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Physicochemical Characteristics of Single Asian Dust Storm Particles

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Abstract

For the detailed characterization of atmospheric aerosol, the analysis of single particle is highly valuable. In this study, to investigate the characteristics of single Asian dust storm particles, scanning electron microscope (SEM) coupled with an energy dispersive X-ray microanalyzer (EDX) and micro-PIXE were applied. Sampling was performed at Kyoto University located in Kyoto, Japan, in spring of 1999. Mass concentration during Asian dust storm events was higher roughly 3~5 times than that measured in the season of the highest concentration. Single particles were generally sharp-edged and irregular in shape and contained mostly crustal elements. Significant amount of S in coarse fraction was detected in individual particles. A large number of single particles in coarse fraction existed as the mixture of soil components and S. A good agreement between the result of SEM-EDX analysis and that of micro-PIXE analysis was obtained in this study.

Key words : Asian dust storm, single particle analysis, SEM-EDX, micro-PIXE- Inner structure

1. INTRODUCTION

Asian dust storms (hereafter called "ADS"), which are generated at desert and loess areas in the northwest of China, have been a well-known meteorological phenomenon in Korea and Japan especially in the spring. The origin is yellow sands from vast deserts in China and Mongolia. 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 the China Continent, this ADS have led to the significant environmental change in East Asia and North Pacific ocean for a long time.

A large number of studies on the bulk ADS aerosols have been reported (Ma *et al.*, 1999; Nishikawa *et al.*, 1991; Braaten *et al.*, 1986; Darzi *et al.*, 1982; Duce *et al.*, 1980). Some of studies on the ADS aerosols as single particle, which can provide detailed information about the nature and composition of single particle were reported (Ma *et al.*, 2000; Zang *et al.*, 1998; Iwasaka *et al.*, 1988).

Investigation of the properties of single aerosol particle is an essential prerequisite for understanding chemical reactions in the atmosphere (Hinz *et al.*, 1998). Single particle analysis has advantages of providing a great amount of information that can not otherwise be

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obtained using methods of bulk analysis. And single particle analysis needs the short sampling time and the 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" of diverse aerosols. However, it has the disadvantage of being very time consuming.

In this study, to determine the nature of ADS particles as single particle in Japan, we measured morphology, elemental composition and concentration of single particle. Furthermore, an attempt was made to acquire more detailed information such as inner-structure and mixing state in the single particle by micro-PIXE analysis.

2. MATERIAL AND METHODS

2. 1 Sampling

For the single particle analysis, the short sampling time and the small sampling mass are needed. For sampling of ambient aerosols, 2-stage filter pack sampler was operated at a height of 20 m above ground level of the Kyoto University building located in Uji, Japan during ADS events from end of March to April, 1999. The surroundings of this sampling site are residential and agricultural areas with no major point sources. There are no nearby structures taller than sampling site. A highway, with usually moderate traffic, is located 1 km south of the sampling site. Location of aerosol sampling site indicated by filled circle is given in Fig. 1.

The 2-stage filter pack sampler without size selective inlet collected coarse and fine fractions of the aerosol separately on the first stage filter (a 47 mm diameter, 8 μm pore size Nuclepore polycarbonate filter) and the second stage filter (a 47 mm diameter, 0.4 μm pore size Nuclepore polycarbonate filter), respectively with 25 l min^{-1} flow rate. The equivalent aerodynamic cut-off diameter of the first stage filter at this flow rate was estimated to be about 1.2 μm (Kasahara *et al.*, 1996).

During this sampling period, the range of wind speed

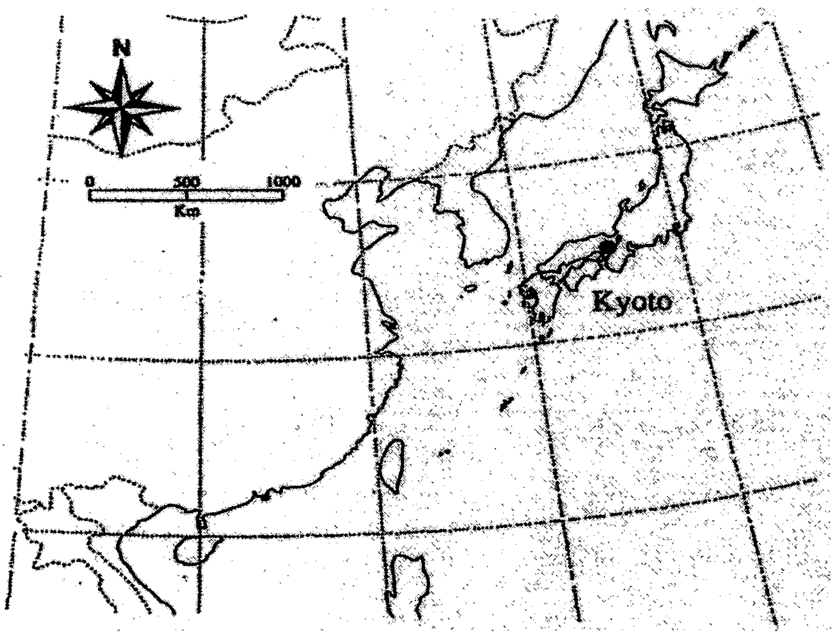

Fig. 1. A location of aerosol sampling site in this study.

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%.

2. 2 Single particle analysis

2. 2. 1 SEM-EDX analysis

A Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray microanalyzer (EDX) has been used for quantitative element analysis of single particle in many air pollution studies (Haapala *et al.*, 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 particle was performed by a SEM S-2000 equipped with a Be 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 sputtering (HITACHI E102 Ion Sputter). For calibration of energy, Al-Cu auto calibration method was applied in this study.

Cu (Kα = 8.04 keV) standard plate laid on the Al (Kα = 1.486 keV) sample stage was analyzed under the 25 kV and about 2000 cps analytical condition. The working conditions of SEM-EDX were 15 kV for the energy dispersive analysis and 100 seconds for X-ray collection. Standardless quantitative electron microscopy techniques which correct for the interaction of X-rays with neighboring atoms (matrix effects) are used to measure relative concentrations of elements in a particle (Haapala *et al.*, 1998; Huang *et al.*, 1994; Paoletti *et al.*, 1991; Farn *et al.*, 1990).

Particle compositions are determined relative to a reference element and corrections are made for the differences in electron backscatter and energy loss as a function of atomic number (Z), the absorption of X-rays by the elements in the surrounding matrix (A) and the fluorescence of secondary X-rays produced by primary X-rays in the surrounding matrix (F) (Huang *et al.*, 1994). Standardless ZAF correction method can be simply summarized as follows:

$$C_A = K_A \cdot (Z \cdot A \cdot F)_A$$
$$= K_A \left[\frac{f(X)_A^{unk}}{f(X)_A^{std}}\right] \cdot \left[\frac{R_A^{unk}}{R_A^{std}} \cdot \frac{S_A^{std}}{S_A^{unk}}\right] \cdot \left[1 + \frac{I_{A(F)}}{I_{A(d)}}\right]$$

where, K_A is the ratio of X-ray energy of A element to those of total elements, f(x) is the correcting factor of the absorption effect occurred by atoms of samples, R is the factor of back scattering effect of incident electron, S is the factor of stopping power, $I_{A(F)}$ is the received intensity of total fluorescence incident to A element from other elements, $I_{A(F)}$ is the first X-ray intensity of standard sample, unk and std = unknown sample and standard sample, respectively.

2. 2. 2 Micro-PIXE analysis

To acquire more detailed information such as inner-structure and mixing state in the single particles, micro-PIXE analytical measurements in the present work performed with the facilities of the Takasaki Ion Accelerators for Advanced Radiation Application, Japan. Unlike the SEM-EDX, which needs the pretreatment of the samples, micro-PIXE can analyze the original samples without pretreatment. And advantages of micro-PIXE are its high sensitivity and non destructive analysis for many elements of environmental samples. The 1∼2 μm beam diameter and >100 pA beam current allowed us to analyze single particle independent of sample thickness.

Fig. 2 shows 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 com-

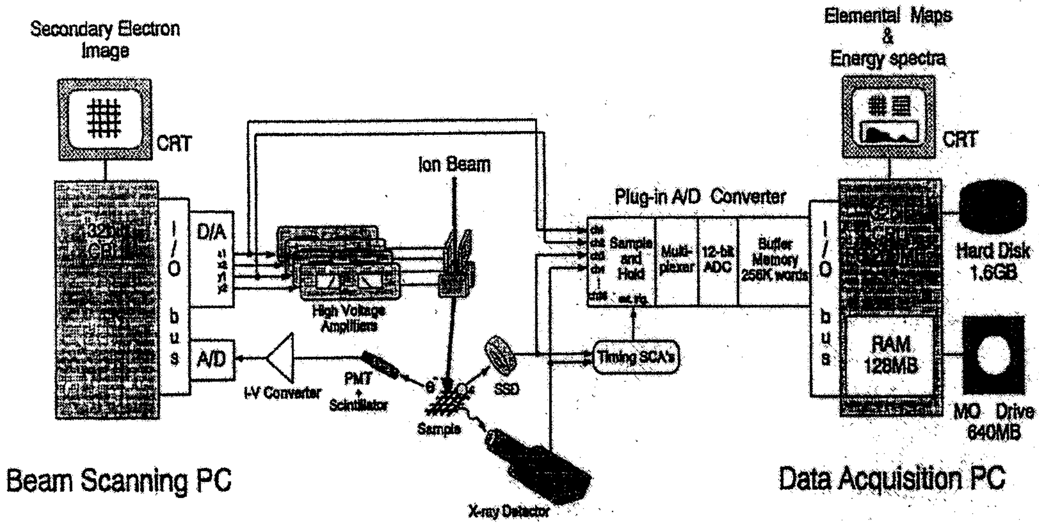

Fig. 2. A schematic diagram of the beam scanning and data acquisition system of micro-PIXE.

puter 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)

Simultaneous PIXE and RBS elemental mapping and ion beam induced charge (IBIC) imaging on fine structure diodes have been demonstrated with this system. The PC installed the date acquisition and processing software is capable of reading and processing the data, displaying maps or spectra and storing raw or sorted data.

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 1~2 μm and >100 pA, respectively. After selecting process of ideal portion by digital microscope, sample attached on 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 detection the transmitted beam amount, i.e. proton energy loss after irradiation of very weak beam current. It is common use 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.

3. RESULTS AND DISCUSSION

One of the ADS events was measured by a Lidar at Tokyo University of Mercantile Marine (TUMM) in our sampling period. Fig. 3 shows an averaged lidar data taken at TUMM. The time of observation by the Lidar was 21 : 30~21 : 37 (JST) Mar. 31, 1999. Apparently, ADS exists from 1.5 km to 10 km in altitude.

Mass concentration (fine+coarse) was 51.7~100.1 μg m^{-3} during ADS events. Although, nearly always the highest mass concentration was reported in December in Japan, mass concentration during ADS events was higher roughly 3~5 times than that measured in

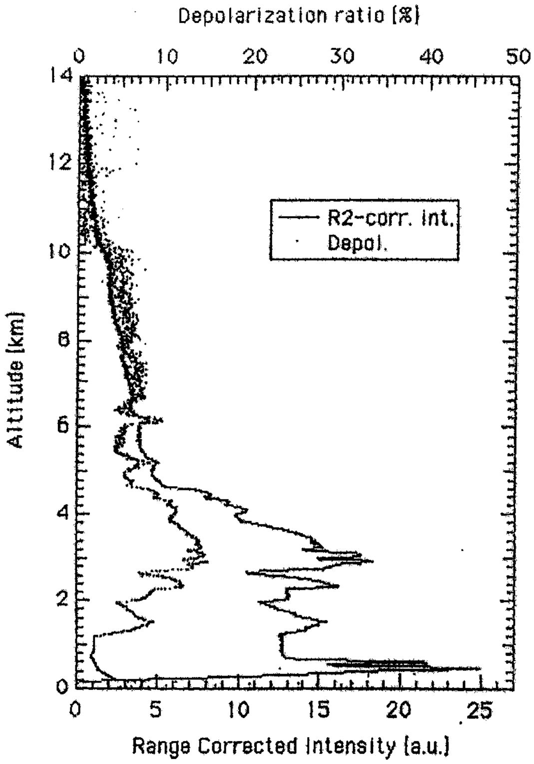

Fig. 3. A diagramor lidar observation Asian dust storm (TUMM).

December, 1998 by Ma *et al.* (1999). This result was relatively low compare to that of strong ADS event. It is easy to neglect the effects of weak ADS event because meteorological observations can not detect the 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 can not 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. 4 illustrates example of the morphology and X-ray spectrum of a coarse particle collected on Nuclepore filter during ADS period. For each sample, 100 particles were randomly selected using the sample moving function of SEM on the screen for elemental analysis by SEM-EDX.

Particles were generally sharp-edged and irregular in shape and contained mostly crustal element such as Si, Fe, Ca and Al. Even though C and O were detected by SEM-EDX analysis, they were not considered in the data analysis because they are major blank components of Nuclepore polycarbonate filters used in this study. After finishing the quality analysis, selected component can be dotted on the particle image by the ROI (Regions of Interest) mapping function of EDX. By means of this method, it is possible to show the distribution of components in and/or on the single particle. In Fig. 4, the black peaks mean spectrum of a non-ADS single particle, and the white dots in figure (b) are the portions, which detected Si in and/or on the single particle sampled during ADS event by X-ray energy. Si was distributed nearly all portion of single ADS particle.

Fig. 5 shows the distribution of elemental concentrations in and/or on coarse particles (≥ 1.2 μm) during ADS and on non-ADS days. But unfortunately, owing to the resolution problem of SEM, this study was restricted to particle whose diameter was greater than 1.2 μm for elemental analysis by SEM-EDX. The maximum measured size of aerosol in coarse fraction using SEM was about 28 μm. During ADS event the major components of coarse particles were Ca, Si and Al. And wt % concentration range of those was wide compared with other elements. In particular, Ca and Si concentrations show the wide range of particle-to-particle variation. On the other hand, on non-ADS days Na, Cl, and Ga show the high distribution of elemental concentrations compared with other elements. And every elements do not show severe particle-to-particle variation. It is suggested that high Ga concentration was derived from local emission source and coating material for SEM-EDX analysis. The maximum concentration of Na and Cl on non-ADS days were 23.2% and 23.9%, respectively. Though sampling site is far

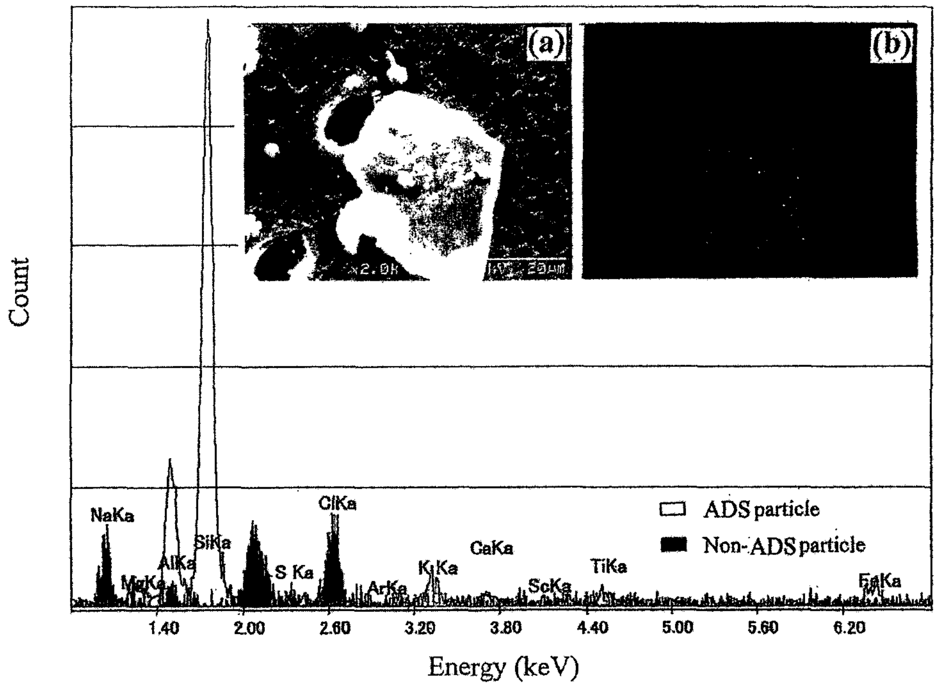

Fig. 4. An example of the morphology and X-ray spectrum of a single ADS particle.

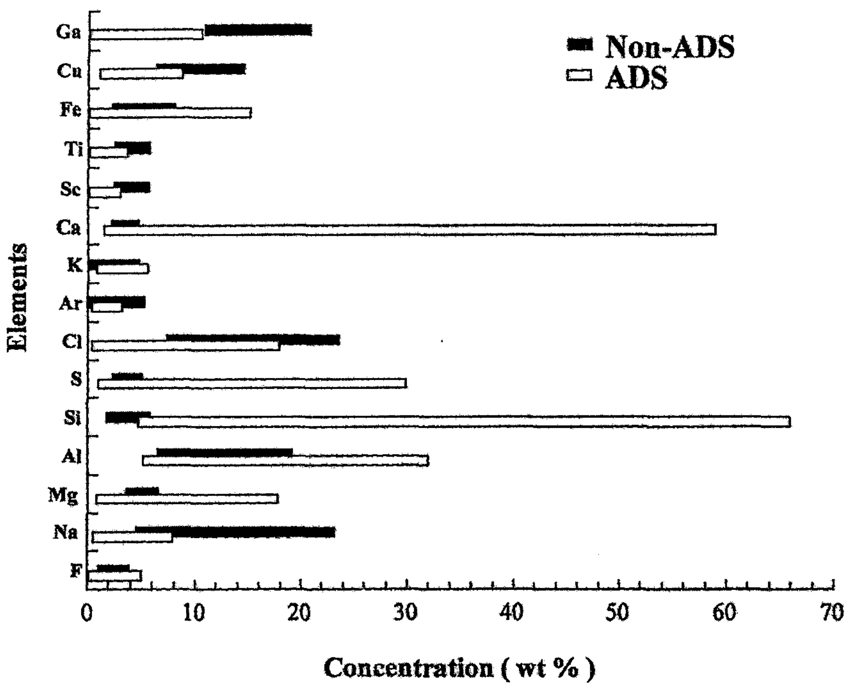

Fig. 5. A distribution of elemental concentration of single coarse particles in ADS events and non-ADS days (n = 208)

about 40 km from ocean, major source of airborne Na and Cl on non-ADS days in this study may be originated by marine sources.

The maximum S concentration (29%) during ADS events was higher about 5 times than that (5%) of on non-ADS days. A large number of single particles sampled during ADS events contain sulfur and chlorine. On the one hand, S in soils of the desert and loess areas of China was not detected as the bulk sample (Wang *et al.*, 1996). The reason of high S concentration in and/or on ADS particles might be 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.

Due to the large available surface area in the coarse fraction compare to that in fine fraction, SO_2 and sulfuric acid deposition rate of the coarse fraction is larger than that of the fine fraction (Nishikawa *et al.*, 1991). And Wang *et al.* (1996) reported that large fraction of sulfate to be associated with the coarse fraction during ADS events through his investigation about the composition distribution of aerosol particles sampled in Beijing. This result is in agreement with that estimated during ADS event in Seoul, 1999 by Ma *et al.* (1999).

Coarse fraction Cl suggests that dust particles are absorbed or coalesced with particles containing sea salt during the long-range transport. High frequencies of chlorine were reported in other areas of Japan during ADS event (Zhang *et al.*, 1998).

While on the other, as discussed above, high Cl concentration on non-ADS days compared with that of during ADS events in this study, may be caused by marine components transported from Osaka bay (about 40 km south-west from the Kyoto sampling site) by south-west winds on non-ADS days.

Added to the elemental analysis of single particle by SEM-EDX, under the assumption that each element

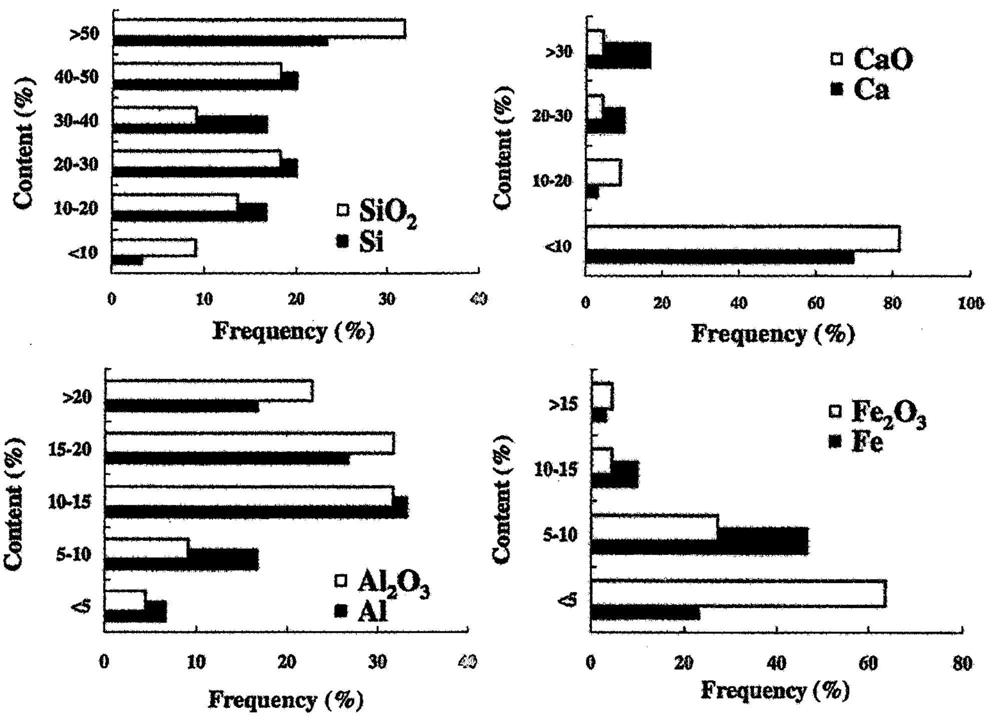

Fig. 6. A frequency histogram of major soil originated components in coarse single particles in ADS events (n = 208).

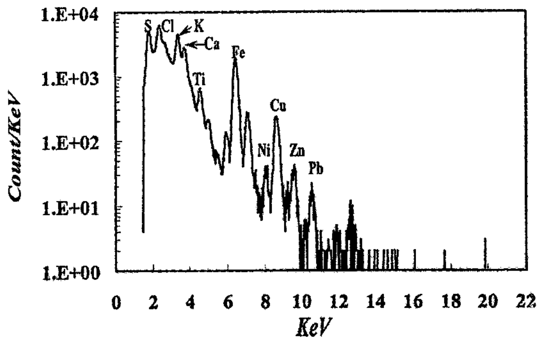

Fig. 7. A micro-PIXE spectrum of the single ADS particles.

exists as oxide, standardless quantification method of oxide was applied to the analysis of oxides in and/or on single ADS particle. Total 14 oxides including SiO_2 and Al_2O_3 were analyzed.

Fig. 6 shows frequency of wt % of major elements and oxides analyzed by SEM-EDX with ZAF standardless elemental analysis method and standardless oxide analysis method, respectively.

Si comprised nearly 50% of coarse single particles during ADS events. Main concentration range of Al in single particles during ADS events was 10~20%, and those of Ca and Fe were below 10%.

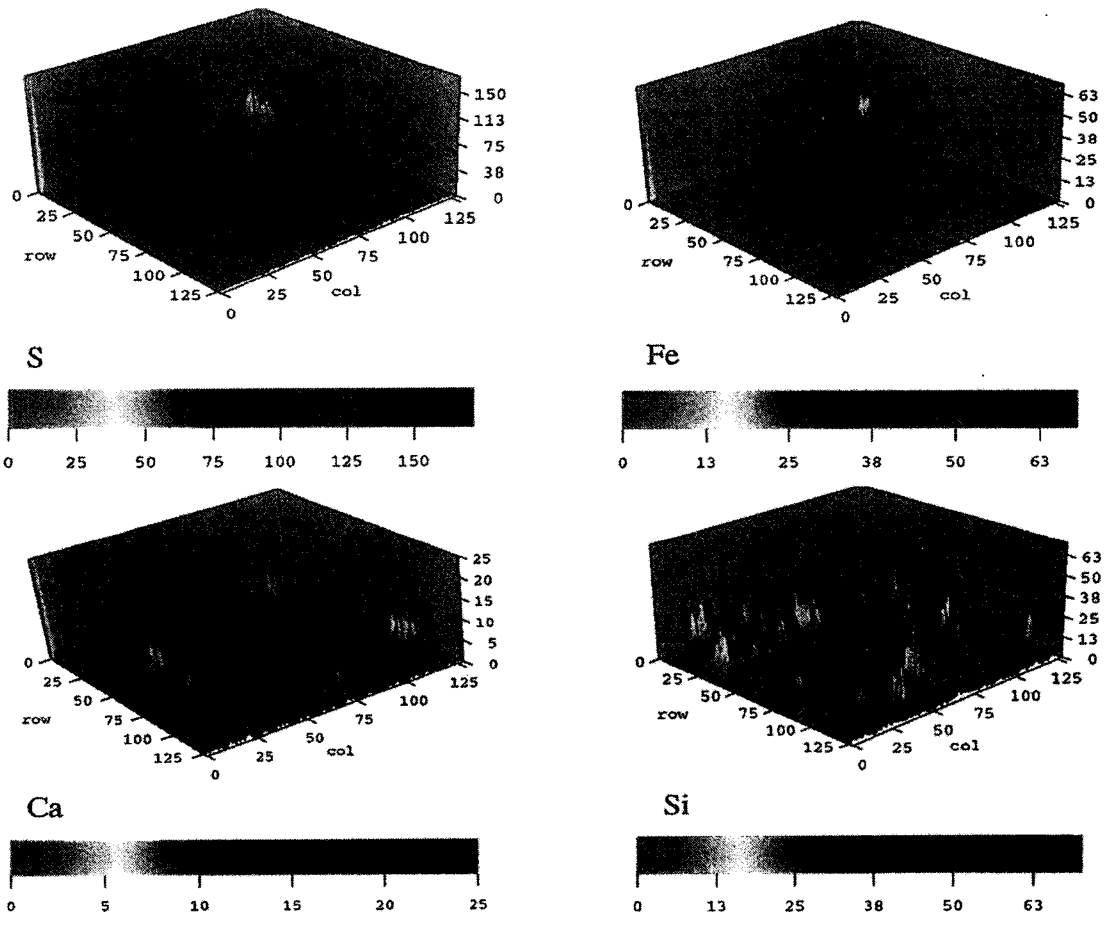

Fig. 8. A micro-PIXE elemental maps (scanning area : 60 μm × 60 μm) taken on the separate single ADS particles (≥ 1.2 μm).

To acquire more detailed information about the single particle, Micro-PIXE analytical measurements was performed with the facilities of the Takasaki Ion Accelerators for Advanced Radiation Application, Japan.

Separate single particle appearing in the full spectral area maps taken on 60 μm × 60 μm scanning area was subjected to individual spectrum measurements for Micro-PIXE elemental analysis. Fig. 7 shows the Micro-PIXE spectrum of the single ADS particles.

Fig. 8 shows the Micro-PIXE elemental maps taken on separate single particles collected on the coarse fraction of 2-stage filter pack. Row and col mean pixels for corresponding the beam scan area. Scale bar shows the number of beam counts. Soil components such Ca, Fe, and Si were found to be the most abundant component in and/or on each single particle.

S was found to be quite distributed in and/or on many single particles. A large number of single particles 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.

4. CONCLUSIONS

To characterize of ADS particles as the single particle, we measured the morphology, elemental composition and concentration of single particles. Furthermore, an attempt was made to acquire more detailed information such as inner-structure and mixing stage in the single particles by Micro-PIXE analysis. Mass concentration during ADS events was higher roughly 3~5 times than that measured in the highest concentration season in Japan. Single ADS particles were generally yellowish sharp-edged and irregular in shape. Soil components such as Si, K, Ca and Fe showed significant concentration in coarse fraction during ADS events. Even though S in the soils of the desert and loess areas in northwest of China was not detected, significant amount of S in coarse fraction during ADS events was detected. It seems reasonable to suppose that a large number of single coarse particles collected during 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. Even though the elemental composition of single particle was determined through the micro-PIXE analysis in this study, attempts at obtaining relative or absolute elemental concentration of single particle was not possible at the present micro-PIXE technical level. Further study such as quantitative analysis of single particle using micro-PIXE is in progress to acquire more detailed information of single particle.

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