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Characteristics of single particles sampled in Japan during the Asian dust–storm period

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Abstract

To investigate the characteristics of Asian dust storm particles as single particles in Japan, we measured morphology, composition and concentration of single particles using Scanning Electron Microscope (SEM) coupled with an energy dispersive X-ray microanalyzer (EDX), particle induced X-ray emission (PIXE) and micro-PIXE. Particles were sampled in Kyoto, Japan from the middle of April to the end of July 1999. Mass concentration in Asian dust–storm events was roughly 3–5 times higher than that of the highest concentration measured in non-Asian dust storm seasons. Single particles were generally sharp-edged and irregular in shape and contained mostly crustal elements such as Si, Fe, Ca and Al. Particles which have more than 40% Si content comprised nearly 50% of coarse single particles in Asian dust storm events. Main concentration range of Al in single Asian dust storm particles was 10–20%, and those of Ca and Fe were below 10%. Even though S and Cl in soils of the desert and loess areas in northwest of China were not detected, significant concentration of S and Cl in coarse fraction in Asian dust storm event were detected in single particles. Especially, the maximum concentration of S in Asian dust storm event was about 5 times higher than that in non-Asian dust storm days. Every single particle in coarse fraction existed as the mixing state of soil components and S. Good agreement between the results of SEM–EDX analysis and that of micro-PIXE analysis was obtained in this study.

Keywords: Asian dust storm; Single particle; Long-range transport; Micro-PIXE; Mixing state

1. Introduction

Asian dust–storm (hereafter called "ADS") often occurs at desert and loess areas in northwest of China traverses China continent and can be extended to Pacific ocean, passing through Korea and Japan in every spring time. This dust is blown up by strong wind behind the cyclone and delivered in free troposphere by westerly jet. Even though ADS is a peculiar phenomenon occurred in China continent, this ADS have led to the significant environmental change in East Asia and North Pacific ocean for a long time.

Although ADS can cause many disasters, it is said that ADS make a contribution to the neutralization of acid rain caused by consumption of a large amount of fossil fuels. By use of a simplified reaction model between SO_2 and NO_2 in the ambient air and various oxides in a ADS particle, Kim et al. (1997) predicted that K_2O, Na_2O and CaO in a 9 μm ADS particle are consumed as much as 51.3, 30 and 9.8%, respectively, by reacting with SO_2 and NO_2 in the atmosphere during the long-range transport through East Asia. ADS particles, therefore, play the role of both bringing SO_2 and NO_2 with them from China and neutralizing SO_2 and NO_2 over Korea and Japan.

A large number of studies on the ADS aerosols have been reported (Duce et al., 1980; Darzi et al., 1982; Braaten et al., 1986; Iwasaka et al., 1988; Nishikawa et al., 1991; Zhang et al., 1998; Ma et al., 1999). However, only a few studies on the ADS aerosols as the single particles,

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which can provide detailed information about the nature and composition of single particles were reported.

Investigation of the properties of single aerosol particles is an essential prerequisite for understanding chemical reactions in the atmosphere (Hinz, 1998).

Single-particle analysis has the advantage of providing a great amount of information that cannot be otherwise obtained using methods of bulk analysis. And single-particle analysis needs a short sampling time and a small sampling mass for analysis. This allows for a better determination of the temporal variation of the component concentrations in aerosol particles. Moreover, in some cases the single-particle analysis data can be used for "finger printing" diverse aerosol, natural as well as anthropogenic.

In this paper, to determine the nature of ADS particles as single particles in Japan, we measured morphology, composition and concentration of single ADS particles. And concentration of soil samples collected at two loess areas and one desert area in China was compared to that of single particles collected in ADS events. Added to this, an attempt was made to acquire more detailed information such as inner structure and mixing state in the single particles by micro-PIXE analysis.

2. Experimental

2.1. Sampling

For sampling of ambient aerosols, two-stage filter pack sampler was operated at a height of 20 m above ground level of the Kyoto University building located in Kyoto, Japan from the middle of April to the end of July, 1999. Several weak and moderate ADS events were occurred in the early stages of our experimental period. Locations of sampling sites indicated by filled circles are given in Fig. 1. The surroundings of aerosol sampling site are residential and agricultural areas with no major point sources. There are no nearby structures taller than sampling site. An east–west highway, with usually moderate traffic, is located 1 km south of the aerosol sampling site.

Two-stage filter pack sampler collected the coarse and fine fraction of the aerosol separately on the first stage filter (a 47 mm diameter, 8 μm pore size Nucleopore polycarbonate filter) and the second stage filter (a 47 mm diameter, 0.4 μm pore size Nucleopore polycarbonate filter), respectively, with 25 l min^{-1} flow rate. The nominal thickness of these filters is 10 μm. The equivalent aerodynamic cut-off diameter of the first-stage filter at this flow rate was estimated to be about 1.2 μm equivalent aerodynamic diameter (Kasahara et al., 1996). During this sampling period, the range of wind speed was 3.4–4.5 m s^{-1}, and it was generally blowing from the west. The temperature was around 19.3–27.7°C and relative humidity in those days was around 24.1–36.6%. In our experiment, two-stage filter pack sampler was operated for 6 h. And 12 and 15 set of samples were collected in ADS events and on non-ADS days, respectively.

2.2. Analysis

A scanning electron microscope (SEM) coupled with an Energy-Dispersive X-ray microanalyzer (EDX) has

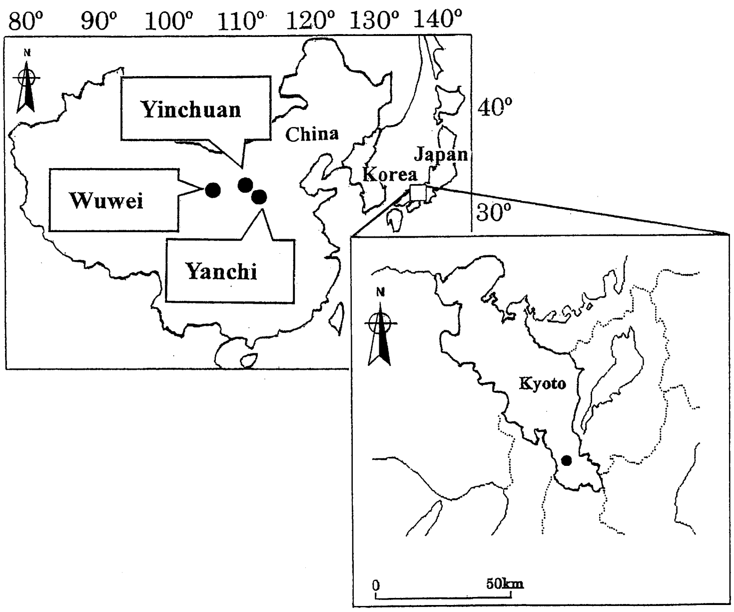

Fig. 1. Aerosol sampling site in Japan and soil collection sites at three desert (loess) areas in China.

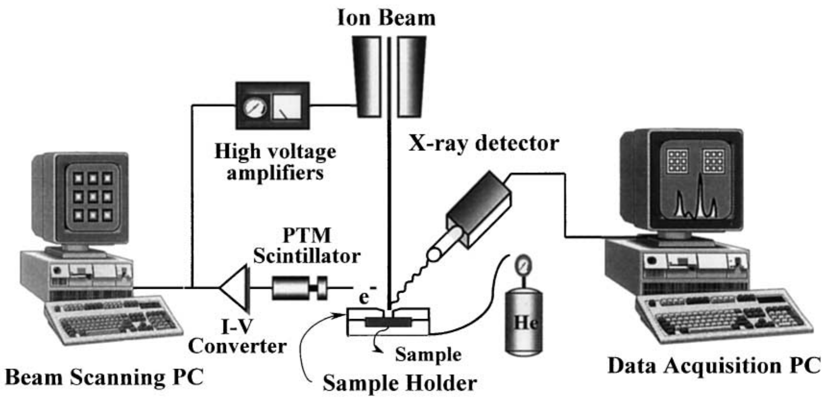

Fig. 2. Schematic diagram of the beam scanning and data acquisition system of micro-PIXE.

been used for quantitative element analysis of single-particles in many air pollution studies (Haapala, 1998). SEM–EDX system can provide single-particle surface morphology, particle number concentration and size distribution, and elemental composition qualitatively and semi-quantitatively (Farn et al., 1990). However, it has the disadvantage of being very time consuming. Furthermore, because particles were subjected to high vacuum (10^{-6} Torr) and an intense electron beam during SEM–EDX analysis, accurate quantitation can be hampered by the loss of volatile components.

In this study, the analysis of the single particles was performed by a SEM S-2000 equipped with a parylene window EDAX DX-prime for X-ray microanalysis by energy dispersion spectrometry. Portions of filters were mounted on SEM sample stubs and then coated with thin platinum film by cathodic sputter (HITACHI E102). For calibration of energy, Al–Cu autocalibration method was applied in this study. Cu ($K_\alpha = 8.04$ keV) standard plate laid on the Al ($K_\alpha = 1.486$ keV) sample stage was analyzed under the 15 kV and about 2000 cps analytical conditions. The working conditions of SEM–EDX were 15 kV for the energy dispersive analysis and 100 s for X-ray collection.

To acquire more detailed information such as inner-structure and mixing state in the single particles, micro-PIXE analytical measurement was performed with the facilities of the Takasaki Ion Accelerators for Advanced Radiation Application, Japan.

Fig. 2 indicates the schematic diagram of the beam scanning and data acquisition system of micro-PIXE. Beam scanning, data acquisition, evaluation and the generation of elemental maps are controlled by a computer on the basis of the system program. *X–Y* beam scanning control signals, which indicate the beam position, are also digitized at the same time. These data are addressed to the 3D matrices in the memory space, that consist of 1024 channels for the energy spectra and 128×128 pixels for corresponding the beam scan area. Real time data processing can be done in addition to this data acquisition by the fast processor with the large memory (Ishii et al., 1996). After selecting the process of ideal portion by digital microscope, the sample was attached onto the sample holder. Target portion was allocated by STIM (Scanning Transmission Ion Microscope) method. This STIM is the method that can get the image of sample thickness by detecting the transmitted beam amount, i.e. proton energy loss after irradiation of very weak beam current. It is commonly used in STIM analysis to improve energy and mass–thickness resolutions by increasing the number of detected ions per scan position (Simons et al., 1997). The field scanned for each sample represents only a very small fraction of the total sample area analyzed by micro-PIXE. Beam collection time was about 30–40 min.

Particle-induced X-ray emission (PIXE) was used for analysis of bulk soil samples collected at three source areas in China. PIXE analysis was performed with a proton beam of 6 mm diameter and 2.0 MeV energy from a Tandem Cockcroft accelerator. Beam intensities from 10 to 60 nA were employed and the total doses were about 20 μC. The calibration method was similar to those described in elsewhere (Kasahara et al., 1993) and was noted here briefly. The relationship of X-ray yield and the mass thickness was measured first using the 18-single-element standard samples that were prepared by a vacuum deposition method. The sensitivity defined by (PIXE yield per unit dose)/(mass thickness) were determined experimentally and theoretically for all objective elements. The more detailed analytical procedures and experimental set-up used for PIXE were described elsewhere (Kasahara et al., 1996).

Table 1
Concentration of each element in soil collected at loess and desert areas in China

	Loess areas				Desert area	
	Yinchuan		Yanchi		Wuwei	
	Conc. ($ng\,mg^{-1}$)	Ratio	Conc. ($ng\,mg^{-1}$)	Ratio	Conc. ($ng\,mg^{-1}$)	Ratio
Si	568.4	1.00	2863.0	1.00	2062.6	1.00
S	—	—	—	—	—	—
Cl	—	—	—	—	—	—
K	34.5	0.06	187.9	0.07	154.5	0.07
Ca	15.2	0.03	115.9	0.04	106.6	0.05
Ti	8.7	0.02	22.9	0.01	14.7	0.01
V	1.3	< 0.01	6.4	< 0.01	4.7	< 0.01
Cr	0.5	< 0.01	3.7	< 0.01	2.2	< 0.01
Mn	1.1	< 0.01	7.9	< 0.01	4.8	< 0.01
Fe	42.8	0.08	227.5	0.08	149.0	0.07
Ni	—	—	2.0	< 0.01	1.1	< 0.01
Cu	0.8	< 0.01	3.5	< 0.01	2.2	< 0.01
Zn	0.1	< 0.01	1.6	< 0.01	0.9	< 0.01
Br	0.9	< 0.01	1.8	< 0.01	1.6	< 0.01
Pb	0.4	< 0.01	3.0	< 0.01	1.7	< 0.01

3. Results and discussion

In order to understand the sources of the many distinct types of single particles observed in the receptor area, it is necessary to investigate sources. It is presumed that ADS particles can be altered by such mechanism of absorption and oxidation during their long-range transport. To find out these variations of ADS components, it is desirable to investigate the soil component in desert and loess areas in China.

In this study, three kinds of soil in desert and loess areas of China (filled circles in Fig. 1) were collected. And bulk soil samples were analyzed by PIXE. Table 1 shows the elemental concentration of each soil collected at two loess areas and at one desert area in China. Unfortunately, Al could not be analyzed by PIXE. As expected Si and other crustal elements showed overwhelmingly high concentration, and S and Cl were not detected at every area. Ratio means the concentration ratio of each element to that of Si.

The range of mass concentration was 51.7–100.1 $\mu g\,m^{-3}$ in ADS events. Although highest mass concentrations were recorded in December 1998 in Japan, mass concentration in ADS events was roughly 3–5 times higher than that measured in December 1998 by Ma et al. (1999). This result was relatively low compared to that of strong ADS event.

It is easy to neglect the effects of weak ADS event because meteorological observations have difficulty in detecting weak ADS. Iwasaka et al. (1988) reported that weak ADS can give an important effect on a global geochemical cycle of soil, since its appearance is extremely frequent in comparison with strong ADS. From this point of view, the effects of weak ADS cannot be negligible. Pueschel (1995) estimated that about ~90% of the natural aerosol emissions originated from desert/loess areas or marine. Thus, both the mineral dust and sea-salt particles have a significant influence on tropospheric chemistry and biogeochemical cycles.

Fig. 3 illustrates typical example of the morphology and X-ray spectrum of the coarse particle collected on Nucleopore filters during the ADS period. For each sample, 30–40 particles were randomly selected for elemental analysis of single particles by SEM–EDX. Particles were generally sharp-edged and irregular in shape and contained mostly crustal elements such as Si, Fe, Ca and Al. Even though, C and O were detected, they were not considered in the data analysis because they are major components of polycarbonate filters.

After finishing the quality analysis, selected component can be dotted on the particle image by the regions of interest (ROI) mapping function of EDX. By means of this method, it is possible to show the distribution of components in and/or on the single particles. In Fig. 3(b), the white dots are the portions, which detected Si in and/or on a single particle sampled in ADS event by X-ray energy. Si was distributed nearly in all the portions of single ADS particle.

Fig. 4 shows the distribution of element concentration of single-coarse particles in ADS and non-ADS days. In

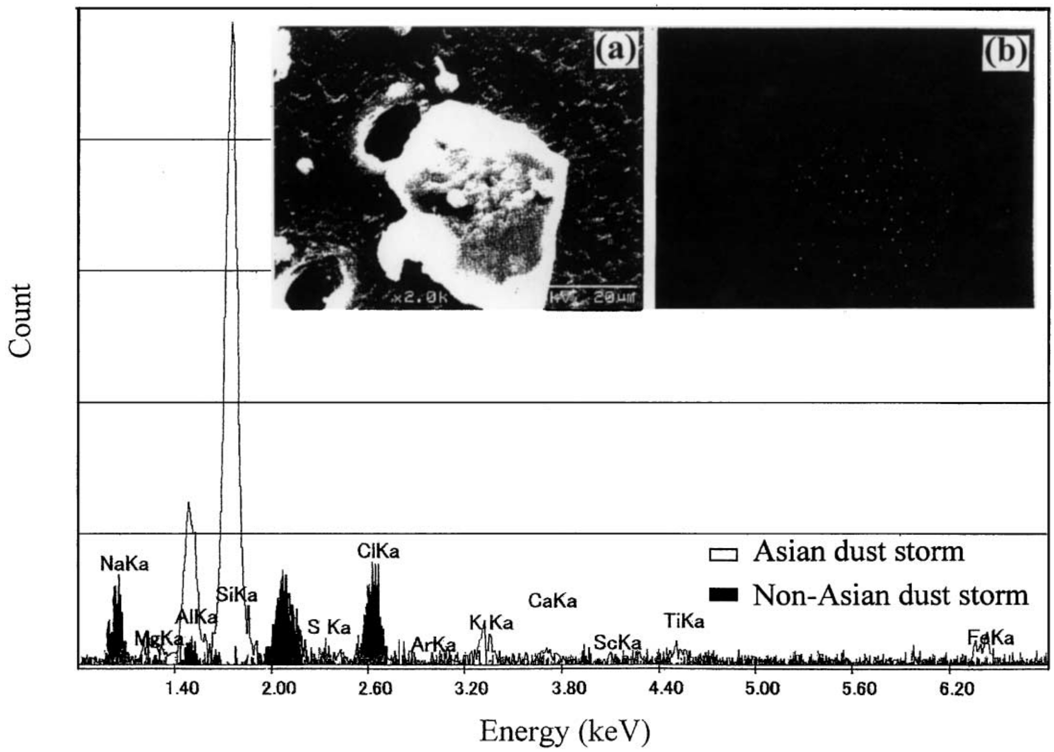

Fig. 3. X-ray spectrum, SEM image (a) and Si map (b) of single coarse particle collected in Asian dust storm event.

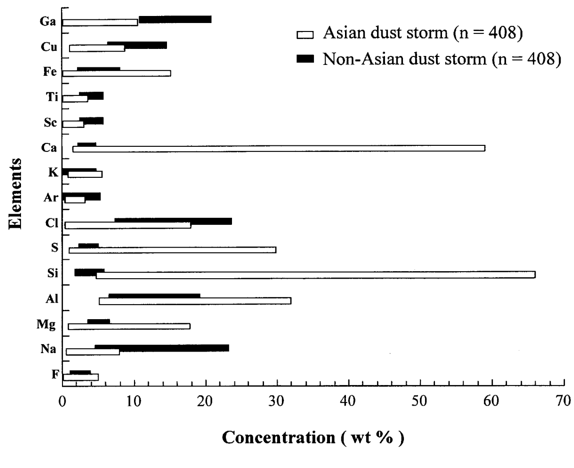

Fig. 4. Distribution of elemental concentration of single coarse particles sampled in Asian dust storm events and non-Asian dust storm days.

ADS event the major component of coarse particles were Ca, Si, Al and S. And wt% concentration range of those was wide compared to other elements.

In particular, Ca and Si concentrations show a wide range of particle-to-particle variation in composition. The maximum concentration of S in ADS events was about 5 times higher than that in non-ADS days. Almost all of single particles sampled on ADS days did contain sulfur and chlorine. In particular, high frequencies of chlorine were reported in other areas of Japan because dust particles are absorbed or coalesced with particles containing sea salt during the long-range transport (Wang et al., 1996).

While on the other, high Cl concentration on non-ADS days compared to that on ADS days in this study, may be caused by marine components transported from Osaka bay (about 40 km southwest from the Kyoto sampling site) by southwest winds on non-ADS days.

Added to the elemental analysis of single particles by SEM–EDX, Standardless quantify oxide method of EDX was applied to analysis of oxides in single-ADS particles under the assumption that each element exists as oxide. Total of 14 oxides including SiO_2 and Al_2O_3 were analyzed. Percentage concentration of each element and oxide detected by SEM–EDX are presented in Table 2. Sum of soil components such as Si, Fe, Ca and Al comprised 69.9%. Marine component was also present on most of the particles in 5.4% (sum of Na and Cl). Sulfur, as one of the major anthropogenic pollutants, was found to be distributed in all particles (3.95% in average). And Fig. 5 shows frequency of wt% of major elements and oxides analyzed by SEM–EDX with ZAF Standardless method and Standardless quantify oxide method, respectively. Particles which have more than 40% Si content comprised nearly 50% of coarse single particles in ADS events. Main concentration range of Al in ADS single particles was 10–20%, and those of Ca and Fe were below 10%.

Furthermore, to investigate more detailed information on single ADS particles individual particles on the two-stage filter pack sampler were analyzed by micro-PIXE. Micro-PIXE measurements was performed with a scanning 2.5 MeV H^+ micro-beam accelerated by 3 MV single-end accelerator. Beam diameter and beam current were 1 to 2 μm and > 100 PA, respectively. This narrow beam diameter allowed us to analyze single particles. Separate single particle appearing in the full spectral area maps taken with 25 μm × 25 μm scanning area were subjected to individual spectrum measurements for elemental analysis.

Table 2
Concentration of each element and oxide of single coarse particles sampled in Asian dust storm events

	Elements (wt%)				Oxides (wt%)		
	Min.	Max.	Average		Min.	Max.	Average
F	—	5.55	1.84	F_2O	0.85	7.13	3.11
Na	0.44	7.42	2.54	Na_2O	—	29.07	5.18
Mg	0.69	16.65	3.67	MgO	—	15.33	3.40
Al	4.82	29.90	14.31	Al_2O_3	4.19	29.53	16.12
Si	4.38	61.79	36.60	SiO_2	6.23	80.50	38.03
S	0.79	27.96	3.95	SO_4	0.50	12.39	3.77
Cl	0.31	16.70	2.84	Cl_2O	0.30	4.39	1.46
Ar	0.33	2.96	1.20	—	—	—	—
K	0.67	5.20	2.87	K_2O	—	3.45	1.61
Ca	1.37	55.36	13.15	CaO	1.19	37.70	6.28
Sc	—	2.86	1.29	Sc_2O_3	—	5.70	1.34
Ti	—	3.29	1.64	TiO_2	—	4.45	1.51
Fe	—	16.63	5.83	Fe_2O_3	1.75	50.68	6.93
Cu	1.04	8.18	4.23	CuO	1.39	9.82	4.08
Ga	—	12.77	5.94	Ga_2O_3	1.66	14.65	6.66

Fig. 6 shows the micro-PIXE elemental maps taken on separate single particles collected on coarse fraction of two-stage filter pack sampler. Row and columns are pixels corresponding beam scan area and the scale bar is the peak count of characteristics X-ray. Soil components such Ca, Fe and Si was found to be the most abundant component in and/or on each single particle. S was detected in and/or on nearly all of single particles. Every single particle existed as the mixing state of soil components and S. Good agreement between the result of SEM–EDX analysis and that of micro-PIXE analysis was obtained in this study. Even though, the composition of single particles was determined through the micro-PIXE analysis in this study, attempts at obtaining relative or absolute element concentration of single particles was not possible at the present micro-PIXE technical level.

Further study such as measurement of absolute elemental concentration is in progress to analyze single particles as a function of their sizes.

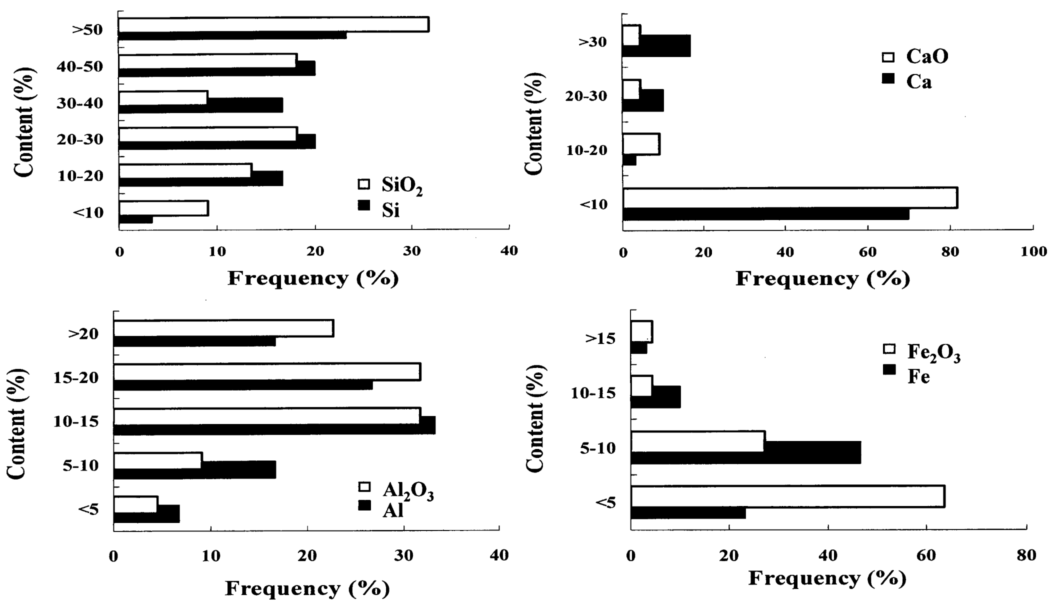

Fig. 5. Frequency histogram of major elements and oxides in and/or on coarse single particles collected in Asian dust storm events.

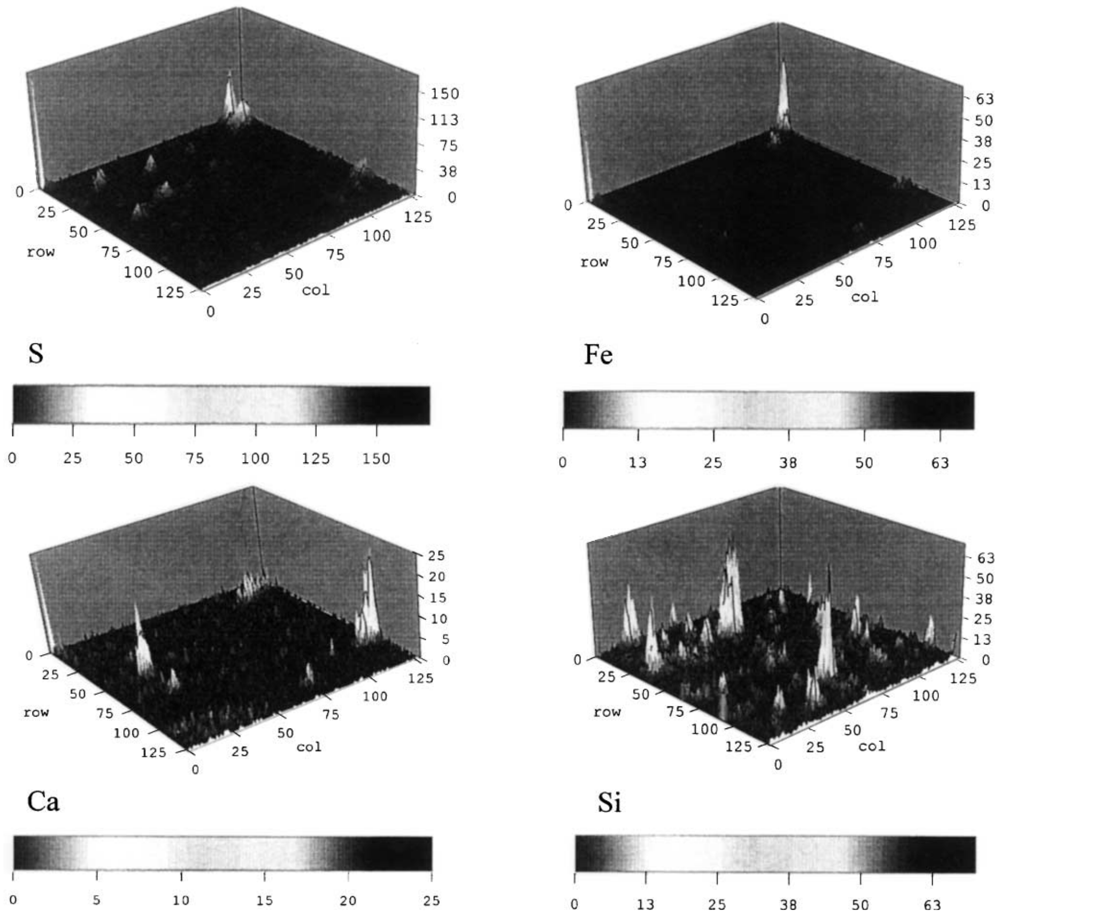

Fig. 6. Micro-PIXE elemental maps (scanning area = 25 μm × 25 μm) taken on the single Asian dust storm particles (⩾ 1.2 μm).

4. Conclusions

Mass concentration in Asian dust-storm events was roughly 3–5 times higher than that of the highest concentration measured in non-Asian dust–storm seasons. Single particles were generally sharp-edged and irregular in shape and contained mostly crustal elements such as Si, Fe, Ca and Al. Particles which have more than 40% Si content comprised nearly 50% of coarse single particles in Asian dust storm events. Main concentration range of Al in single Asian dust-storm particles was 10–20%, and those of Ca and Fe were below 10%. Even though S and Cl in soils of the desert and loess areas in northwest of China were not detected, significant concentration of S and Cl in coarse fraction in Asian dust storm event were detected in single particles. Especially, the maximum concentration of S in Asian dust storm event was about 5 times higher than that in non-Asian dust storm days. It seams reasonable to conclude that S is released to the atmosphere in gaseous form and is deposited onto coarse particles through reactions with water vapor and sunlight forming sulfuric acid during the long-range transport. Our data supports that every single coarse particle collected in ADS events existed as the mixing state of soil components and S. Good agreement between the result of SEM–EDX analysis and that of micro-PIXE analysis was obtained in this study.

Further study such as quantitative analysis of single particles using micro-PIXE is in progress to acquire more detailed information of single particles as a function of their sizes.

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