Mineralogical characteristics of aerosols collected at Matsue and Kanazawa – with a special reference to neutralizing effect on acid pollutants

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Abstract

A high-volume air sampler was used for aerosol sampling in Matsue (Oct. 1992 to Mar. 1994) and Kanazawa (Mar. 27 to Apr. 3, 1994). Snow and rain samples were collected during 1993 to 1995 in Kanazawa. The mineral composition in the aerosols during a one year period from October, 1992 to September, 1993 was analyzed by XRD and SEM-EDX. S-rich particles with a size distribution between 1-1.5μm are abundant in aerosol samples collected during winter (winter type) and its abundance decreased about 2 times in samples collected during summer (summer type). A size peak between 4-5μm of Al, Si-rich particles is always present in winter type and it changed to 2-3 μm in summer type. Major particles (the most is smaller than 10μm) are grouped into aerosol types : crustal minerals (48-68%), fly ash (9-17%), sulfur constituents (4-26%), sea salt (0-3%), biological (1-5%) and miscellaneous particles (3-6%). About 80% of fly ashes had Al and Si as major compositions. A number of submicrometer S-rich particles were detected in aerosols and in snow by SEM-EDX analyses. Calcite and clay minerals were often closely associated with submicrometer S-rich particles, suggesting that they acted as carriers of sulfur pollutants and played an important role in the cycle of S constituents during transport. The experiment of reaction between aerosols and simulated acid rain solutions showed that the aerosol with high Kosa flux had a relatively large neutralizing ability. Calcite in the aerosol played an important role in neutralization of acids in the solution. The result indicates that acid rain is depended not only on the SO_4^{2-}concentration in the atmosphere, but also upon other factors such as the presence of some materials available for neutralizing acids such as calcite.

Key words: mineral aerosol, S-pollutants, long-range transport, acid rain, neutralization, Matsue and Kanazawa

Introduction

Mineral dust, present as suspended particulate matter mainly in size <10μm (Kasahara, 1988), is an important constituent in atmospheric aerosols. It has been demonstrated that the mineralogy of atmospheric dust over the North Pacific is similar to that of the underlying deep sea sediments and that the primary source of clay minerals in these sediments is eolian soil material transported from the Asian arid regions (Rex and Goldberg, 1958 ; Windom, 1969 ; Prospero, 1979 ; Blank et al., 1985). The transport of soil dust from Asia to the tropical north Pacific Ocean has been reported (Duce et al., 1980 ; Uematsu et al., 1983). Recent years, the influence of soil dust on marine micro–organism and climate change has been given specific attention (Angelis et al., 1987 ; Charlson and Wigley, 1994 ; Tanaka, 1994). In Japan, eolian soil dusts in sediments were reported frequently (Naruse and Inoue, 1983 ; Inoue et al., 1991 ; Xiao et al., 1993 ; Zhang et al., 1994). During spring, Kosa particles are frequently transported from the Asian desert areas to the Islands of Japan (Iwasaka et al., 1988 ; Okada et al., 1990 ; Tazaki et al., 1990 ; Nishikawa et al., 1991). On the Japan Sea side of Japan, acid precipitation with pH ranging between 4–5 prevail in winter and it has been revealed that acid precipitation is mainly caused by high concentration of SO_4^{2-} in atmosphere in the Japan Sea coast (Hirai et al., 1991 ; Kitamura et al., 1991 ; Tamaki and Koyama, 1991 ; Iida et al., 1995 ;

Tazaki et al., 1995). Some reports have indicated a significant role of neutralizing acids by minerals contained in Kosa particles (Inoue et al., 1991 ; Nishikawa et al., 1991).

Recent years, industrialization of the Asian countries has been rapidly developed. Particularly, in China coal combustion is a dominant energy source, which causes a serious air pollution (Zhao et al., 1988). It was expected that about 2500 Mt SO_2 will be emitted in China in 1995 (Denchuken, 1994). Because the monsoon prevails during spring and winter, this air pollution is not limited only in the Asian countries. It will give a global effect, particularly in the northern hemisphere (Charlson and Wigley, 1994).

Based on the importance of mineral dust in atmospheric aerosols, Al concentration in aerosols was frequently used as an indicator of mineral aerosol concentration in some reports (Duce et al., 1980 ; Uematsu et al., 1983 ; Sekine et al., 1992). Several studies on mineral compositions and abundance variation of minerals in aerosols are reported (Arima et al., 1995 ; Sato et al., 1995), but their numbers are much smaller compared with the study on the chemistry of aerosols. The purposes of this study are to characterize behaviors of mineral aerosols in atmosphere and investigate relations between mineral aerosols and SO_2-related acid pollutants. For this reason, a high-volume air sampler was used for aerosol sampling in Matsue, Shimane Prefecture and Kanazawa, Ishikawa Prefecture, both located at the Japan Sea side. Snow and rain samples were collected in Kanazawa. In order to evaluate the influences of mineral aerosols and the acids on terrestrial and aquatic ecosystems, experiments of reaction between aerosols and simulated acid rain solutions were carried out. In this paper, the abundance variation of major minerals and S constituents in aerosols over an extended time was presented and the neutralization ability of aerosols was discussed.

Samples and methods

Samples

Atmospheric aerosol was collected weekly with a high-volume air sampler (HVC-1000) on the roof of the building (8 stories) of Faculty of Science, Shimane University in Matsue, Shimane Prefecture, Japan, located at the Japan Sea side (Fig. 1). Matsue city has a population of approximately 140,000. There is no large pollution source compared with most cities on the Pacific Ocean coast of Japan (Yamaguchi et al., 1991). Glass fiber filters (Toyo, GRB 100 R, 203X245 mm) were fitted with the sampler. Weekly sampling was done with a flow rate of 1000 l min^{-1} from October, 1992 to March, 1994. The filters were changed every Monday and kept in a refrigerator before analysis.

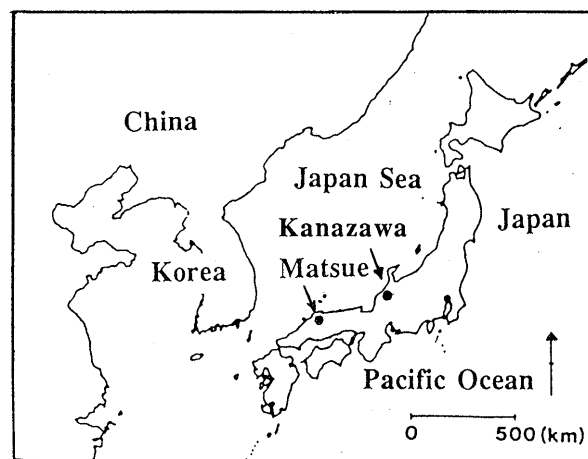For one week period from March 28 to April 4, 1994,

Fig. 1. Map showing eastern Asian area and the sampling sites on Matsue and Kanazawa, Japan.

atmospheric aerosol samples were collected daily at the balcony of 7th floor of the building of Faculty of Science, Kanazawa University using a high-volume air sampler (HVC-500) with a flow rate of 500 l min^{-1}. Snow and rain samples were collected in a polyethylene container (50×35×10 cm) on the campus of Kanazawa University, around where there are no large pollution emissions. After collection, snow and rain water were filtered with a membrane filter (0.45 μm of pore diameter) using an aspirator. Residual solid particles were analyzed by XRD and SEM-EDX. The filtered solution was evaporated slowly at the temperature lower than 60℃, and solid material left behind evaporation was analyzed by SEM-EDX to investigate water soluble components.

Individual particle analyses and size distribution measurement

Morphology and identification of individual particles were examined by SEM-EDX. A small square filter (5×5 mm) cut from sample was stuck to the carbon tape on a Cu-Zn or a plastic stud and was coated in vacuum with a thin layer of carbon. For selected samples, 5-10 random fields of view were chosen and about 200-400 particles were analyzed. The analysis includes particle size, shape and specify elements analyzed of the particle. Based on the elemental content and morphology, particles were assigned to one of several types such as clay minerals, quartz, calcite, gypsum, coal and oil fly ash, sea salt, biological particles (pollen, diatom, plant debris) and miscellaneous particles rich in Zn, Cu, V, Al elements (mostly of anthropogenic sources). This classification was useful to evaluate abundance of major particle types in aerosols. Among the aerosols, 12 samples collected in different months in Matsue were selected for the examination of particle size distribution. The particle numbers counted range from 256 to 312. Although this classification is not perfect due to the precision limited by SEM-EDX analysis, espe-

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cially in cases of mixed particles, particles in 5-10 random fields of view were analyzed by manual operation, therefore it was possible to avoid confusion of mixed particles. XRD results were generally used as references in mineral classification.

Mineral composition analysis

Atmospheric aerosol samples collected during a one year period from October, 1992 to September, 1993 were used to investigate seasonal variation of major minerals. In order to know primary abundance of minerals and to protect some water soluble minerals in aerosols from dissolution and recrystallization during water extraction, an area with 2×2 cm was cut from a filter, attached to a glass slide and analyzed by X-ray powder diffraction (XRD) with a Rigaku, Rint 1200 system X-ray diffractometer with CuKα generated at 40 kV and 30 mA. Relative abundances of major minerals were expressed by peak intensity (CPS : Counts per Second) of the strongest reflection of each mineral.

Elemental concentration measurements

Major elemental concentrations were measured in the area of $400 \times 300 \mu$m on the 1×1 cm square filter which was analyzed by XRD. Elemental concentration measurements were conducted using a Philips–EDAX PV 9800 STD energy dispersive X–ray analyzer attached to a JEOL–JSM–5200 LV scanning electron microscope. Operational conditions were as follows : an accelerating voltage of 15 kV and an analytical time of 200 s. With this method, concentration measurements were limited to elements with $Z > 11$, but if a particle was made mainly of lighter elements such as C and O in pollen or elemental carbon particle, a relatively low peak to background ratio and low count rate for its X–ray spectrum will occur. Conversion of intensities into concentrations was accomplished using a standardless ZAF correction program set in computer. The concentration of elements were normalized as wt %.

Reaction experiment of simulated acid rain with aerosols

To evaluate the neutralization capacities of atmospheric aerosols during a long–range transport and after deposition, simulated acid rain solutions with pHs 3, 4 and 5 were prepared using H_2SO_4 solution (10 μl ml^{-1}) added by $(NH_4)_2SO_4$. Seven atmospheric aerosol samples including the sample collected in Kosa period (March 29–April 4, 1993) were selected in this experiment. Four pieces of aerosol filter (2.5×2.5 cm) of each sample were immersed with 200 ml of distilled water and simulated acid rain solution, pHs 3, 4 and 5, respectively. After samples were stood different time at room temperature, the pH and electrical conductivity (EC) was measured using a Twin Cont pH and EC meters (HORIBAR).
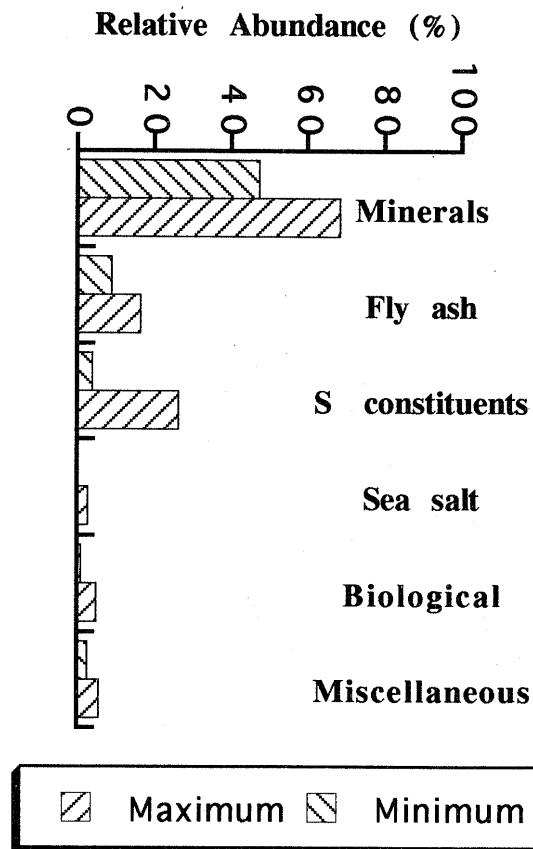
Relative Abundance (%)

Fig. 2. Major particle types in aerosols by individual particle analyses. Analytical particle numbers for several selected samples were 200-400.

Results

1 Major particle types and size distribution in aerosols

Fig. 2 summarizes the major particle types in aerosols by individual particle analyses. Some specific morphologies are the basis to distinguish the particles with similar chemical composition. Al, Si-rich fly ash, for example, has a similar chemical composition to clay minerals but its typical morphology of smooth sphere is easy to be distinguished from the later (Mamane et al., 1986). Pollen and diatom could also be identified by their specific shapes and low peak to background ratio. Major particle types include crustal minerals (clay minerals, quartz, feldspars, carbonate minerals and iron oxide minerals), fly ash, sulfur constituents (include sulfur-rich particles and sulfates), sea salt, biological particles and miscellaneous particles. About 48-68% of aerosols are composed of minerals in which the common includes clay minerals, quarts, feldspars and calcite. Other parts of aerosols are composed of fly ash (9-17%), sulfur constituents (4-26%), sea salt (0-3%), biological (1-5%) and miscellaneous particles (3-6%). Table 1 lists number concentrations of fly ashes which were counted by individual particle analyses in aerosol, snow and rain

Table 1. Relative abundance of fly ashes detected by individual particles in samples.*

Sample	Relative abundance(%)**	Al Si-rich fly ash(%)	Fe-rich fly ash(%)	Ti-rich fly ash(%)	S-rich fly ash(%)
Aerosol	13	83	7	---	10
Snow	17	73	9	9	10
Rain	9	86	11	2	---

* Aerosol (March 31, 1994), snow (December 15, 1993) and rain (June 13, 1994) were collected in Kanazawa.
**Total numbers measured by SEM-EDX analysis are 397 for aerosol, 410 for snow and 376 for rain samples.

samples. The abundance of particle numbers ranges from 9-17%. About 80% of fly ashes have Al and Si as major compositions.

Twelve samples collected in different months in Matsue were selected for the examination of size distribution. Their sampling periods and main elemental concentrations detected by area analysis of SEM-EDX are listed in Table 2. As individual particle analysis by SEM-EDX revealed a lot of particle types, for size distribution examination, we selected only four particle types to made curves considering that these particle types are more representative in characterization of aerosols. Fig. 3 A and B show size distributions of aerosols collected during Oct. 1992–Sept. 1993.

The curves could be generally divided into winter type and summer type. The winter type includes the samples collected from November to May. They are characterized by (1) a relatively high abundance of sulfur-rich particles with a size peak between 1–1.5 μm ; (2) Al, Si-rich particles characterized mainly by soil dust showing two relatively high abundance with size peaks between 4–5μm and >10μm, respectively ; (3) considerable abundances of Al, Si-rich fly ash and

Fe-rich particles. They all show similar patterns with a size peak at 2μm. Summer type is composed of samples collected from June to October. In the comparison with the winter type, an apparent difference is that concentration of sulfur-rich particles decrease sharply, although the sample from June still show a higher concentration which could be explained as the effect from Kosa season during late spring (Iwasaka et al., 1988 ; Tanaka et al., 1989). Al, Si-rich particles only display one peak abundance near 2-3μm, showing a relatively small particle size. The peak abundance >10μm are almost not present, except for the case of sample collected in June. Al, Si-rich fly ash and sulfur-rich particles show weak peaks and the amounts have decreased about two times compared with the winter type. This result indicates that particle size and abundance are largely affected by season. That is the wind direction which controlled the pattern of size distribution of aerosols in air.

2 Seasonal variation of major minerals in aerosols

Fig. 4 shows the seasonal variation of major minerals in aerosol samples, collected in Matsue during a

Table 2. Sampling periods and main elemental concentration of selected samples for the examination of size distribution (wt.%).

Samples	Al	K	Fe	S	Cl
Oct. 5-11, 1992	5.0	3.3	0.7	3.0	6.4
Nov. 9-15	9.3	5.1	3.7	14.7	3.3
Dec. 7-13	6.8	3.6	2.4	11.6	10.5
Jan. 18-24, 1993	5.2	3.5	1.7	5.5	5.4
Feb. 1-7	8.9	5.3	6.0	10.9	4.4
Mar. 29-Apr. 4	11.5	5.5	8.7	8.1	6.3
Apr. 12-18	10.4	6.4	5.9	19.9	3.0
May 10-16	11.3	5.7	7.0	8.3	1.0
Jun. 28-Jul. 4	4.2	3.5	0.8	3.3	2.5
Jul. 26-Aug.1	3.6	3.9	0.4	3.3	3.0
Aug. 23-29	5.0	4.2	1.7	6.5	0.8
Sept. 13-19	5.8	4.6	2.8	9.5	1.0

* Elemental concentrations were detected by area analysis of EDX described in the Samples and Method Section

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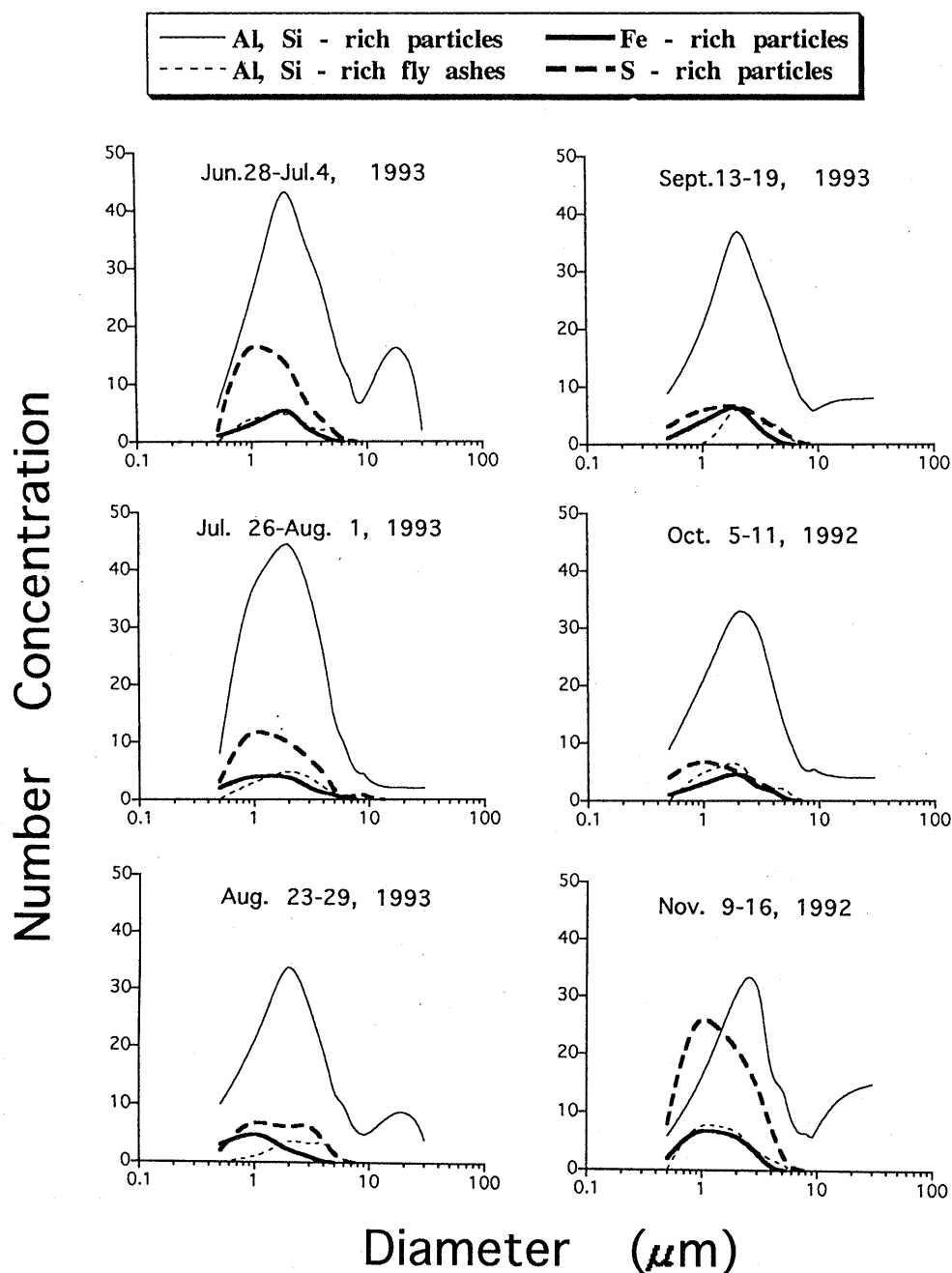*Jour. Geol. Soc. Japan,* 102 (9)　　　Neutralizing effect on acid pollutant　　　791

Fig. 3. Size distribution of four particle types in aerosols collected during Oct. 1992–Sept. 1993 in Matsue. Curves could be divided into winter (November to May) and summer (June to October) types.

one year period, by XRD analysis and S concentration in the same samples by EDX area analysis described in the Sample and Methods section. Arrows show the Kosa phenomena (March 8–14, 1993, March 29–April 4, 1993 and May 10–16, 1993) recorded by the Meteorological Station of Shimane Prefecture. The frequency of wind directions observed on the Oki Islands near Matsue (Mukai et al., 1990) was set to correlate the S concentration and mineral abundances. The most apparent variation in abundance is quartz which shows a highly broad peak in spring (March–May) and a small peak in early winter (late

November – early December). Similar patterns are displayed by clay minerals and gypsum, although the peaks of higher abundances in gypsum do not continuously occur compared with quartz and clay minerals. Clay minerals were mainly characterized by kaolin minerals, illite, chlorite and mixed layer minerals. Fig. 5 shows XRD patterns of one of the aerosol samples collected during March 29–April 4, 1993 in Matsue. No-treated pattern shows that the sample is mainly composed of clay minerals, gypsum, lepidocrocite, quartz, feldspars, calcite and halite. The sample was treated with ethylene glycol (E.G.)
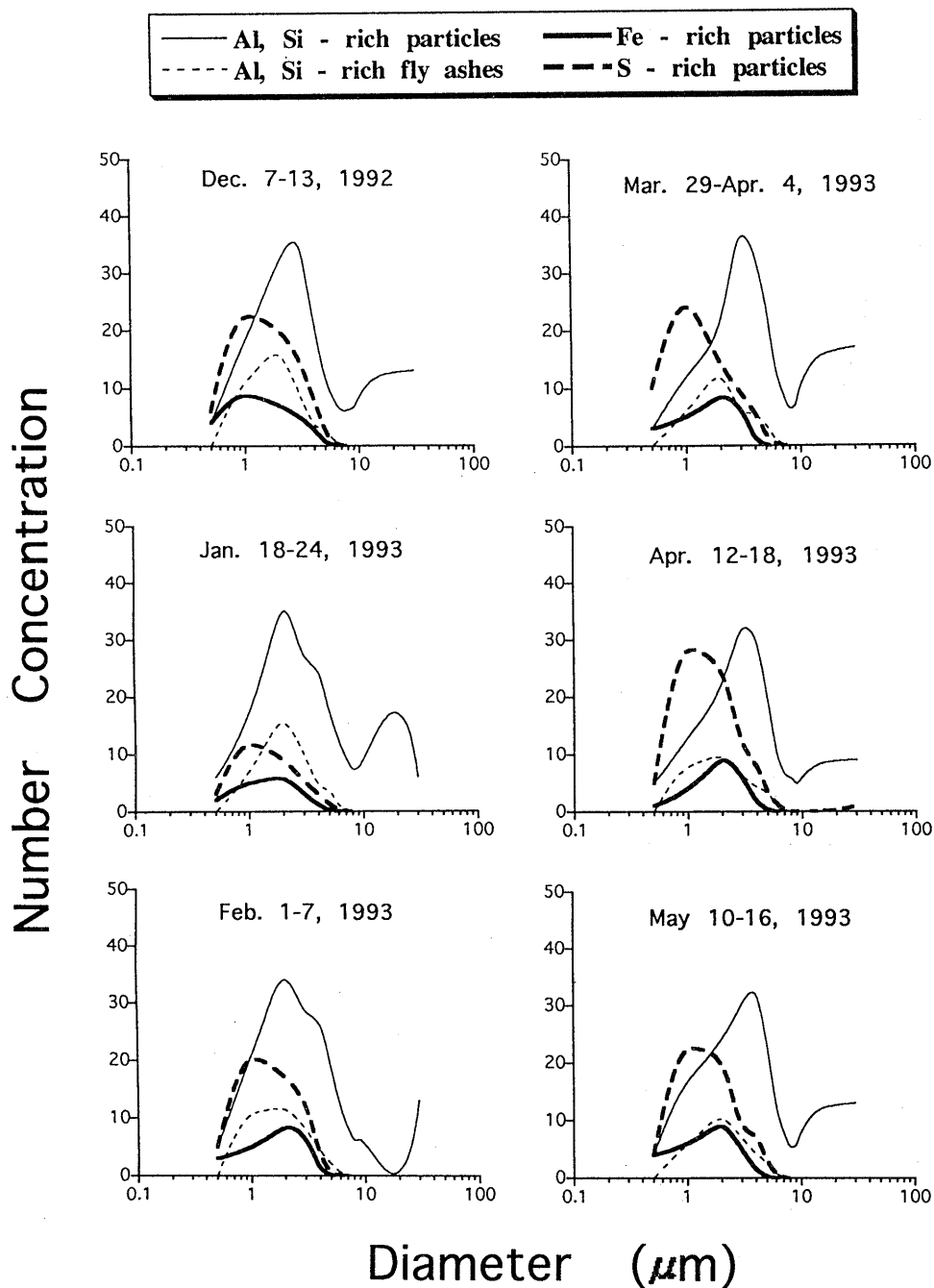
Fig. 3. Continued.

saturation and heated at 600℃ for 2 hours to identify clay minerals. The result shows that clay minerals include mainly chlorite, illite, kaolinite and illite/smectite interlayer minerals. Calcite does not show apparent peaks in both spring and early winter, although a small peak was observed during spring. Halite did displayed a pattern different from others, as it had a high concentration during winter.

3 Behavior of sulfur pollutants in aerosols

Elemental measurements by EDX showed that S concentration had a seasonal variation similar to those of the major mineral aerosols (Fig. 4). Although the total S concentrations should include a contribution from gypsum, the pattern of S concentration was not well correlated with the abundance pattern of gypsum, particularly in late winter (Fig. 4). This indicated the presence of sulfur bearing phases other than gypsum in aerosols. A number of sub-micrometer S-rich particles were found in aerosols and in snow by SEM-EDX analyses. These S-rich particles were generally found with fly ash and soil particles (Fig. 6 A, B). EDX analyses showed that besides the major compositions of fly ash and silicate minerals such as Na, Mg, Al, Si, K, Ca and Fe, considerable amounts of S components were detected from the surface of fly ash and soil particles. These S-

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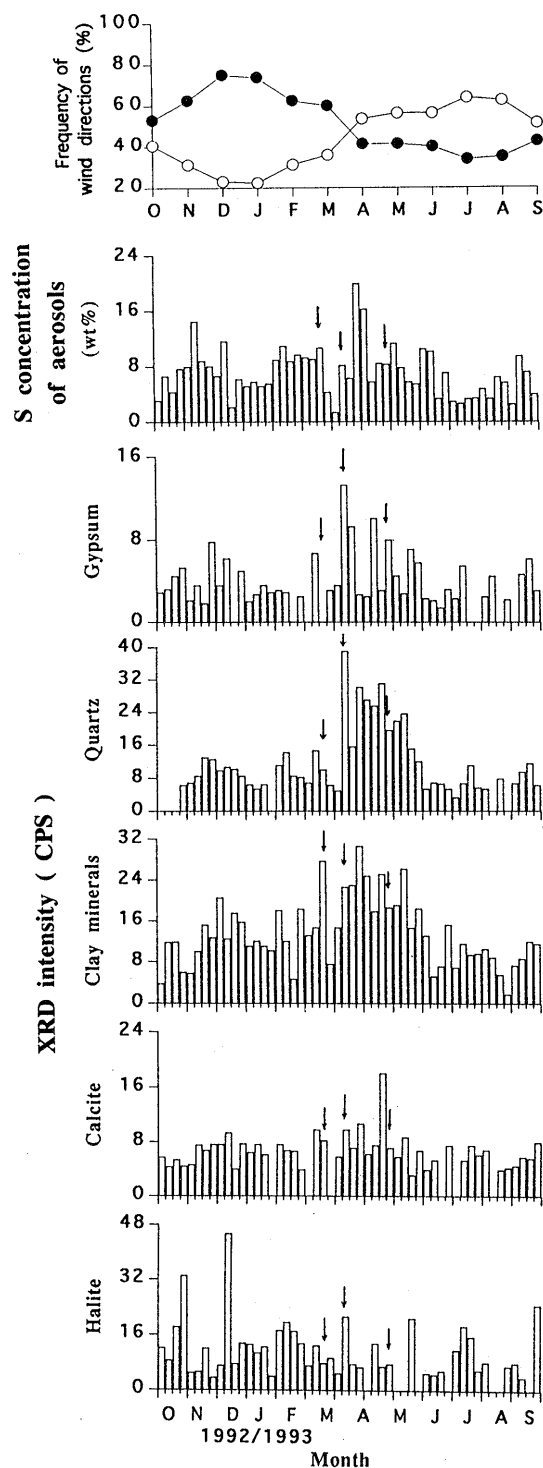
Fig. 4. Seasonal variation of major minerals in aerosols and S concentration during a one year period. Arrows show the Kosa phenomena (March 8–14, 1993, March 29–April 4, 1993 and May 10–16, 1993) recorded by Meteorological Station of Shimane Prefecture, Japan. The frequency of the wind directions was observed on the Oki Islands near Mastue for 10 years. ○ : from the main land of Japan, ● : from the direction of the Asian continent. The data are calculated from the table by The Japan Meteorological Agency (1977), (after Mukai et al., 1990).

bearing aggregates of submicrometer particles showed a high background (Fig. 7 A). TEM observation showed that these S-bearing aggregates of submicrometer particles were carbon particles which were identified as carbonaceous soot according to their morphologies (Fig. 8) (Tazaki et al., 1989 ; Parungo and Nagamoto, 1993 ; Sato et al., 1995). The experiment of dissolving aerosols with distilled water showed that most sulfur substances were water soluble (Zhou and Tazaki, 1996), therefore, sulfur was considered as coatings on the surface of fly ash or silicate minerals (Parungo and Nagamoto, 1993). Spherical particles with S as an only element detected by EDX were commonly found in snow samples (Fig. 7 B). As limited by EDX analyzer in this study, we could not detected some lighter elements such as O, C and N, but a lower peak to background ratio could suggest some lighter elements such as O and C contained in these S-bearing aggregates of submicrometer particles. It has been proved that many S-substances coated on the surface of other particles have the morphology characteristic of H_2SO_4 or NH_4HSO_4 as identified by using an electrostatic aerosol sampler with the film of $BaCl_2$ (Ferek et al., 1983 ; Mukai et al., 1990). Therefore it could be considered that most of water soluble S-substances are present as H_2SO_4 and NH_4HSO_4, which are produced by the conversion from SO_2 (Mukai et al., 1990).

Several samples were selected to examine the number concentration of particles attached by S substances. A secondary strong S peak after main elemental peaks, such as Al and Si in clay minerals or fly ash, Ca in calcite was considered as S substances attached to existing particles. Table 3 lists the result which shows that a sequence favorable to be attached by S constituents is calcite (83%) > clay minerals (68%)>fly ash (55%)>quartz and feldspars(36%). Table 4 gives statistical results of number concentrations of S-containing fly ash in aerosol, snow and rain samples. About half of the fly ashs was coated by S constituents in the aerosol sample. This means that fly ashes carried considerable amounts of S substances. Number concentrations in snow and rain samples were low in comparison with those in the aerosol. A part of sulfur substances appeared to have been dissolved during a snowfall or rainfall. Fig. 9 shows the concentration variation of elements in solid residues after filtration and filtered snow water, respectively in a snow sample. Filtered snow water contain usually Na, Mg, S, Cl, K, Ca. The amount of S in the filtered snow water was more than that in the solid residues after filtration. This suggested that most sulfur substances were water soluble.

4 Reaction of aerosols with simulated acid rain solutions

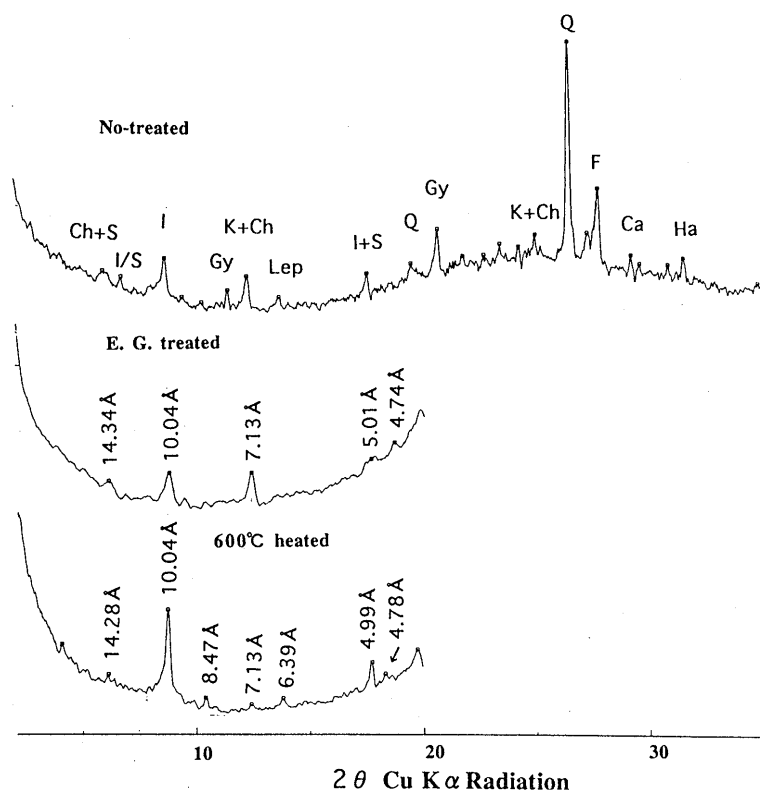Table 5 lists the abundances of major minerals and

Fig. 5. XRD patterns of aerosol samples collected in March 29 – April 4, 1993 in Matsue. Sample was treated with ethylene glycol (E.G.) saturation and heating at 600℃ for 2 hours. Ch : chlorite ; S : smectite ; I : illite ; K : kaolinite ; I/S : illite/smectite interlayer ; Lep : lepidocrocite ; Gy : gypsum ; Q : quartz ; F : feldspars ; Ca : calcite ; Ha : halite

S concentration in aerosol samples used in this reaction experiment. Fig. 10 shows the variation of pH and electrical conductivity (EC) with time after aerosols were immersed with distilled water. Initial pHs (10 min.) were different for each sample, but the sample with high Kosa flux showed a relatively high pH at 6.8. After 10 hours, pHs increased near 7 for most samples, however the sample with high Kosa flux showed a relatively high pH at 8.6, displaying an alkaline reaction. After a long period (from 10 hours –24 days), pHs of most samples were balanced near 7, only showing a slightly increase (Fig. 10 A). It could be observed that during all reactions, the sample with high Kosa flux always showed pHs higher than other samples. EC of the solutions showed a similar trend to the pH. It appeared that EC was partially related to S concentration as well as gypsum and calcite contents in aerosols (Table 5). Although the sample with high Kosa flux showed a relatively high pH, it had a relatively low EC (Fig. 10 B). This might be related to relatively high contents of gypsum and calcite contained in Kosa aerosol (Table 5).

Fig. 11 shows the change in pH of the system when aerosols reacted with simulated acid rain solutions of pHs 3, 4 and 5, respectively. The solutions of pHs 4 and 5 were significantly neutralized by aerosols (Fig. 11 A and B). Especially for the sample with high Kosa flux, the solution of pH 5 was neutralized quickly at 6.7 (10 min.) and 7.2 after one day (Fig. 11 A), and the solution of pH 4 was neutralized at 5.6 (10 min.) and 6.6 after one day (Fig. 11 B). Whereas the solution of pH

3 was only slightly neutralized by the sample with high Kosa flux as indicated by an increase in pH from 3 to 4.4 after one day's reaction (Fig. 11 C). After 13 days, it was neutralized at pH 6.8. Generally, following characteristics could be observed. (1) initial pHs (10 min.) of the immersing solutions depended on not only aerosol themselves but also pHs of simulated acid rain solutions ; (2) pHs increased rapidly in one day's reactions, then increased slowly with time ; (3) with different simulated acid rain solutions, the sample with high Kosa flux always showed relatively high pH.

The immersing solutions of aerosol samples were filtered with a membrane filter and the residues after filtration were measured by EDX area analysis. Fig. 12 shows average relative proportions of elements dissolved in the immersing solutions. It is apparent that dissolved Ca in the sample with high Kosa flux was much more than that in other samples. The ratios of Ca/S or (Ca+Mg+K+Na)/S also showed the same result. It could be found from Table 5, the sample with high Kosa flux contain relatively high gypsum and calcite, whereas relatively low S. The higher Ca/S ratio could be related with the abundances of both gypsum and calcite.

Discussion

Transport of acid pollutants by mineral aerosols from the Asian continent to the Japanese coast

As shown in the results, two abundance peaks of major minerals except for halite in aerosols almost
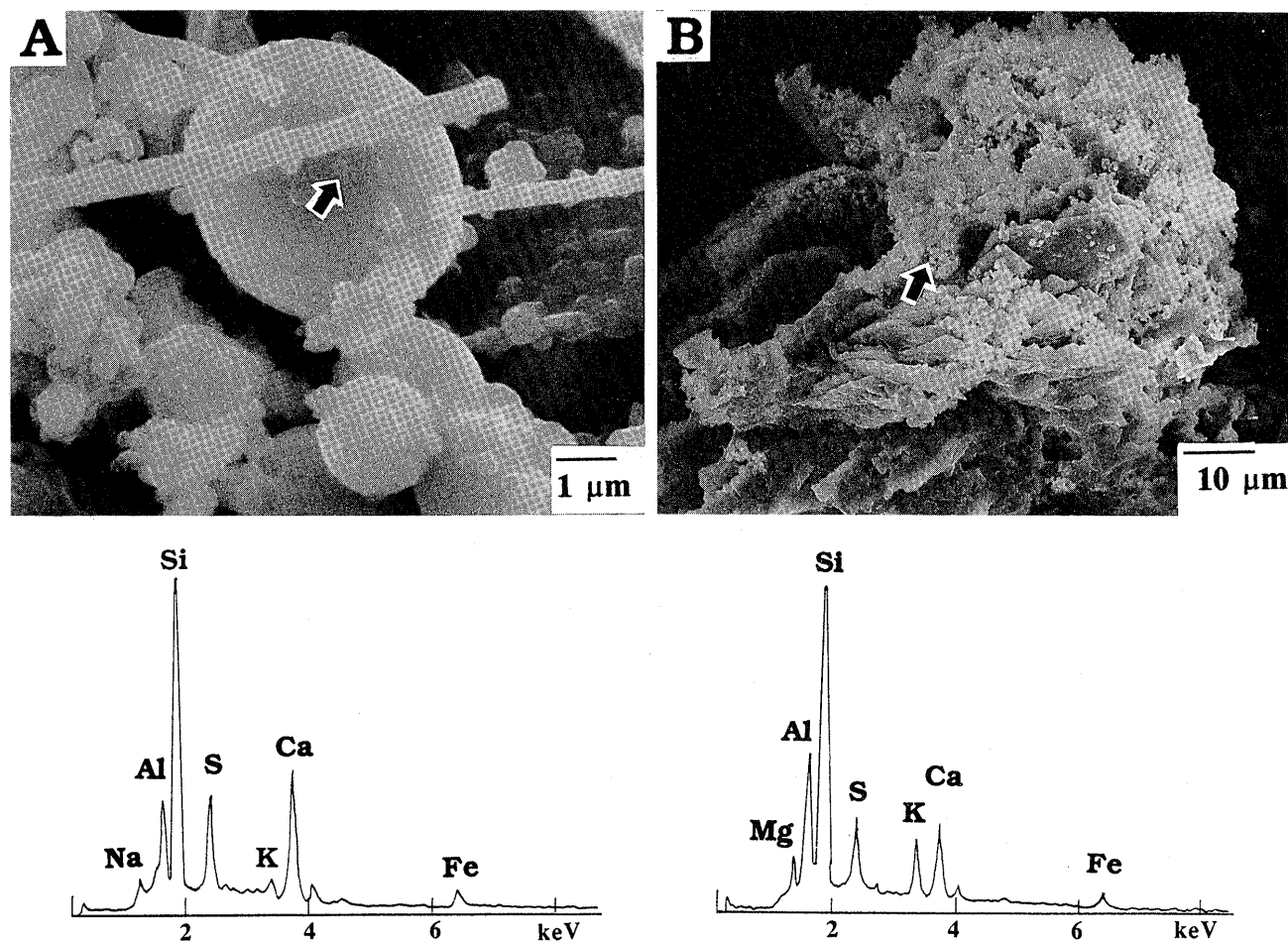
Fig. 6. Scanning electron micrographs and results of energy dispersive X-ray analyses of aerosols, showing submicrometer S-rich particles covering on the surface of fly ashes (A) and soil particles (B). The fine fibrous matters in Fig. 6 A are come from the filter paper. Sample was collected in the period from November 30 – December 6, 1992 in Matsue. Arrows indicate the place of spot analysis by EDX.

occurred in spring and early winter, and S concentration variation also showed the same patterns (Fig. 4). These abundance peaks are consistent with the number of dust storm reports in China reported by WMO (World Meteorological Organization) (Merrill et al., 1989). The number of dust storm reports in China has a broad maximum from February to late May with the largest peak occurring in late April or early May. Secondary peaks occur in October, November or December in some years. Above results were also very similar to those reported by Sekine et al. (1992). In their report, soil dust in Beijing, China displayed two higher abundances in spring and winter. Apparently, the effect of seasonal wind on the transport of mineral aerosols is obvious. Size distribution of aerosols with larger size peaks between 4-5μm in winter type and 2-3μm in summer type also suggests that size of aerosols is largely controlled by seasonal wind. Higher numbers of dust storm reports are correlated with the seasons of northwestern monsoon prevailing during which soil dust is easy to be transported to the

Islands of Japan (Tanaka et al., 1989). The typical large scale weather configuration of the Japan Sea side of Japan in winter shows a strong high pressure system on the Asian continent and a low pressure system over the north-western Pacific Ocean (Hirai et al., 1991). This weather configuration directs a flow of cold continental air masses to the main Islands of Japan. On the Japan Sea side of Japan, wind direction apparently changes with season because of the monsoon (Mukai et al., 1990 ; Kitamura, 1993). Surface wind directions are classified into the wind from the main land of Japan (NE-E-S-WSW) and from the direction of the Asian continent (W-NW-N) by Japan Meteorological Agency (Fig. 4). About 60-75% of wind directions in winter and early spring (November-March) are from the direction of the Asian continent, whereas in summer (May–September) the wind from the main land of Japan is dominant (Fig. 4). According to the calculation by Sekine et al. (1992), residence time of soil dust (according to the diameter of Kosa particles ranging from 3.8-4μm) in Beijing
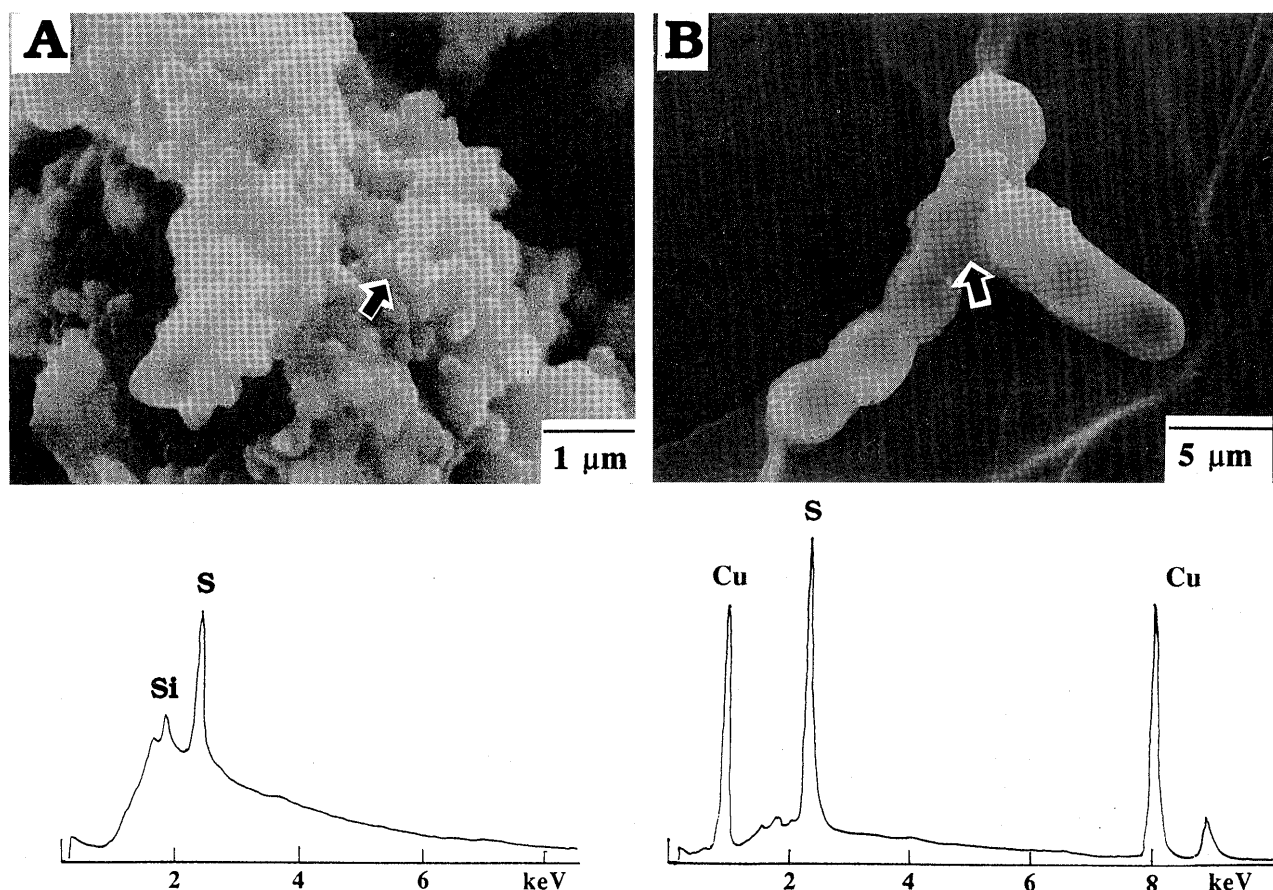
Fig. 7. Scanning electron micrographs and results of energy dispersive X-ray analyses of aerosols, showing aggregates of submicrometer particles with S as a dominant component and a high background (A) and spherical particles in snow collected in January 14, 1995 in Kanazawa using a TEM grid (B), only S element was detected in EDX spectrum and another two strong peaks of Cu are resulted from the TEM grid. Arrows indicate the place of spot analysis by EDX.

was about 2.5 days in high dust season (March–May) and was about 0.5 day in low dust season (July–September). If 2.5 days are considered as an average residence time of the soil dusts (3.8–4μm) in high dust season in north part of Chinese continent, the soil dusts from the Asia continent could contribute to the long-range transport over Japan by northwestern monsoon (Uematsu et al., 1983 ; Sekine et al., 1992). Higher mean concentrations of major minerals and S constituent of aerosols in spring and winter suggested a large influence from northwestern monsoon. High abundance of halite in winter also suggested a strong effect from the Japan Sea, as the cold continental air masses pass the Japan Sea, they pick up the moisture of sea. This indicated that in spring and winter a large part of mineral aerosols was transported from the Asian continent. As pointed out by Merrill et al. (1989), mineral aerosol is a good natural tracer of air movement because it is relatively inert, it has a residence time long enough to allow transport over great distances. High concentrations of Al and Ca in the atmosphere were observed in all sampling stations in NASN (National Air Surveillance Network) every spring from March to May when Kosa phenomenon was observed in Japan, and the contribution of soil dust transported by Kosa phenomenon to the total soil dust in each city in Japan is 56-80% with the highest (80%) in Matsue (Tanaka et al., 1989). As shown in Fig. 4, relatively high S concentration in winter was probably related to these mineral aerosols. The correlation between S constituents and mineral aerosols indicated that during spring and winter, a considerable amount of sulfur-related pollutants was transported with mineral particles and fly ashes. These particles were coated by water or solution containing SO_4^{2-} and could absorb various atmospheric gases (Iwasaka et al., 1988 ; Okada et al., 1990). They can be transported to a long distance until deposition (Parungo and Nagamoto, 1993 ; Charlson and Wigley, 1994). Soil dusts associated with S-related pollutants
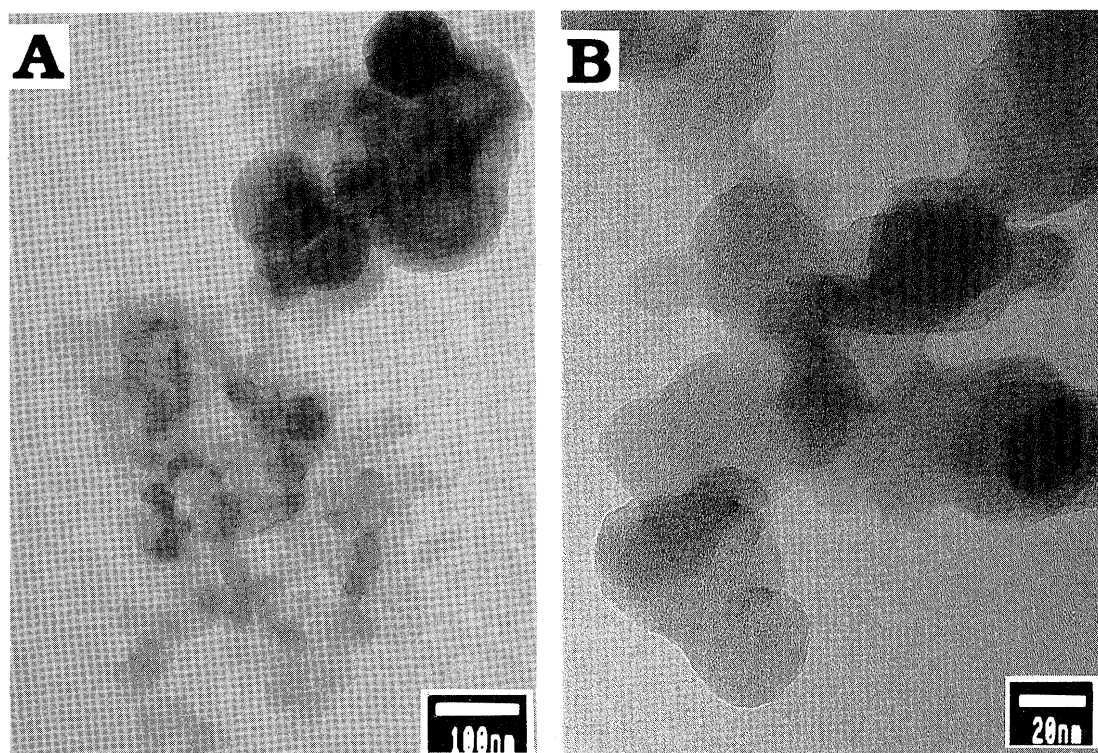
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Fig. 8. Transmission electron micrographs of S-bearing aggregates of submicrometer particles coated on the surface of fly ashes (A) and the enlarged image showing morphologies of chain-like carbon particles (B).

have been found in Arctic aerosols (Parungo et al., 1990 ; Parungo and Nagamoto, 1993).

Sulfur pollutants is one of the origins of acid rain and snow

Coal combustion is a major source of air pollution in China with the most common air pollutants being particulate and SO_2. Coal and oil accounted for 74% and 19%, respectively of total energy consumption in China (Zhao et al., 1988). Coal is burned generally in medium- and small-sized boilers and household stoves which have a small holding capacity. Mukai et al. (1990) indicated that the ratio of excess-SO_4^{2-}/non-soil V (total V-soil V, according to the abundance ratio of V to Al in crust) changed seasonally on the Oki Islands with $3,740 + 1,120 \mu g$ m^{-3} in winter and $2,470 + 720 \mu g$ m^{-3} in summer on average. As in Japan most SO_2 is derived from oil burning, V is a characteristic component in oil, whereas it is not so enriched in coal. Therefore, the higher ratio of excess-SO_4^{2-}/non-soil V in winter suggests that these excess-SO_4^{2-} resulted mainly from coal combustion. According to Iida et al. (1995), in winter the ratio of {NO_3^-}/{nss-SO_4^{2-} + NO_3^-} and that of {nss-Ca^{2+}}/{nss-SO_4^{2-} + NO_3^-} in the shore of Japan Sea are consistent with those in northern China. As indicated above, about 80% of fly ashes were rich in Al and Si which are one of the dominant composition of coal (Fisher et al., 1978 ; Makino, 1989 ; Tazaki et al., 1989 ; Okazaki, 1993). The difference of chemical composition between coal- and oil-fired fly ashes indicates that 75%

of Al, Si-rich fly ashes results from coal combustion (Mamane et al., 1986), suggestig a major source from the Asian continent. The study on the sulfur isotopic ratios ($\delta^{34}S$) of the atmospheric sulfate deposition in the Japan Sea coast has revealed nearly similar distribution to that of $\delta^{34}S$ values of SO_2 emitted from Chinese coal combustion, and it was estimated that sulfate produced by coal combustion in China has higher contribution (20%) in winter (Kitamura et al., 1993 ; Ohizumi et al., 1994). In northern China, relative contributions to aerosols by coal burning and wind-blown dust are 2 : 3 in the summer and 3 : 2 in the winter (Zhao et al., 1988). The high ratio in the winter contributes largely the air pollution resulted from SO_2 emissions. Statistical analysis of individual particles by SEM-EDX showed that calcite and clay minerals were often associated with S constituents rather than other particles. This suggests that the reaction between SO_2 and particle surface depends on the chemistry of particles, property for water absorption as well as time available for the reaction (Navakov et al., 1974). Mineralogical properties of calcite and clay minerals make them easily to be absorbed by solutions. Wet surfaces provide an attractive nucleating site for SO_2 absorption and deposition of submicrometer S constituent. During the transport, these minerals and fly ash particles acted as carriers of the pollutants. They played an important role in the cycle of S constituents, as chemical reaction sites or as carriers during transport. Particularly

Table 3. Statistical result of S-containing particles in the aerosol sample.

Particle Types	Total numbers measured by EDX	Numbers of S-containing particles	Percentage (%)
Calcite	23	19	83
Clay minerals	92	63	68
Fly ash	53	29	55
Quartz+Feldspars	73	26	36

* Sample was collected in March 31, 1994 in Kanazawa.

during winter, acid pollutants were incorporated by droplets in snow and caused the acidity of wet precipitation.

Neutralization of mineral aerosols

It is apparent that mineral aerosols carried a considerable amount of acid pollutants from the Asian continent to the Islands of Japan. In the same time, mineral aerosols, as nuclei of acid rain and snow, partially neutralized the acidity of these precipitations during the long-range transport (Inoue et al., 1991 ; Nishikawa et al., 1991). pH of immersing solution of aerosols is depended on the amount of total aerosols and soluble substances contained in aerosols (Inoue et al., 1991 ; Nishikawa et al., 1991). The different mass weight of aerosols in each piece of filter used in this experiment could give an effect on the pH, although the difference of mass weight among the filter pieces are very small. The most important factor controlling pH of immersing solution could be water soluble substances, especially the balance between cation and anion ions (Nishikawa et al., 1991). Different pHs of immersing solutions could be a result affected by both aerosol amounts and dissolved ions in the filter pieces. For the sample with high Kosa flux, a higher pH correlated to a lower EC (Fig. 10), suggesting that ion balance is apparently in the side of cations and the sample also showed a relatively large neutralization ability. This may related to the content of calcite and gypsum contained in this sample (Table 5). As shown in Fig. 12, a relatively high proportion of Ca in the immersing solution of
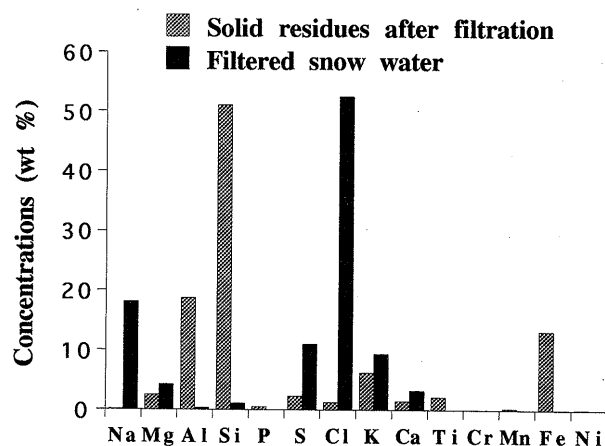

Fig. 9. Elemental concentrations of solid particles in snow and filtered snow water. Sample was collected in December 18, 1993 in Kanazawa. The amount of S in filtered snow water was more than that in the solid residues after filtration, suggesting that most sulfur pollutants were water soluble.

sample with high Kosa flux were measured. Average relative abundance of calcite in aerosols collected in Matsue was 5.8 (cps) for winter (averaged from 14 samples ; n=14), 7.7 (cps) for spring (n=14), 4.1 (cps) for summer (n=13) and 4.7 (cps) for autumn (n=13). Solutions of the aerosols immersed with distilled water gave an average pH of 6.8 for winter samples (n=4), 7.2 for spring ones (n=5), 6.7 for summer ones (n=4) and 6.9 for autumn ones (n=4). This suggested that aerosols in spring contained more alkaline mate-

Table 4. Statistical result of S-containing fly ashes in samples.

Sample	Total numbers measured by EDX	Numbers of S-containing fly ashes	Percentage (%)
Aerosol	53	29	55
Snow	83	26	31
Rain	88	22	25

* Aerosol (March 31, 1994), snow (December 15, 1993) and rain (June 13, 1994) were collected in Kanazawa.

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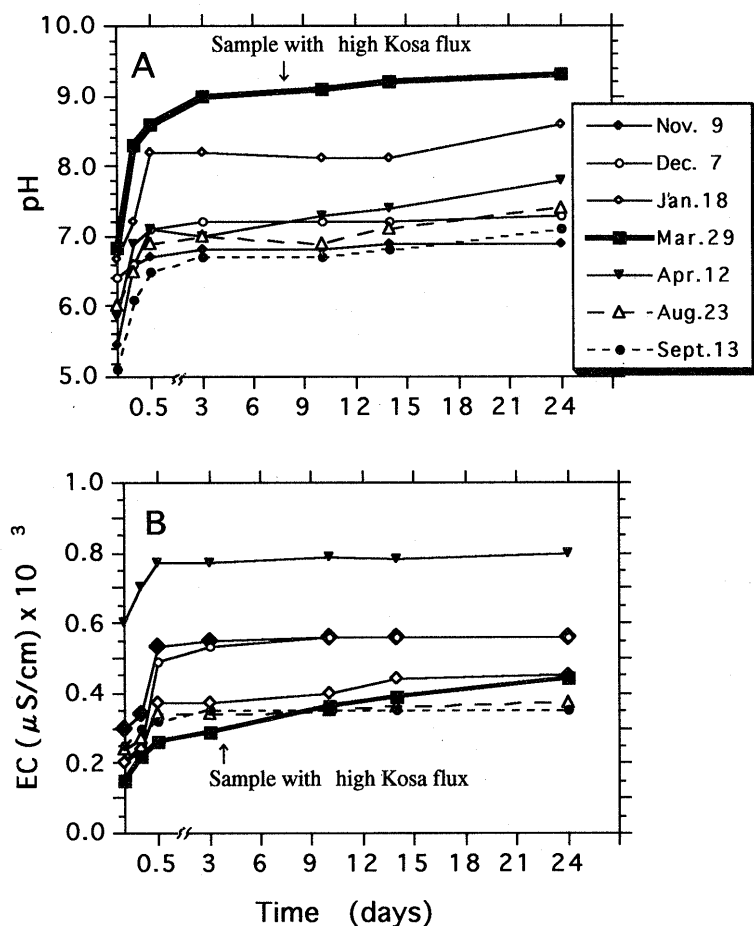
Fig. 10. The changes of pH (A) and electrical conductivity (EC) (B) of the immersing solutions of aerosols with distilled water with time.

rials or carbonate minerals than those in other seasons. According to Zhao et al. (1988), average pHs of solutions of aerosols immersed with distilled water were 8.2 and 5.8 for Beijing and Guiyang samples, respectively. These pHs were apparently related to carbonate minerals, especially calcite, in aerosols. Nishikawa et al. (1991) indicated that Ca^{2+} occupied 80% of the total cations dissolved after the reaction of Kosa aerosols with simulated acid rain

solutions, suggesting a considerable amount of calcites being dissolved. During the initial period (10 min.) of the reaction in this experiment pH increased rapidly, suggesting that alkaline materials or carbonate minerals contained in aerosols effectively neutralized the acidity in relatively short period of time. It is important for the partial neutralization of acids by mineral aerosols during long-range transport. This may be favorable for the protection of soil

Table 5. Concentrations of S and major minerals in aerosol samples.*

Sample	S (wt%)	Gypsum (cps)	Calcite (cps)	Clay minerals (cps)	Quartz (cps)	Halite (cps)
Nov. 9-15, 1992	14.4	3.6	7.5	9.9	8.5	5.3
Dec. 7-13	11.5	6.2	9.3	12.4	10.7	45.4
Jan. 18-24, 1993	5.5	2.9	0.0	10.1	0.0	4.0
Mar. 29-Apr. 4**	8.1	13.3	9.8	22.6	39.1	21.3
Apr. 12-18	19.9	2.7	10.7	30.6	30.2	6.7
Aug. 23-29	6.4	0.0	3.9	5.5	7.8	0.0
Sept. 13-19	9.4	4.7	5.8	8.6	9.5	3.8

* Samples were used in the experiment of reaction between aerosols and simulated acid rain solutions.
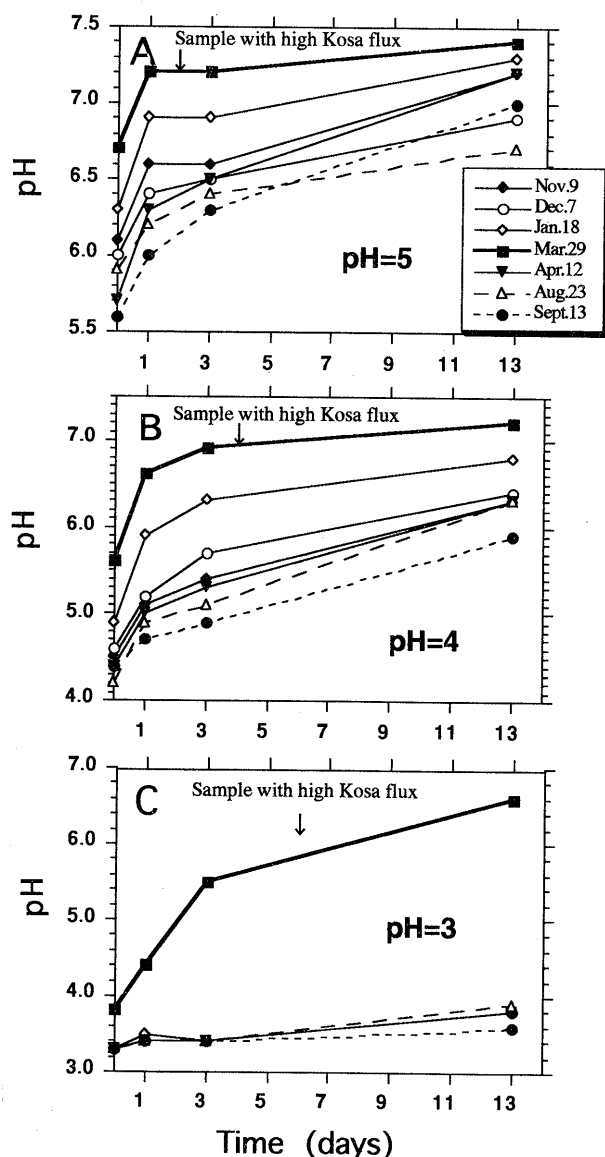** Kosa phenomenon was recorded during this period.

Fig. 11. pH change after the reaction of mineral aerosols with simulated acid rain solutions of pHs 3, 4 and 5, respectively with time.
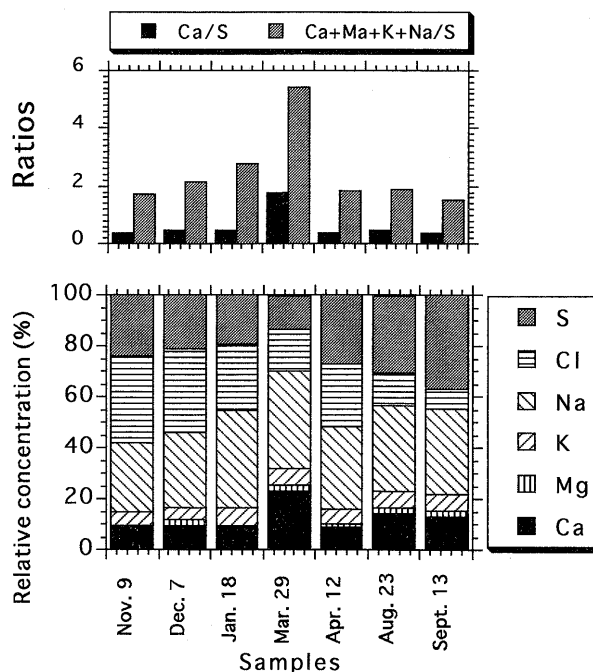

Fig. 12. Average relative proportions of elements dissolved in the immersing solution with distilled water after 24 days measured by EDX analysis.

ing. Ion balance is also in the side of anion ions. This may be the major reason why the pH of snow and rain water in winter is lower on the Japan Sea side of Japan than that in northern cities of China (Hirai et al., 1991 ; Kitamura et al., 1991 ; Kitamura, 1993 ; Kitada, 1994 ; Tazaki et al., 1995). Above results indicated that acid wet precipitation is depended not only on the SO_4^{2-} concentration in the atmosphere, but also on other factors such as the presence of alkaline materials or carbonate minerals available for neutralizing acids.

Conclusions

The mineral composition in the aerosols during a one year period from October, 1992 to September, 1993 was analyzed. Seasonal variations of major minerals were observed. Individual particle analyses led us to a better understanding of the relationship between aerosols and sulfur pollutants. Major conclusions may be summarized as follows.

1. About 48-68% of aerosols were composed of minerals, indicating that soil or crustal dusts had an important effect on the atmospheric quality. About 80% of fly ashes were rich in Al and Si, indicating that coal combustion was a major source.

2. A large amount of S constituents was detected in aerosols. They showed similarly seasonal variation to mineral aerosols and generally as submicrometer particles attaching to the surface of minerals and fly ashes. The association with mineral aerosols indicated that these S pollutants were transported by

and vegetation from rapid acidification and damage due to acid precipitates.

In some northern cities of China, such as Beijing and Tianjing, there are high SO_2 emissions which cause serious air pollutions, but no acid rain (Zhao et al., 1988). As shown in Table 6, rain water in Beijing and Tianjing contain SO_4^{2-} as nearly high concentration as in Chongqing and Guiyang where acid rain prevails, but the differences in NH_4^+ and Ca^{2+} concentrations among these regions lead pH in rain water different. Ion balance is apparently in the side of cation ions for the rain water in Beijing and Tianjing, whereas in the side of anion ions for those in Chongqing and Guiyang. In Kanazawa and Matsue, general ion concentrations in rain and snow water are lower than in China, but SO_4^{2-} is still higher in concentration than NH_4^+ and Ca^{2+} in comparison with Beijing and Tianj-

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Table 6. Concentrations of major ions and pH in the precipitations (μ eq/l).

Cities	Beijing	Tianjin	Chongqing	Guiyang	Kanazawa	Matsue
Years	1982	1982	1982-1984	1982-1984	1984-1989	1985-1988
pH	6.74	6.26	4.14	4.07	4.68	4.67
H^+	0.18	0.55	72.4	84.5	24.1	18.9
SO_4^{2-}	337.5	317.7	307.0	411.0	52.5	70.7
NO_3^-	81.0	29.2	31.6	21.0	6.7	16.2
Cl^-	59.1	183.1	15.0	8.2	139.9	160.9
NH_4^+	224.4	125.6	106.0	78.9	9.6	20.3
Ca^{2+}	760.0	287.0	110.0	231.2	16.7	28.4
Na^+	77.4	175.2	51.4	10.1	128.8	133.7
K^+	38.2	59.2	7.4	26.4	4.8	5.1
Mg^{2+}	---	---	48.3	56.5	18.5	37.8
Total anions	477.6	530.0	353.6	440.2	199.1	247.8
Total cations	1100.0	647.0	323.1	403.1	178.4	225.3
Ion balance	+622.4	+117.0	-30.5	-37.1	-20.7	-22.5
Data sources	Zhao et al., 1988	Zhao et al., 1988	Zhao et al., 1988	Zhao et al., 1988	Hirai and Chyouji, 1994	Yamaguchi et al., 1991

mineral aerosols during winter and spring.

3. Calcite and clay minerals were often closely associated with S constituents, suggesting that the former acted as carriers of sulfur pollutants and played an important role in the cycle of S constituents during transport.

4. Sample with high Kosa flux had a relatively large neutralization ability. This may related to a relatively high concentration of calcites contained in the sample. It is important not only for the partial neutralization of acids in a relatively short period of time during the long-range transport, but also for the protection of soil and vegetation from rapid acidification and damage due to acid precipitates.

Acknowledgments

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* : in Japanese with English abstract

** : in Japanese

（要　旨）

Zhou, G. and Tazaki, K., 1996, Mineralogical characteristics of aerosols collected at Matsue and Kanazawa - with a special reference to neutralizing effect on acid pollutants. *Jour. Geol. Soc. Japan,* 102, 787-803. （周　国平・田崎和江，1996，松江と金沢で採集したエアロゾルの鉱物学の特徴—特に酸性物質に対する中和作用の評価．地質雑，102，787-803.）

　ハイボリューム・エアサンプラーを用いて松江と金沢でエアロゾルを，また，金沢において雪および雨を採集し，その中の個体粒子を XRD および SEM-EDX で分析した．主要な粒子は地殻を構成する鉱物（48-68%），フライアッシュ（9-17%），イオウ微粒子（4-26%），海塩（0-3%），生物起源の粒子（1-5%）のほか，Zn，Cu，Al，V を含んでいる人為的な粒子（3-6%）とで構成されている．そのうち，フライアッシュ中には Al, Si を主成分とする粒子が 80% 存在する．SEM の観察結果より，イオウ微粒子はカルサイトおよび粘土鉱物に付着しており，これらはキャリアとしてイオウ汚染物質をアジア大陸から日本へ輸送する重要な役割を果たす．エアロゾルと人工酸性雨溶液の反応実験は，黄砂エアロゾルが大きな中和能力を持っていることを示した．また，雨の酸性度は単に大気中の SO_4^{2-} 濃度だけではなく，エアロゾル中に存在する粘土鉱物とカルサイトにも影響されることが示唆された．