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SEASONAL VARIATION OF GYPSUM IN AEROSOL AND ITS EFFECT ON THE ACIDITY OF WET PRECIPITATION ON THE JAPAN SEA SIDE OF JAPAN

GUOPING ZHOU and KAZUE TAZAKI
Faculty of Science, Kanazawa University, Kanazawa 920-11, Japan

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Abstract—Variations of mineral concentrations in aerosols collected weekly for a 1 yr period (from October 1992 to September 1993) on Matsue, Shimane Prefecture, Japan, were investigated by X-ray powder diffraction (XRD) analysis. Major elemental concentrations were measured by energy dispersive X-ray analysis (EDX). Sulfate minerals in aerosol include gypsum, ferricopiapite, metavoltine and glauberite. Gypsum showed two high concentration peaks during spring and early winter, which was consistent with that of clay minerals and quartz. The ratios of gypsum to clay minerals, quartz and calcite, respectively, showed an increase of gypsum in spring. A non-agreement of concentration distribution between calcite and other soil minerals during spring implies a conversion of calcite to gypsum during transport. Individual particle analyses by EDX revealed large amounts of S-rich submicrometer particles coated on the surface of minerals. A sequence favorable to be attached by S constituents was calcite (83%) > clay minerals (68%) > fly ash (55) > quartz and feldspars (36%) The reaction between calcite and simulated acid rain solution with pHs of 3, 4 and 5 showed a formation of gypsum in 12 h, indicating that the conversion of calcite to gypsum is possible in the presence of sulfuric acid or $(NH_4)_2SO_4$ aerosols during transport from the Asian continent to the Japan Islands. Copyright © 1996 Elsevier Science Ltd

Key word index: Seasonal variation of gypsum, long-range transport, sulfur coatings, calcite, neutralization.

1. INTRODUCTION

In recent years, air pollutants such as S-related compounds have caused some serious environmental problems. Especially on the Japan Sea side of Japan and the Pacific Ocean, the long-range transport of air pollutants from the Asian region has been given special attention (Duce *et al.*, 1980; Uematsu *et al.*, 1983; Dod *et al.*, 1986; Iwasaka *et al.*, 1988; Mukai *et al.*, 1990; Okada *et al.*, 1990; Tazaki *et al.*, 1990; Hirai *et al.*, 1991; Nishikawa *et al.*, 1991; Sekine and Hashimoto, 1991; Satake and Yamane, 1992; Kitamura *et al.*, 1993; Sekine *et al.*, 1993). Higher deposition rates of nss-sulfate in winter and early spring at Shimane, Toyama and Ishikawa, Japan and on the Oki islands in the Japan Sea have been reported (Mukai *et al.*, 1990; Hirai *et al.*, 1991; Yamaguchi *et al.*, 1991; Satake and Yamane, 1992). On the other hand, higher concentrations of nss-Ca^{2+} in rain water and snow during winter and especially early spring have also been observed on the Japan Sea side of Japan and the Pacific Ocean (Ichikuni, 1978; Suzuki and Tsunogai, 1988; Hirai *et al.*, 1991; Yamaguchi *et al.*, 1991; Satake and Yamane, 1992; Kitamura *et al.*, 1993). But these studies are almost on the basis of chemical analytical data of rain water and filtered snow water or water-soluble components of aerosol. The data about the concentration variation of calcite in aerosol have rarely been reported. Particularly gypsum has not been given large attention. The concentration variation of gypsum and a relationship between gypsum and calcite may contribute very important information on the conversion of acid pollutants such as SO_2 during transport.

The aims of this study are to characterize the concentration of gypsum in aerosols, its seasonal variation and relations to other mineral aerosols. For these reasons, the mineral composition in aerosols collected on Matsue, Shimane Prefecture, during a 1 yr period from October 1992 to September 1993 has been investigated. To investigate the conversion history of acid pollutants, experiments of reaction between calcite and simulated acid rain solutions were conducted.

2. SAMPLES AND METHODS

Samples. Aerosols were collected weekly with a high-volume air sampler (HVC-1000) on the roof (25 m from ground level) of the building of the Faculty of Science, Shimane University in Matsue, Shimane Prefecture, located on the Japan Sea side of Japan (Fig. 1). The sampling site is about 25 km from the Japan Sea. Matsue city has a population of approximately 140,000. There is no large pollution

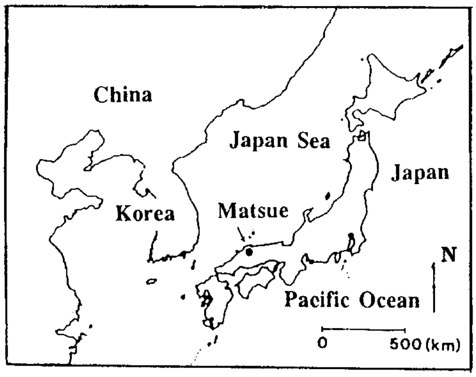

Fig. 1. Map showing the eastern Asian area and the sampling site on Matsue, Shimane Prefecture, Japan.

source compared with most cities on the Pacific Ocean coast of Japan (Yamaguchi *et al.*, 1991). Glass fiber filters (Toyo, GRB100R, 203 x 245 mm) were fitted with the sampler. Weekly sampling was done with a flow rate of 1000 $\ell \mathrm{min}^{-1}$ from October 1992 to March 1994. The filters were changed every Monday and kept in a refrigerator before analysis.

Mineral composition analysis. Aerosol samples collected during a 1 yr period from October 1992 to September 1993 were used to investigate a seasonal variation of major minerals. In order to know the primary concentration of minerals and to protect some water-soluble minerals in aerosols from dissolution and recrystallization during water extraction, an area with 2 x 2 cm was cut from each filter, attached to a glass slide and measured by X-ray powder diffraction (XRD) with a Rigaku, Rint 1200 system X-ray diffractometer with a CuKα radiation and accelerating voltage of 40 kV and an electric current of 30 mA. Relative concentrations of major minerals were expressed by peak intensity (CPS: counts per second) of the strongest reflection of each mineral. Determinations of the minerals were made according to the cards published by the Joint Committee of the Powder Diffraction Standard (JCPDS).

Elemental concentration measurement. To complement XRD results, major elemental concentrations were measured in the area of 400 x 300 μm on the 1 x 1 cm filter which was analyzed by XRD. Elemental concentration measurement was conducted using a Philips-EDAX PV9800 STD energy dispersive X-ray analyzer (EDX) attached to a JEOL-JSM-5200LV scanning electron microscope (SEM). Operational conditions were as follows: an accelerating voltage of 15 kV and an analytical time of 200 s. The analyses were limited to elements with Z (atomic number) > 11. Conversion of intensities into concentrations was accomplished using a standardless ZAF (Z = atomic number, A = absorption, F = fluorescence) correction program set in a computer. Concentrations of elements were normalized as wt%.

Reaction experiment of calcite with simulated acid rain solutions. To investigate the conversion of calcite to gypsum during long-range transport, simulated acid rain solutions with pHs 3, 4 and 5 were prepared using H_2SO_4 solution ($10\,\mu\mathrm{l\,ml}^{-1}$) added by $(NH_4)_2SO_4$. 0.01 g of pure calcite powders (5 μm size on the average) were immersed with 20 ml simulated acid rain solutions with pHs 3, 4 and 5, respectively. After samples were stood for different times at room temperature, the pH of the solutions was measured using a Twin Cont pH meter (HORIBA). The solution after 12 h reaction was filtered with a membrane filter (0.45 μm of pore diameter) using an aspirator and evaporated slowly at a temperature lower than 60°C. Solid materials left behind after evaporation were analyzed by SEM-EDX.

3. RESULTS AND DISCUSSION

3.1. *Major sulfate minerals in aerosols*

Major sulfate minerals detected by XRD analysis with the help of SEM-EDX analysis in this study are listed in Table 1. Other associated minerals include clay minerals, quartz, feldspars, iron oxide minerals, calcite and halite. Gypsum was detected in most of the samples which showed aggregates of irregular particles. It associated generally with soil, fly ash and glauberite particles (Fig. 2a). Glauberite showed typically needle-like crystals and generally formed radical aggregates (Fig. 2b). Gypsum results generally from the following major sources: (1) the spatter of wave-produced bubbles at the sea surface (Andreae *et al.*, 1986); (2) arid soils (Tanaka *et al.*, 1985; Chang *et al.*, 1995); (3) desulfurization by electric power plants in Japan (Satake and Yamane, 1992); and (4) by-products from coal combustion (Fisher *et al.*, 1978). Glauberite is a widespread constituent of salt deposits both of oceanic and lacustrine origin (Dana, 1951). It is also found in clastic sediments and salty clay layers formed in arid regions. Metavoltine and ferricopiapite were characterized by small irregular particles and associated with soil particles. These minerals generally occurred as secondary minerals in some ore areas such as coal mines and soils. Ferricopiapite can be formed by the oxidation of sulfides, especially pyrite. They can also be formed from some iron oxide hydroxides such as lepidocrosite (FeO(OH)) when sulfur compounds are present (Dana, 1951). Among sulfate minerals, gypsum showed a significant seasonal variation in concentration.

Table 1. Major sulfate minerals detected by XRD analysis

Minerals	Chemical composition	Major *d*-values
Gypsum	$CaSO_4 \cdot 2H_2O$	7.60 Å, 4.27 Å, 3.06 Å
Glauberite	$CaNa_2(SO_4)_2$	3.13 Å, 3.11 Å, 3.18 Å
Ferricopiapite	$Fe_{4.67}(SO_4)_6(OH)_2 \cdot 20H_2O$	9.60 Å, 5.58 Å, 3.58 Å
Metavoltine	$Na_6K_7Fe_9(SO_4)_{12}O_2 \cdot 18H_2O$	9.08 Å, 3.76 Å, 3.29 Å

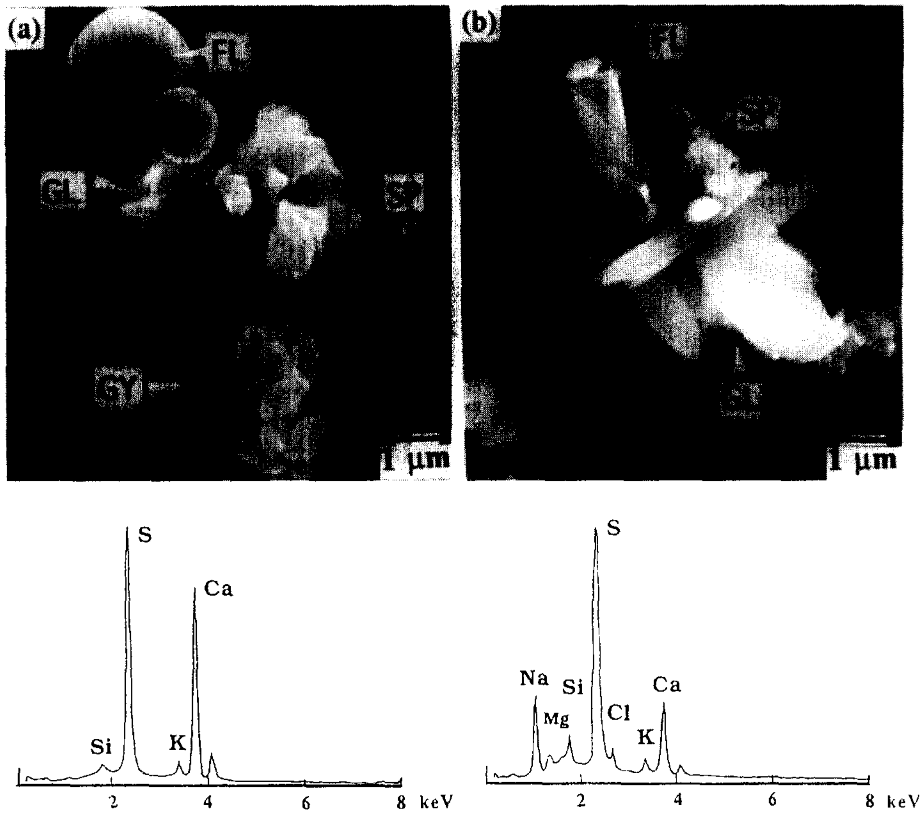

Fig. 2. Scanning electron micrographs and energy dispersive X-ray analyses of aerosols collected in the period from 29 March to 4 April 1993 on Matsue. (a) Gypsum aggregates (GY) associate with soil particles (SP), glauberite (GL) and fly ash (FL). (b) Radical aggregates of glauberites (GL) were attached by small soil particles (SP) and fly ash (FL). EDX spectra were obtained by spot analyses on the center of both gypsums and glauberites.

3.2. *Concentration variation of gypsum in aerosols*

Figure 3 shows concentration variations of gypsum, clay minerals, calcite, quartz and halite in aerosols during a 1 yr period. Arrows show the Kosa phenomena recorded by the Meteorological Station of Shimane Prefecture. Table 2 lists the average concentrations of major minerals (detected by XRD analysis) and S, Al, Fe elements (measured by EDX analysis) of aerosols in different seasons. Gypsum concentration showed two higher peaks during spring and early winter, respectively. This variation trend was generally consistent with that of quartz and clay minerals. Particularly, the average concentration of gypsum was nearly two times higher in spring than other seasons (Table 2). Kosa phenomena were principally characterized by higher concentrations of clay minerals and quartz. EDX analysis also showed that Al and Fe concentrations were lower in non-Kosa seasons and increased sharply in spring (Table 2). In this study, XRD results did not show very high concentrations of calcite during the periods that Kosa phenomena were recorded. Calcite only showed slightly higher trends during spring and early winter in comparison with other soil minerals. Halite had a different pattern, showing a higher concentration during winter.

3.3. *A relative increase of gypsum during long-range transport*

As shown in Fig. 3, calcite did not show a high concentration as other soil minerals in spring. This non-agreement may suggest two possibilities. (1) The concentrations of calcite or gypsum largely depended on soil dust sources. Soils from Chinese loess plateau are poor in gypsum (Liu, 1988; Tazaki *et al.*, 1990; Nishikawa *et al.*, 1991; Zhang *et al.*, 1994), whereas soils from some arid deserts are rich in gypsum (Tanaka *et al.*, 1985; Chang *et al.*, 1995). For example, gypsum is one of the most commonly occurring sulfate minerals in the desert soils of Tarim Basin, northwest of China (Chang *et al.*, 1995). It is possible that the small-sized gypsum particles are blown up into the atmosphere in association with soil dust when the dust storm particles are transported from arid deserts. (2) It could imply a conversion of calcites to gypsum during transport. It can be found from Table 2 that the mean concentration of gypsum is 2.2 times higher in spring than in summer, whereas calcite is only 1.87 times. It is also lower than quartz (3.5 times) and clay minerals (2.2 times). Figure 4 shows changes in ratios of gypsum to clay minerals, quartz and calcite, respectively, in aerosols in Matsue, Japan.

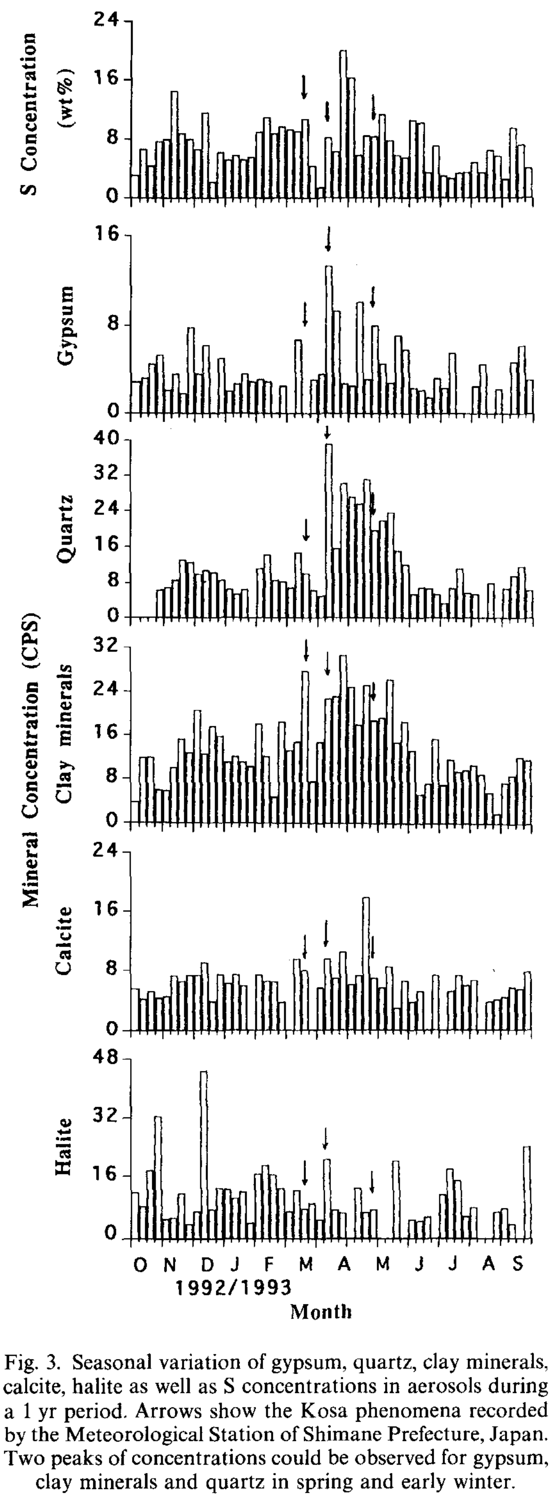

Fig. 3. Seasonal variation of gypsum, quartz, clay minerals, calcite, halite as well as S concentrations in aerosols during a 1 yr period. Arrows show the Kosa phenomena recorded by the Meteorological Station of Shimane Prefecture, Japan. Two peaks of concentrations could be observed for gypsum, clay minerals and quartz in spring and early winter.

The same ratios in road dust in northern cities of China (Beijing, Shengyang and Dalian), Seoul, Korea, and Matsue, Japan, were plotted as different lines in the graph. Firstly, the ratios in aerosol in Matsue are generally higher than that in road dust in any area, suggestive of a relative increase of gypsum during transport. The following factors could increase partially the concentration of gypsum in aerosol during transport: (1) coarser quartz, calcite, and partial clay minerals may deposit more closely to the continent; (2) an addition of sulfates from the Japan Sea; (3) an addition of local dust containing gypsum in Matsue. Especially, the increase of gypsum in autumn and early winter could be related to the desulfurization of power electric plants in Japan (Satake and Yamane, 1992). But all the ratios show higher peaks during spring, suggesting that the increase of gypsum in spring is related to northwestern monsoons which could transport a part of gypsum with soil dust from Asian desert areas.

However, if we consider Al_2O_3 as a representative composition of clay minerals in arid soils, in spring the mean ratio (0.30) of gypsum/clay minerals in aerosols in Matsue was 10 times higher than the ratio (0.03) of $CaSO_4/Al_2O_3$ (calculated from the data of Nishikawa *et al.*, 1991) in surface soil from the Taklamakan desert. Such a high concentration of gypsum during spring could not be completely contributed by desert soil dust. This leads us to infer that partial gypsum could have resulted from the reaction between calcite and H_2SO_4 during transport. Other investigators also reported the possibility by S/Ca ratios, individual particle analyses and ion equivalent balance in water-soluble constituents of Kosa aerosol (Iwasaka *et al.*, 1988; Winchester, 1989; Okada *et al.*, 1990; Nishikawa *et al.*, 1991; Yamaguchi *et al.*, 1991; Satake and Yamane, 1992). In this study, a reaction experiment was conducted to investigate the possibility.

3.4. *Conversion of calcite to gypsum during transport*

Figure 5 shows changes in the pH of the system when calcite reacted with simulated acid rain solutions with pHs 3, 4 and 5, respectively, at room temperature. Initial reactions were quick and solutions with pHs 3, 4 and 5 were neutralized at pHs of 7.0, 7.1 and 7.3, respectively. After 2 h, these solutions all showed pHs at 7.4. They were all saturated at pHs of 7.6–7.7 after 10 h. This trend was kept continuously in the latter 12 h except for the solution with pH 3 displaying a slight increase in pH. Figure 6 shows a SEM photograph of needle-like gypsums crystallized from the filtered solution with pH 3 after 12 h reaction. If we consider that 24 h is an average time for soil dust transported from the Asian continent to the Japan Islands (Iwasaka *et al.*, 1988), a part of calcites could be converted to gypsum through the reaction with acid pollutants. For some northern cities of China, such as Beijing and Tianjin, rain water contains very high SO_4^{2-} (162.5–337.5 $\mu eq\,l^{-1}$) (Zhao *et al.*, 1988), suggesting a relatively high concentration of sulfur compounds present in the atmosphere. They could be transported associated with soil dust during the period of northwestern monsoon prevailing. SEM observations and EDX analyses of aerosols in Matsue revealed that about half of the fly ash particles and

Table 2. Mean concentrations of major minerals and S, Al, Fe elements of aerosols in different seasons

Mineral and element	Gypsum[a] (CPS)	Quartz[a] (CPS)	Clays minerals[a] (CPS)	Calcite[a] (CPS)	Halite[a] (CPS)	S[a] (wt%)	Al[a] (wt%)	Fe[a] (wt%)
Spring[b]	5.5	20.4	20.6	7.7	8.5	9.38	8.88	5.22
Summer[b]	2.5	5.9	9.5	4.1	6.4	5.29	4.39	1.26
Autumn[b]	3.8	6.8	9.6	4.7	11.2	6.70	6.27	2.56
Winter[b]	2.6	8.2	13.6	5.6	14.5	7.34	6.31	2.99

[a] Arithmetic mean concentration; [b] spring (March–May); summer (June–August); autumn (September–November); winter (December–February).

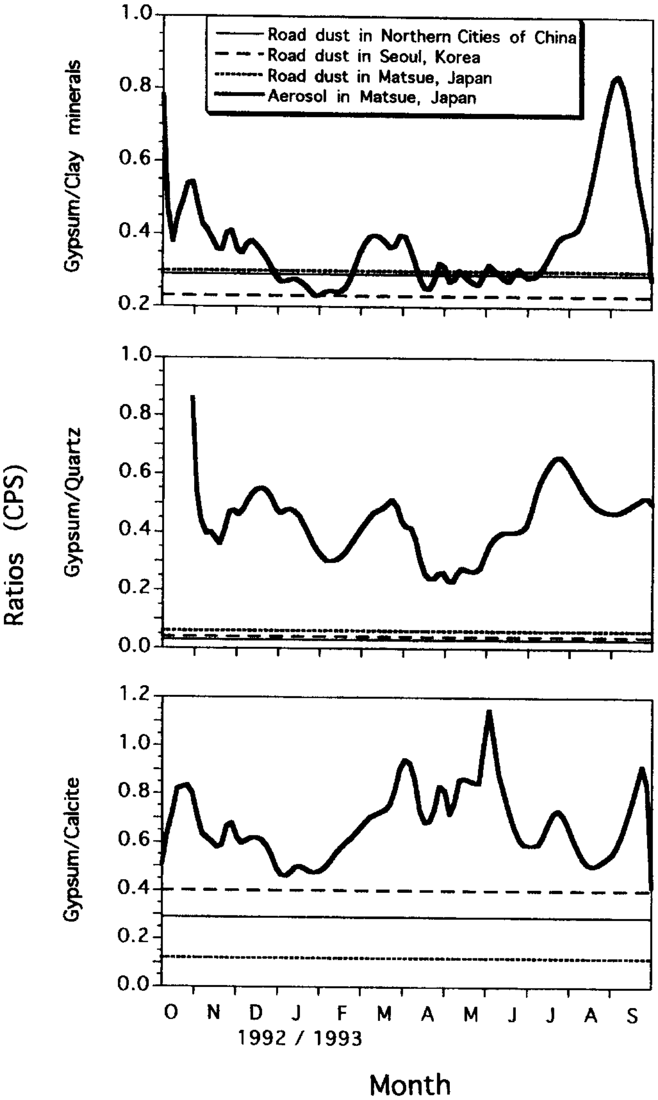

Fig. 4. Changes in the ratios of gypsum to clay minerals, quartz and calcite, respectively, in aerosols in Matsue, Japan. The same ratios in road dust from northern cities of China, Seoul, Korea and Matsue, Japan, are plotted as different lines. The ratios are mean values of four samples for China and Korea, and two samples for Matsue. It is apparent that all the ratios have peaks in spring corresponding to Kosa periods (March–May).

most of the carbonaceous soots were covered by S constituents on the surface (Zhou and Tazaki, 1996). A part of the soil particles, mainly calcite and clay minerals, were found to be coated by S-rich fine particle aggregates. A statistical analysis of individual particles of SEM-EDX showed the following sequence favorable to be attached by S constituents: calcite (83%) > clay minerals (68%) > fly ash (55)

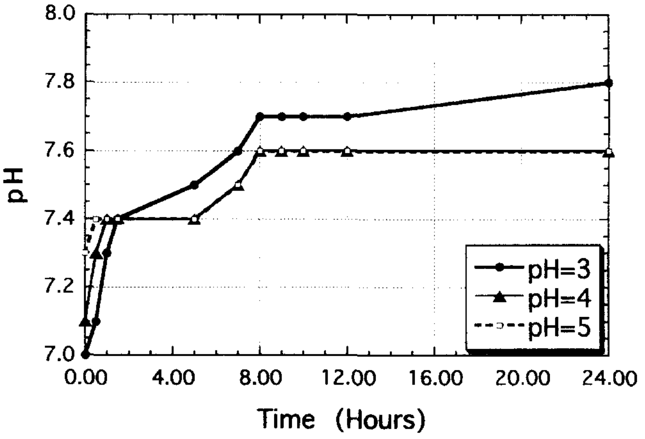

Fig. 5. pH changes in the system when calcite reacted with simulated acid rain solutions with pHs 3, 4, and 5, respectively, at room temperature. Experimental conditions were described in Section 2. The solutions were quickly neutralized in the initial reactions and were saturated at pHs of 7.6–7.7.

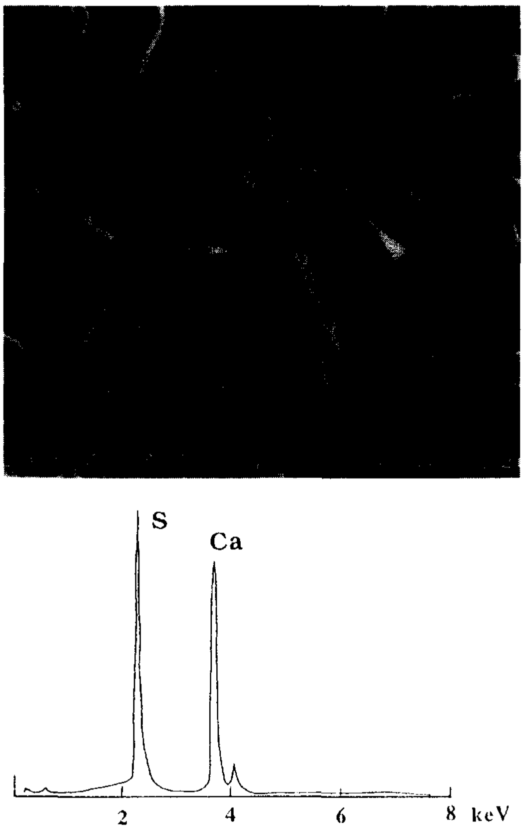

Fig. 6. A scanning electron micrograph and the result of energy dispersive X-ray analysis, showing needle-like gypsums crystallized from a filtered solution with pH 3 after 12 h reaction. The EDX spectrum is from the spot analysis on one of the gypsum crystals (arrow). Granular particles are ammonium sulfate crystals.

> quartz and feldspars (36%) (Zhou and Tazaki, 1996). Figure 7a shows fine S-rich particles coating the surface of soil particles. A spot analysis by EDX on the center of S-rich particles showed a strong S peak and a high background. Observations by a transmission electron microscope revealed that these S-rich particles were submicrometer carbonaceous soots coated with sulfur films on the surface. During winter, spherical or irregular particles with S as the only composition were commonly observed in snow samples collected directly using a Cu grid of transmission electron microscope (Fig. 7b). These results indicated that a considerable amount of S constituents were transported with soil particles to Japan. It could be considered that soil particles played an important role as carriers or reaction sites during transport.

As demonstrated by this experiment, gypsum could form from the reaction between calcite and sulfur compounds during transport. Therefore, an increase of gypsum in spring revealed that a part of acid pollutants could have been neutralized by calcite. This may be important for lowering the acidity of a wet precipitation on the Japan Sea side of Japan and for the protection of soil and vegetation from the damage due to acid precipitation.

5. CONCLUSIONS

From our study of the mineral compositions of aerosols collected in Matsue, Shimane Prefecture, the major conclusions are summarized as follows.

(1) Gypsum, as a common sulfate mineral in aerosols, shows two higher concentrations during spring and early winter. The same tendency of seasonal variation with quartz and clay minerals indicates that a part of the gypsums was transported from Asian deserts.

(2) Sulfur coatings on the surface of minerals were commonly observed by SEM-EDX analyses. Calcite

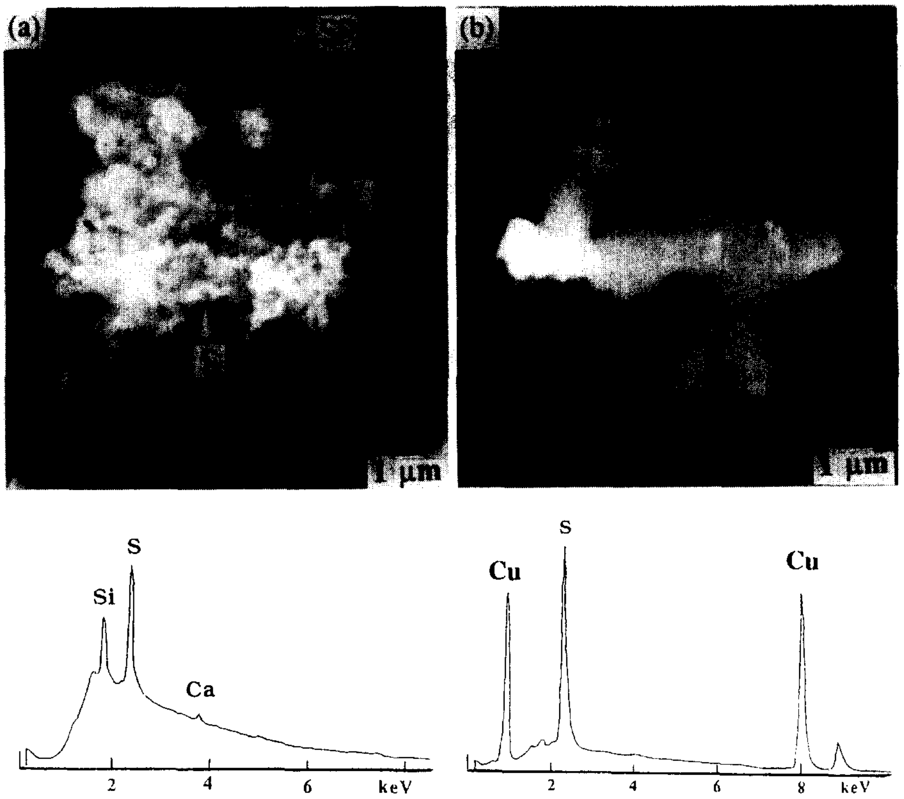

Fig. 7. Scanning electron micrographs and the results of energy dispersive X-ray analyses. (a) Aerosols collected in the period from 9–15 November 1992 on Matsue, showing fine S-rich particles (S) covering the surface of soil particles (SP). A spot EDX analysis of fine S-rich particles shows a strong S peak with a high background. Si and Ca peaks are from soil particles. (b) Sulfur compounds in snow collected on 14 January 1995 in Kanazawa using a Cu grid of transmission electron microscope, showing only the S peak in the EDX spectrum and two other strong peaks of CuKα and CuKβ are from the Cu grid.

was the most favorable to be attached by S constituents, which implies a possibility of reaction between calcite and S constituents.

(3) A non-agreement of concentration distribution between calcite and other soil minerals could imply a part of the calcites being converted to gypsum during long-range transport. The experiment in this study indicated that after 12 h, gypsum formed from the reaction of calcite with simulated acid rain solutions. This duration is in the scale of average time (24 h) for soil dust transported from the continent to the Japan Islands.

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