked particle in (a). Cu in the spectra was caused by the sampling mesh frame.

continent, similar to Asian dust storm particles, a large fraction of Ca in particulate matter collected in the downwind areas of China, such as Korea and Japan, might be from anthropogenic emissions. Notice that there were a large number of the Ca particles in the polluted atmosphere, no matter whether the pollutants are from eastern China (this study) or local emissions (Wang and Hu, 2001; Zhang *et al.*, 2001). Therefore, Ca should not be a good indicator of Asian dust from natural sources in the downstream areas of China.

Observations by aircraft over the Sea of Japan and at mountain sites close to the sea revealed that atmospheric particulate matter sometimes contained a large ratio of Ca in summer and autumn when no Asian dust storm was reported or recorded at the source areas (Kanamori et al., 1991; Iwasaka *et al*., 1996; Mori

et al., 1998; Kido *et al.*, 2001; Matsuki *et al.*, 2003). Furthermore, some case data in Korea indicated an increase of Ca concentration in the range of diameter smaller than 1 μm (Kim and Park, 2001). There were no solid data to clarify whether the observed Ca in those studies was from natural or anthropogenic sources, although it was attributed to Asian dust in those studies. The results of this study indicate that it is improper to attribute the total Ca simply to Asian dust. The sources of Ca observed in the downstream areas of China must be identified before discussing whether it represents the output from the continent. Otherwise, ignorance of the anthropogenic emission may result in large discrepancies in the evaluation of natural dust storms. However, if we can confidently separate anthropogenic Ca from natural Ca in the downstream areas, the Ca particles do probably provide a useful indicator of the dispersion of anthropogenic emissions in East Asia.

4. Summary

Through the analysis and comparison of mineral particles collected at Beijing and Qingdao during non-dust-storm and dust-storm periods, the following conclusions can be drawn about calcium in atmospheric particles in North and East China.

(1) Anthropogenic emissions were significant sources of calcium in the urban atmosphere in cities like Beijing. They contributed a large fraction of calcium to total particulate matter. In particular during non-dust-storm periods, Ca particles were the major mineral particles in the polluted urban atmosphere.
(2) A large number of the Ca particles were in the range of diameter smaller than 1 μm, where usual mineral particles and natural dust were rarely detected.
(3) The Ca particles showed the same characteristics as soil particles for sulfate and nitrate formation. Because of their large number fraction, their enhancement of particulate sulfate and nitrate formation in polluted urban atmosphere may considerably exceed that of soil particles during non-dust-storm periods. In particular, Ca particles provided a major medium for particulate sulfate formation in the range of diameter $<1\mu$m.

Constant emission of similar particles from other cities was also confirmed, and the particles dispersed out of the continent similar to Asian dust particles. In this respect, Ca in particles collected in the downstream areas of the continent probably contained a large fraction of anthropogenic calcium besides the origin of desert dust. If Ca is utilized as the indicator of Asian dust, ignorance of the anthropogenic contribution may result in large discrepancies in the evaluation of Asian dust. To avoid this, reliable methods to identify anthropogenic Ca and natural Ca are necessary. However, because of the unique shapes, elemental composition and wide diameter ranges of the particles, such particles might provide a possible indicator of the dispersion of anthropogenic pollutants in East Asia in the future.

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References

Arimoto, R., Duce, R. A., Ray, B. J. and Unni, C. K.: 1985, 'Atmospheric trace elements at Enewetak Atoll, 2, Transport to the ocean by wet and dry deposition', *J. Geophys. Res.* **90**, 2391–2408.

Bishop, J. K. B., Davis, R. E. and Sherman, J. T.: 2002, 'Robotic observations of dust strom enhancement of carbon biomass in the North Pacific', *Science* **298**, 817–821.

Duce, R. A., Unni, C. K., Ray, B. J., Prospero, J. M. and Merrill, J. T.: 1980, 'Long-range atmospheric transport of soil dust from Asia to the Tropical North Pacific: temporal variability', *Science* **209**, 1522–1524.

Gao, Y., Arimoto, R., Duce, R. A., Zhang, X. Y., An, Z. S., Chen, L. Q., Zhou, M. Y. and Gu, D. Y.: 1997, 'Temporal and spatial distributions of dust and its deposition to the China Sea', *Tellus* **49B**, 172–189.

Fan, X., Okada, K., Niimura, N., Kai, K., Arao, K., Shi, G., Qin, Y. and Mitsuta, Y.: 1996, 'Mineral particles collected in China and Japan during the same Asian dust-storm event', *Atmos. Environ.* **30**, 347–351.

Fung, Y. Y., Meyn, S. K., Tegen, I., Doney, S. C., John, J. and Bishop, J. K. B.: 2000, 'Iron supply and demand in the upper ocean', *Global Biogeochem. Cycles* **14**, 281–295.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C., Cadle, S., Chan, T. and Mulawa, P.: 2001, 'The characteristics of $PM_{2.5}$in Beijing, China', *Atmos. Environ.* **35**, 4959–4970.

Huebert, B., Wang, M. and Lu, W.: 1998, 'Atmospheric nitrate, sulfate, ammonium and calcium concentrations in China', *Tellus* **40B**, 260–269.

Iwasaka, Y., Shi, G., Yamada, M., Matsuki, A., Trochkine, D., Kim, Y., Zhang, D., Nagatani, T., Nagatani, M., Nakata, H., Shen, Z., Chen, B. and Li, G.: 2003, 'Importance of dust particles in the free troposphere over Taklamakan Desert: Electron microscopic experiments of particles collected with balloon-borne particle impactor at DunHuang, China', *J. Geophys. Res,* **108**(D23), 8644, doi:10.1029/2002JD003270.

Iwasaka, Y., Minoura, H. and Nagaya, K.: 1983, 'The transport and spatial scale of Asian dust-storm clouds: a case study of the dust-storm event of April 1979', *Tellus* **35B**, 189–196.

Iwasaka, Y., Yamato, M., Imasu, R. and Ono, A.: 1988, Transport of Asian dust (KOSA) particles; importance of weak KOSA events on the geochemical cycle of soil particles, *Tellus* **40B**, 494–503.

Kanamori, S., Kanamori, N., Nishikawa, M., Higuchi, T.: 1991, 'The chemistry of KOSA', in *KOSA* (eds WRI of Nagoya Univ.), pp.124–156, Kokin Syoin press, (in Japanese).

Kido, M., Osada, K., Matsunaga, K. and Iwasaka, Y.: 2001, 'Diurnal variation of ionic aerosol species and water-soluble gas concentrations at a high-elevation site in the Japanese Alps', *J. Geophys. Res.* **106**(D15), 17335–17345.

Kim, B. and Park, S.: 2001, 'Transport and evolution of a winter-time Yellow sand observed in Korea', *Atmos. Environ.* **35**, 3191–3201.

Langner, J. and Rodhe, H.: 1991, 'A global three-dimensional model of the tropospheric sulfur cycle', *J. Atmos. Chem.* **13**, 225–263.

Matsuki, A., Iwasaka, Y., Osada, K., Matsunaga, K., Kido, M., Inomata, Y., Trochkine, D., Nishita, C., Nezuka, T., Sakai, T., Zhang, D. and Kwon, S.: 2003, 'Seasonal dependence of the long-range transport and vertical distribution of free tropospheric aerosols over East Asia: On the basis of aircraft and lidar measurements, and isentropic trajectory analysis', *J. Geophys. Res.* **108**(D23), 8663, doi:10.1029/2002JD003266.

Mori, I., Nishikawa, M., Morita, M., Tanimura, T. and Quan, H.: 2001, 'Chemical characteristics of KOSA aerosol collected in China and Japan', *Proc. 18th Symp. Aerosol Sci. & Tech.*, 102–103 (in Japanese).

Mori, I., Iwasaka, Y., Matsunaga, K., Hayashi, M. and Nishikawa, M.: 1998, 'Chemical characteristics of free tropospheric aerosols over the Japan Sea coast: aircraft-borne measurements', *Atmos. Environ*. **33**, 601–609.

McInnes, L., Covert, D. and Baker, B.: 1997, 'The number of sea-salt, sulfate, and carbonaceous particles in the marine atmosphere: EM measurements consistent with the ambient size distribution', *Tellus* **49B**, 300–313.

Nishikawa, M., Kanamori, S., Kanamori, N. and Mizoguchi, T.: 1991, 'Kosa aerosol as eolian carrier of anthropogenic material', *Sci. Total Environ*. **107**, 13–27.

Okada, K. and Kai, K.: 1995, 'Features and elemental composition of mineral particles collected in Zhangye, China', *J. Meteor. Soc. Japan* **73**, 947–957.

Okada, K., Naruse, H., Tanaka, T., Nemoto, O., Iwasaka, Y., Wu, P., Ono, A., Duce, R., Uematsu, M. and Merrill, J.: 1990, 'X-ray spectrometry of individual Asian dust-storm particles over the Japanese islands and the North Pacific Ocean', *Atmos. Environ.* **24**, 1369–1378.

Okada, K., Heintzenberg, J., Kai, K. and Qin, Y.: 2001, 'Shape of atmospheric mineral particles collected in three Chinese arid-regions', *Geophys. Res. Lett.* **28**, 3123–3126.

Okada, K. and Kai, K.: 1995, 'Features of elemental composition of mineral particles collected in Zhangye, China', *J. Meteor. Soc. Japan* **73**, 947–957.

Okdada, K. and Kai, K.: 2003, 'Atmospheric mineral particles collected in the Taklamakan Desert, China', submitted to *Atmos. Environ*.

Qian, G. W., Tanaka, H., Yamato, M. and Ishizaka, Y.: 1991, 'Multiple thin film method for simultaneous detection of sulfate and nitrate ions in individual particles and its application to atmospheric aerosols', *J. Meteor. Soc. Japan* **69**, 629–640.

Sokolik, I. and Toon, O.: 1996, 'Direct radiative forcing by anthropogenic airborne mineral aerosols', *Nature* **381**, 681–683.

Sokolik, I. and Toon, O.: 1999, 'Incorporation of mineralogical composition into models of the radiative properties of mineral aerosol from UV to IR wavelengths', *J. Geophys. Res.* **104**, 9423–9444.

Sokolik, I., Winker, D. M., Bergametti, G., Gillette, D. A., Carmichael, G., Kaufman, Y.J., Gomes, L., Schuetz, L. and Penner, J.P.: 2001, 'Introduction to special section: Outstanding problems in quantifying the radiative impacts of mineral dust', *J. Geophys. Res.* **106**, 18015–18027.

Tegen, I., Lacis, A. and Fung, I.: 1996, 'The influence on climate forcing of mineral aerosols from disturbed soils', *Nature* **380**, 419–422.

Uematsu, M., Duce, R. A., Prospero, J. M., Chen, L., Merrill, J. T. and McDonald, R. L.: 1983, 'Transport of mineral aerosol from Asia over the north Pacific ocean', *J. Geophys. Res*. **88**, 5343–5352.

Wang, M. and Hu, M.: 2001, 'Major inorganic compositions in fine and coarse particles of ambient aerosol at Qingdao', Environmental Science **22**, 35–38 (in Chinese with English abstract).

Xie, S., Zhang, Y. and Tang, X.: 2000, 'Current situation and trend of motor vehicle exhaust pollution in urban areas of China', *Res. Environ. Sci.* **13**, 22–26 (in Chinese with English abstract).

Yamato, Y. and Tanaka, H.: 1994, 'Aircraft observations of aerosols in the free marine troposphere over the North Pacific Ocean: Particle chemistry in relation to air mass origin', *J. Geophys. Res.* **99**, 5353–5377.

Zhang, D. and Iwasaka, Y.: 1999, 'Nitrate and sulfate in individual Asian dust-storm particles in Beijing, China in springs of 1995 and 1996', *Atmos. Environ.* **33**, 3213–3223.

Zhang, D. and Iwasaka, Y.: 2001, 'Chlorine deposition on dust particles in marine atmosphere', *Geophys. Res. Lett.* **28**, 3613–3616.

Zhang, D., Iwasaka, Y. and Shi, G.-Y.: 2003, 'Recent results of individual Asian dust particles analysis', *Proc. 2*nd *International Workshop on Mineral Dust*, 10–12 September, 2003, Paris, France.

Zhang, J., Wu, Y., Liu, C., Shen, Z., Yu, Z. and Zhang, Y.: 2001, 'Aerosol characters from the desert region of Northwest China and the Yellow Sea in spring and summer: observations at Minqin, Qingdao, and Qianliyan in 1995–1996', *Atmos. Environ.* **35**, 5007–5018.

Zhang, X., Arimoto, R., An, Z., Chen, T., Zhang, G., Zhu, G. and Wang, X.: 1993, 'Atmospheric trace elements over source regions for Chinese dust: Concentrations, sources and atmospheric deposition on the loess Plateau'. *Atmos. Environ.* **27**, 2051–2067.

Zhou, M., Okada, K., Qian, F., Wu, P., Su, L., Casareto, B. and Shimohara, T.: 1996 'Characteristics of dust-storm particles and their long-range transport from China to Japan – case studies in April 1993', *Atmos. Res.* **40**, 19–31.