NOTES AND CORRESPONDENCE

A Method for the Identification of Asian Dust-Storm Particles Mixed Internally with Sea Salt

By Noriko Niimura

University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Kikuo Okada

Meteorological Research Institute, Tsukuba, Ibaraki 305, Japan

Xiao-Bio Fan

Institute of Atmospheric Physics, Beijing 100029, China

Kenji Kai

University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Kimio Arai

Nagasaki University, Nagasaki 852, Japan

and

Guang-Yu Shi

Institute of Atmospheric Physics, Beijing 100029, China

(Manuscript received 18 February 1994, in revised form 9 August 1994)

Abstract

A method for the identification of Asian dust-storm particles mixed internally with sea salt was developed on the basis of electron microscopic analysis by using an energy-dispersive X-ray spectrometry and dialysis (extraction) of water-soluble material. The method was applied to samples collected in Nagasaki (Japan) and Beijing (China) during the spring of 1991. Dust particles containing Na and Cl or with Na/Si weight ratios larger than 0.25 (even if Cl was not detected) were identified to be Asian dust-storm particles mixed internally with sea salt.

1. Introduction

Asian dust-storm particles originating from the desert and loess areas in China are often transported over Japan and the North Pacific Ocean during the spring season (*e.g.*, Ishizaka and Ono, 1982; Iwasaka *et al.*, 1983; Uematsu *et al.*, 1983). These dust parti-

cles influence the cloud-physical and radiative transfer processes in the atmosphere.

Asian dust-storm particles act as ice nuclei (Isono *et al.*, 1959). Tanaka (1987) suggested, on the basis of measurements on ice nuclei collected at Mt. Fuji, that Asian dust-storm particles are present as particles containing water-soluble material (mixed particles). Okada *et al.* (1987) found, on the ba-

sis of electron microscopic examinations, that Asian dust-storm particles collected in Japan were present as mixed particles. Knowledge of the chemical composition and hygroscopic properties is important to assess the mode of ice crystal formation on the dust particles.

Moreover, the change in composition of dust particles during long-range transport is important in the field of atmospheric chemistry. The modification of dust-storm particles has been studied with respect to 1) their chemical reactions with acidic gaseous material (*e.g.*, Wu and Okada, 1994), and 2) their incorporation of sea salt. The information is not sufficient at present.

The presence of mineral particles mixed with sea salt has been reported previously by several investigators. Andreae *et al.* (1986) reported that a large fraction of dust particles collected in the atmosphere over the equatorial Pacific Ocean was internally mixed with sea salt. Parungo *et al.* (1986) collected some Sahara dust particles containing sea salt over the Atlantic Ocean. Sea salt was also detected in Asian dust-storm particles which were transported to northern Japan (Sakurai, 1989), to the North Pacific Ocean (Okada *et al.*, 1990), and to the western Pacific Ocean (Zhou *et al.*, 1992). However, these studies were based on analysis using an energy-dispersive X-ray (EDX) spectrometry alone.

Since mineral particles such as Asian dust-storm particles contain a small amount of mineral Na (sodium of mineral origin is called "mineral Na" in this note) (Nishikawa *et al.*, 1991), it is necessary to evaluate the mineral Na content in order to determine the amount of sea salt in the individual dust particle and the mixed properties. Examination by using the EDX spectrometry alone can not distinguish between sea salt Na and mineral Na. The aim of this report is to propose a method to identify Asian dust-storm particles mixed internally with sea salt by using the EDX spectrometry and dialysis of water-soluble material.

2. Method

Aerosol particles were collected in Nagasaki, Japan and in Beijing, China during the spring of 1991. Samples used in this study are those collected in Beijing (18:13–18:23 JST on 30 April and 14:02–14:12 JST on 7 May) and in Nagasaki (12:45–12:55 JST on 27 April and 14:23–14:33 JST on 2 May). Samples were taken at about 30 m above the ground surface. Aerosol particles were collected on electron-microscope grids covered with carbon-coated nitrocellulose (collodion) film using an impactor of 1-mm diameter jet at an air flow rate of 1.3 l min^{-1} with a collection time of 10 min. This impactor has a collection efficiency of 100 % for aerosol particles with radii more than $0.55 \text{ }\mu\text{m}$. The collection efficiency

Fig. 1. Relative weight ratios of Al, Si and Ca for all the dust particles collected in Beijing (before dialysis) (a), Nagasaki (before dialysis) (b) and Nagasaki (after dialysis) (c). The sum of the weight ratios of Al, Si and Ca is equal to 1. The number of particles used in this figure is 151 in Beijing (a), 74 in Nagasaki (b) and 66 in Nagasaki (c). Samples used in these figures are those collected in Beijing (18:13–18:23 JST on 30 April and 14:02–14:12 JST on 7 May) and in Nagasaki (12:45–12:55 JST on 27 April and 14:23–14:33 JST on 2 May).

Fig. 2. Electron micrographs of aerosol particles before (a) and after (b) dialysis. The sample was collected in Nagasaki during the period from 12:44 to 12:54 JST on 27 April 1991. The X-ray spectra obtained from particle "A" before (c) and after (d) dialysis. Particles indicated by arrows were sea salt.

was evaluated by using experimental results by Ranz and Wong (1952) on the assumption of spherical particles with a density of 2.6 g cm^{-3} (Ishizaka, 1972).

After collection, aerosol particles on the electron-microscope grid were coated with Pt/Pd alloy at a shadowing angle of $\arctan 0.5$ and examined using an electron microscope (Hitachi, H-600 and H-6010) equipped with an EDX analyzer (Kevex, delta 5). The X-ray spectrum was obtained through a Kevex UTW (ultra thin window) with a counting time of 50 sec. The electron beam was irradiated at the center of a particle at an accelerating voltage of 50 kV. For quantitative analysis of the individual particles with the EDX analyzer, a thin film method (Cliff and Lorimer, 1975) was applied using Kevex QuantexTM software for energy-dispersive microanalysis. The weight percent of elements was calculated on the basis of the characteristic X-ray fitted with a Gaussian distribution, not the peak in-

tensity. Particles with radii larger than $1 \mu\text{m}$ were mainly used in this study.

At first, the individual particles were analyzed by using the EDX spectrometry. After then, water-soluble material contained in individual dust particles was removed by floating the electron-microscope grid on distilled water, with the collecting surface upward (Mossop, 1963; Tanaka, 1980; Okada, 1983). In the present study, the dialysis was performed for 3 hours. Temperature of the distilled water was approximately 40°C . It was confirmed that the sea-salt component was removed completely from particles using this technique. After dialysis, particles were also analyzed quantitatively by using the EDX spectrometry mentioned above.

3. Results and Discussion

Relative weight ratios of Al, Si and Ca for all the individual dust particles collected in Beijing and

Fig. 3. Electron micrographs of dust particle "B" before (a) and after (b) dialysis. The sample was collected in Nagasaki during the period from 14:23 to 14:33 JST on 2 May 1991. The X-ray spectra were obtained from particle "B" before (c) and after (d) dialysis.

Nagasaki were examined in order to see features of these samples (Fig. 1). The weight ratios in Beijing (Fig. 1a) and Nagasaki (Fig. 1b) were obtained before dialysis. Particles with relative weight ratios of $\text{Ca} \geq 0.2$ occupy 14 (10–19) % of all the dust particles in Beijing. The number in parenthesis is the range obtained from the evaluation of the counting error, $\pm(N)^{-1/2} \times 100$, where N is number of particles counted. For the particles collected in Nagasaki, the number proportion of the particles of which the ratio of $\text{Ca} \geq 0.2$ before dialysis is 42 (30–57) % of all the collected particles. This proportion is relatively high. As shown later, the dust particles collected in Nagasaki contained sea salt. Hence, the weight ratio obtained after dialysis is also shown in Fig. 1c. From Fig. 1c, particles with the ratios of $\text{Ca} \geq 0.2$ comprise 22 (13–33) % of all the particles. It is known that Chinese desert and loess soil particles contain Ca (e.g., Hseung and Jackson, 1952), which was not found abundantly in Japanese soil (Tanaka *et al.*,

1986). As found in Fig. 1, the ratios for particles after dialysis in Nagasaki showed a similar distribution to those in Beijing. Therefore, dust particles collected on 27 April and 2 May in Nagasaki would be Asian dust-storm particles. Note that, the dialysis was not applied to the samples collected in Beijing, because dust particles containing both Na and Cl were present at very low number proportions (less than 2 %).

Dust particles which did not change their morphological features and X-ray spectra before and after dialysis were present in the samples. Figures 2a and 2b show the electron micrographs of particles before and after dialysis, respectively. The micrographs were taken originally at a low magnification of $\times 300$. Particles indicated by arrows were sea salt, because the X-ray spectra of these particles (though not shown here) showed strong peaks of Na and Cl, along with small peaks of Mg, S, K and Ca. On the other hand, the particle marked by "A" is made

Fig. 4. Electron micrographs of dust particle "C" before (a) and after (b) dialysis. The sample was collected in Nagasaki during the period from 12:44 to 12:54 JST on 27 April 1991. The X-ray spectra were obtained before (c) and after (d) dialysis.

up of an electron-opaque material with an irregular shape. The morphological appearance does not change by dialysis, indicating that the particle is water-insoluble. X-ray spectra of particle "A" before and after dialysis are shown in Figs. 2c and 2d, respectively. The X-ray spectrum of particle "A" (Fig. 2c) shows peaks of Na, Mg, Al, Si, S, K, Ca and Fe. No change in the spectrum is found before and after dialysis. The particle is identified to be mineral. The peak of Na after dialysis was the same value with that before dialysis, indicating that the Na is originating from soil, not sea salt. Water-insoluble Na was detected in bulk samples collected during an Asian dust-storm episode (Nishikawa *et al.*, 1991). As reported by Ishizaka and Ono (1982), the dust-storm particles contain feldspar. One of the kinds of feldspar is albite ($\text{NaAlSi}_3\text{O}_8$) which is present in surface soil of China (O. Nemoto, private communication). It should be noted that dust particles without Na were also found, as indicated later in Table 1.

Figures 3a and 3b show the electron micrographs

of aerosol particles before and after dialysis, respectively. The morphology of particle "B" changed after dialysis. The X-ray spectra of the particle before and after dialysis are shown in Figs. 3c and 3d, respectively. Before dialysis, particle "B" contains mineral Al, Si, Ti and Fe, along with Na, S and Cl. After dialysis, Na, S and Cl are not detected in the particle. Sea salt is composed of the mixture of water-soluble material with main components of Na and Cl, along with minor components of Mg, K, Ca and S. Usually, Na and Cl would be absent in most of the dust-storm particles in China, although the presence of dust with halite (NaCl) was reported (*e.g.*, Wake *et al.*, 1993). As mentioned previously, dust particles containing both Na and Cl were present at very low number proportions (less than 2 %) in the samples collected in Beijing. Since collected particles were well separated on the film, the probability of coagulation of the mineral particle with the other sea-salt particles on the film would be small. Then, dust particles which contain both Na and Cl could be identified to be the particles in-

Table 1. Number of analyzed dust particles in Nagasaki and Beijing for given Na/Si weight ratios (w). Dialysis (extraction) of water-soluble material was applied to the samples in Nagasaki.

Location	Period		Na/Si weight ratio			Total
			$w = 0$	$0 < w < 0.25$	$0.25 \leq w$	
Nagasaki	12:44–12:54 JST 27 April 1991	before dialysis	18	9	14	41
		after dialysis	24	17	0	41
Nagasaki	14:23–14:33 JST 2 May 1991	before dialysis	0	10	23	33
		after dialysis	13	12	0	25
Beijing	18:13–18:23 JST 30 April 1991	before dialysis	89	6	0	95
Beijing	14:02–14:12 JST 7 May 1991	before dialysis	42	14	0	56

Fig. 5. Relation between Na/Si weight ratios in individual dust particles before and after dialysis. The data are obtained from the particles containing Na collected in Nagasaki during the periods of 12:44 to 12:54 JST on 27 April and 14:23 to 14:33 JST on 2 May. Number of particles in this figure is 48. Although not shown in the figure, only one particle (before dialysis) had an Na/Si ratio of more than 10.

ternally mixed with sea salt, which were formed in the atmosphere.

Figures 4a and 4b show the electron micrographs of particle "C" before and after dialysis, respectively. Morphology of particle "C" changed due to dialysis. The X-ray spectra before and after dialysis are shown in Figs. 4c and 4d, respectively. The particle contained Na, Mg, Al, Si, S, K, Ca and Fe before dialysis. As found in Fig. 4d, Na was extracted completely from the particle by dialysis. Moreover, large amounts of Mg, S and Ca were also found to be water soluble. This result suggests that the Na is originating from sea salt, although any Cl was not found in the particle. Complete Cl loss (deficiency) in sea-salt particles could occur through chemical reactions with acidic material (*e.g.*, Ikegami *et al.*, 1994). Then, this particle is also identified to be a dust particle mixed with sea salt.

According to the results by bulk analyses (*e.g.*, Miyake *et al.*, 1956; Liu *et al.*, 1985), Na/Si weight ratio for Asian dust-storm particles is lower than 0.08. However, the ratios for individual dust particles would be scattered over a wide range. All the dust particles examined in this study contained Si which is regarded as water-insoluble material. Then, the amount of mineral Na can be evaluated by Na/Si weight ratios in individual dust particles before and after dialysis.

Figure 5 shows the relation between Na/Si weight ratios of individual dust particles before and after dialysis. The ratio after dialysis corresponds to the weight ratio of mineral Na to Si. The Na/Si ratio before dialysis mainly ranges from 0 to 5. On the other hand, after dialysis, the ratio is lower than 0.25. Approximately 60 % of the particles shown in

Fig. 5 have Na/Si ratios of 0.1–2 before dialysis and lower than 0.03 after dialysis. Table 1 shows the number of dust particles in Nagasaki and Beijing for different Na/Si weight ratios. On 27 April and 2 May in Nagasaki, there are 37 particles with Na/Si ratios larger than 0.25 before dialysis. After dialysis, however, Na/Si ratios for all the particles are lower than 0.25. This indicates that water-soluble Na was extracted from these particles by dialysis. Approximately 40 % of the particles collected on 27 April do not contain Na. Table 1 also shows the Na/Si weight ratio (before dialysis) in dust particles in Beijing. The ratios for all the particles in Beijing are lower than 0.25. Na was not detected in most of the particles. For the sample collected on 2 May in Nagasaki, the number of examined particles before dialysis (33 particles) is different from that after dialysis (25 particles), because the collecting film on the electron-microscope grid was broken by dialysis. These results showed that the weight of mineral Na in individual Asian dust-storm particles is evaluated to be less than 25 % of that of Si. If the Na/Si weight ratio is larger than 0.25, this particle can be identified to be an Asian dust-storm particle mixed internally with sea salt. This Na/Si ratio of 0.25 is nearly equal to the value for albite.

The mixed dust particles would be formed through cloud physical processes during long-range transport, as suggested by Andreae *et al.* (1986). The formation of these particles will be studied in detail in separate paper.

4. Conclusion

A method for the identification of Asian dust-storm particles mixed internally with sea salt was proposed on the basis of electron microscopic analysis by using an energy-dispersive X-ray spectrometry and dialysis (extraction) of water-soluble material. Individual aerosol particles were collected during the spring of 1991 in Nagasaki, Japan and in Beijing, China. Asian dust-storm particles mixed internally with sea salt were identified by the following criteria: 1) the particle contained both Na and Cl, or 2) the particle had an Na/Si weight ratio of ≥ 0.25 , even if Cl was not detected.

Acknowledgments

This study was carried out in the HEIFE (HEIthe river Field Experiment) program supported by the National Natural Science Foundation of China, Chinese Academy of Science, and the Japanese Ministry of Education, Science and Culture. The authors are deeply grateful to Prof. Y. Mitsuta, Disaster Prevention Research Institute, Kyoto University.

References

- Andreae, M.O., R.J. Charlson, F. Bruynseels, H. Strom, R.V. Grieken and W. Maenhaut, 1986: Internal mixture of sea salt, silicates, and excess sulfate in marine aerosols. *Science*, **232**, 1620–1623.
- Cliff, G. and G.W. Lorimer, 1975: The quantitative analysis of thin specimens. *J. Microscopy*, **103**, 203–207.
- Hseung, Y. and M.L. Jackson, 1952: Mineral composition of the clay fraction of some main soil groups of China. *Soil Sci. Soc. Am. Proc.*, **16**, 97–110.
- Ikegami, M., K. Okada, Y. Zaizen and Y. Makino, 1994: Sea-salt particles in the upper tropical troposphere. *Tellus*, **46B**, 142–151.
- Ishizaka, Y., 1972: On materials of solid particles contained in snow and rain water : Part 1. *J. Meteor. Soc. Japan*, **50**, 362–375.
- Ishizaka, Y. and A. Ono, 1982: Mass size distribution of the principal minerals of yellow sand dust in the air over Japan. *Időjárás*, **86**, 249–253.
- Isono, K., M. Kobayashi and A. Ono, 1959: The nature and the origin of ice nuclei in the atmosphere. *J. Meteor. Soc. Japan*, **37**, 211–233.
- Iwasaka, Y., H. Minoura and K. Nagaya, 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.
- Liu, T. *et al.*, 1985: Loess and Environment. *Science Press, Beijing*, 481 pp. (in Chinese).
- Miyake, Y., Y. Sugiura and Y. Katsuragi, 1956: Radioactive fallout at Asahikawa, Hokkaido in April, 1955. *J. Meteor. Soc. Japan*, **34**, 226–230 (in Japanese).
- Mossop, S.C., 1963: Stratospheric particles at 20 km. *Nature*, **199**, 325–326.
- Nishikawa, M., S. Kanamori, N. Kanamori and T. Mizoguchi, 1991: Ion equivalent balance in water soluble constituents of Kosa aerosol. *J. Aerosol Res. Japan*, **6**, 157–164 (in Japanese).
- Okada, K., 1983: Nature of individual hygroscopic particles in the urban atmosphere. *J. Meteor. Soc. Japan*, **61**, 727–736.
- Okada, K., A. Kobayashi, Y. Iwasaka, H. Naruse, T. Tanaka and O. Nemoto, 1987: Features of individual Asian dust-storm particles collected at Nagoya, Japan. *J. Meteor. Soc. Japan*, **65**, 515–521.
- Okada, K., H. Naruse, T. Tanaka, O. Nemoto, Y. Iwasaka, P.-M. Wu, A. Ono, R.A. Duce, M. Uematsu, J.T. Merrill and K. Arao, 1990: X-ray spectrometry of individual Asian dust-storm particles over the Japanese islands and the North Pacific Ocean. *Atmos. Environ.*, **24A**, 1369–1378.
- Parungo, F.P., C.T. Nagamoto and J.M. Harris, 1986: Temporal and spatial variations of marine aerosols over the Atlantic Ocean. *Atmos. Res.*, **20**, 23–37.
- Ranz, W.E. and J.B. Wong, 1952: Impaction of dust and smoke particles on surface and body collectors. *Ind. Eng. Chem.*, **44**, 1371–1381.
- Sakurai, K., 1989: Ice nucleation ability of yellow sand. *Reports of the Taisetsuzan Institute of Science*, **24**, 1–9 (in Japanese).

- Tanaka, S., M. Tajima and Y. Hashimoto, 1986: X-ray fluorescence analysis for major and trace elements in soil of Takla Makan Desert and Japan. *X-ray Chem. Anal. Japan*, **17**, 253–264 (in Japanese).
- Tanaka, T., 1980: Ice nucleating activity and the mode of action of volcanic ash ejected from Mt. Usu in Hokkaido — an improved method to remove hygroscopic materials collected on a membrane filter. *Pap. Meteor. Geophys.*, **31**, 153–171.
- Tanaka, T., 1987: Loess particles as ice nuclei. *Tenki*, **34**, 189–194 (in Japanese).
- Uematsu, M., R.A. Duce, J.M. Prospero, L. Chen, J.T. Merrill and R.L. McDonald, 1983: Transport of mineral aerosol from Asia over the North Pacific Ocean. *J. Geophys. Res.*, **88**, 5343–5352.
- Wake, C.P., P.A. Mayewski, Z. Xie, P. Wang and Z. Li, 1993: Regional distribution of monsoon and desert dust signals recorded in Asian glaciers. *Geophys. Res. Lett.*, **20**, 1411–1414.
- Wu, P.-M. and K. Okada, 1994: Nature of coarse nitrate particles in the atmosphere—a single particle approach. *Atmos. Environ.*, **28**, 2053–2060.
- Zhou, M.-Y., N.-P. Lu, J. Miller, F.P. Parungo, C. Nagamoto and S.-J. Yang, 1992: Characterization of atmospheric aerosols and of suspended particles in seawater in the western Pacific Ocean. *J. Geophys. Res.*, **97**, 7553–7567.

海塩を含む黄砂粒子の同定法

新村典子

(筑波大学)

岡田菊夫

(気象研究所)

樊小標

(中国科学院大気物理研究所)

甲斐憲次

(筑波大学)

荒生公雄

(長崎大学)

石廣玉

(中国科学院大気物理研究所)

電子顕微鏡を用いたエネルギー分散 X 線 (EDX) 分析と水透析法を用いることによって、海塩を含む黄砂粒子の同定の方法について研究した。分析に使用した試料は、1991 年春に長崎と北京で採集されたものである。その結果、Na と Cl が認められるもの、あるいは、Cl は検出されないが、Na/Si の重量比が 0.25 以上である粒子を海塩を含む黄砂粒子とした。