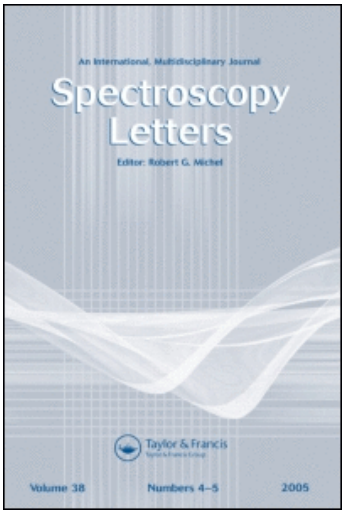

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Characterization of Individual Silicon-Poor Particles in Atmospheric Aerosols by SEM-EDX and Application to Kosa Particle Identification

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Characterization of Individual Silicon-Poor Particles in Atmospheric Aerosols by SEM-EDX and Application to Kosa Particle Identification

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Abstract: Silicon-poor particles, mainly composed of mafic minerals such as olivine or pyroxene, were examined as an indicator of eolian dust particles from China, called the *Kosa aerosol* in Japan. A method of scanning electron microscopy–energy dispersive x-ray microanalysis (SEM-EDX) has been developed to discriminate Kosa-derived, individual Si-poor particles from Japanese igneous rock–derived ones. Prior to single-particle analysis by the SEM-EDX, atmospheric particle samples were ignited at 1000°C for 6 hr, and thereafter the ignited samples were washed in hydrochloric acid, in order to remove organic matter, soluble-formed secondary particles, easily-weathering minerals having medium SiO_2 content, and so forth. Particles having a SiO_2 content of 30–50% in the residue after the acid treatment were defined as Si-poor particles in this study, and the elemental composition was determined by SEM-EDX using a standardless $\varphi(\rho z)$ correction. Si-poor particles are characterized by their high contents of Mg and Fe, so that a correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 was examined for individual Si-poor particles. Atmospheric aerosol sampling was carried out at the northern foot of Mt. Fuji, central Japan, and the distribution areas under the Kosa phenomena in the correlation plot widely differed from

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those of background aerosol at the sampling site. Also, the correlation plot showed a clear temporal variation corresponding to transporting episodes of the Kosa aerosol. The variation of major elements like Mg and Fe in Si-poor particles was wide compared to that of trace impurities (Na and K) in Si-rich particles like quartz. These results indicate that Si-poor particles are an indicator that can be used to identify the Kosa-derived particles grain by grain and to investigate transportation of the Kosa aerosol.

Keywords: Climate change, kosa aerosol, mafic minerals, SEM-EDX, Si-poor particles

INTRODUCTION

The eolian dust particles called the *Kosa* ("yellow sand") *aerosol*[1–3] in Japan originate from arid and semiarid areas of China and reach as far as the northern Pacific Ocean.[4–8] They are an effective indicator of the aridity in the source area and of climate change in eastern Asia. The chemical compositions and the discrimination methods of the Kosa aerosol have been studied by many researchers using bulk analysis.[1–3,9–13] However, as is already well-known, atmospheric aerosols are composed of materials derived from a wide variety of sources[14,15] so that it is very difficult to discriminate the Kosa particles of small or trace amounts in atmospheric aerosol or sediments using bulk analysis that give information only for average compositions. Although, the discrimination of the Kosa particles based on the shape and grain size of minerals has also been often done, it has been reported that continental soil is relatively round quartz[11,16] and most of the grain sizes of the Kosa aerosol reaching Japan are several micrometers.[1,3,6] However, the application of this discrimination to real ambient aerosol seems to be difficult, because detrital particles from Japanese igneous rocks having the shape and grain size characteristics similar to the Kosa coexist in large quantities. Although the elemental compositions of individual Kosa particles have often been investigated by electron probe microanalysis,[6,8,17] most research has been done by concentrating on the chemical reactions or formation of secondary particulates on the particles, and so forth. Thus, a reliable method for the identification and quantification of individual Kosa particles in atmospheric aerosol formed by complex matrix components has not yet been established.

We already reported a new method of scanning electron microscopy–energy dispersive x-ray microanalysis (SEM-EDX) that can identify the Kosa particles grain by grain; a correlation plot between ($Na_2O + K_2O$) and SiO_2 contents was used for individual Si-rich particles having SiO_2 content over 80%, and Kosa-derived Si-rich particles were clearly discriminated from Japanese igneous rock–derived ones.[18] Using the method and lake sediments, the variation of the Kosa flux during the last 8000 years was reconstructed.[19] Eolian dust particles under the Kosa phenomena include many minerals other than Si-rich particles.[6,8,9,17] The aim of this study is to find

other indicators for the discrimination of Kosa particles grain by grain and climate change analysis. The indicator should be not only for Kosa particles identification but also for paleo-climate change analysis using sediments and should be limited to minerals having high chemical stability. Judging from this point, Si-rich particles mainly composed of quartz seem to be the best indicator.[18,19] On the other hand, easily-weathering minerals having medium SiO_2 content such as alkali feldspars, plagioclase, and clay minerals, or soluble-formed secondary particles such as sulfates and nitrates, are not suitable. Therefore, Si-poor particles mainly composed of mafic minerals such as olivine or pyroxene were examined in this study.

Particles having both SiO_2 contents of 30–50% and high chemical stability were defined as Si-poor particles in this study, and the elemental compositions of the individual particles were determined by SEM-EDX using a standardless φ (ρz) correction. Consequently, Kosa-derived individual Si-poor particles in ambient aerosol could be clearly discriminated from Japanese igneous rock–derived by using differences of the distribution areas in a correlation plot between MgO/Fe_2O_3 and MgO/SiO_2.

MATERIALS AND METHODS

Aerosol Sampling

The detail of the sampling location is shown in Fig. 1. Aerosol sampling was done at the Yamanashi Institute of Environmental Sciences (YIES) located at the northern foot (an altitude of 1100 m) of Mt. Fuji, central Japan, from March to May 2000. The YIES is built on lava beds and eruptive materials from Mt. Fuji. The traffic density in this area is very low compared to that in the Kofu Basin (Kofu City). An air sampler was set on the roof of the YIES. Aerosol samples were collected on polycarbonate filters (Millipore, Bedford, MA, USA, ATTP, 0.8-μm pore size, 47 mm in diameter) for 2–16 days by a low-volume air sampler equipped with a cyclone classifier ($<10.0\,\mu m$) (Shintaku Machine Manuf., model S-2) with a flow rate of $20\,L\,min^{-1}$. Mt. Fuji, at an altitude of 3776 m is the largest basaltic stratovolcano in the quaternary period in Japan, and has spewed a tremendous amount of volcanics since the prehistorical age. Therefore, roughly speaking, the foot of Mt. Fuji consists of mainly basaltic rocks.

Japanese Igneous Rocks and Kosa Aerosol Source Materials

In order to grasp the general elemental compositions of individual Si-poor particles in Japanese igneous rocks and Kosa aerosol source materials, the following geological standard materials[20,21] were used; granite (JG-2), granodiorite (JG-1a, JG-3), andesite (JA-1, JA-2), basalt (JB-2, JB-3), China loess (CJ-1), and simulated Asian mineral dust (CJ-2) prepared from Tengger desert

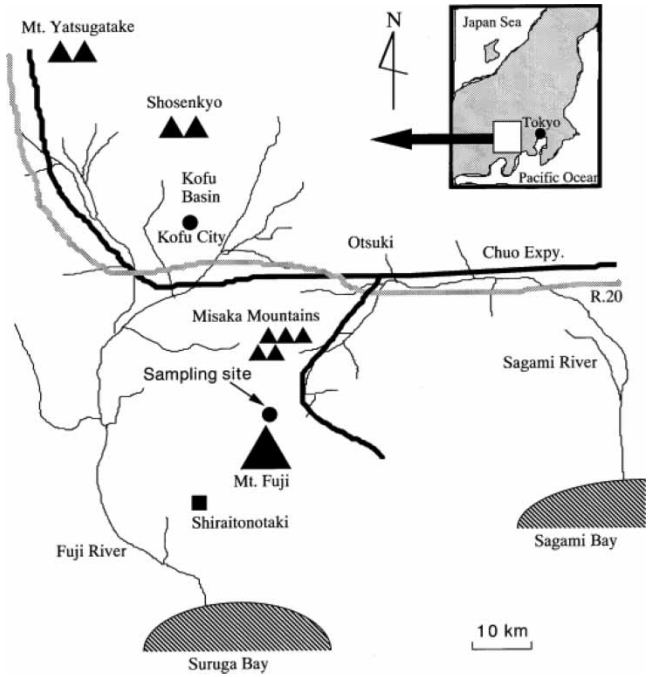

Figure 1. Sampling location.

sand. Because the source region in China of the Kosa aerosol is so wide, the two source materials were used as reference data to be compared. In this study, particles less than 10 μm were used for analysis.

Single-Particle Analysis by SEM-EDX

Atmospheric aerosol samples contain materials derived from a wide variety of sources.[14,15] Therefore, prior to SEM-EDX analysis, aerosol samples were converted to a specimen suitable for single particle analysis. At first, the particles were detached from the sampling filter by ultrasonication for 20 min in ultrapure water (30 mL) and the released particles were air-dried at 110°C for 2 hr. The dried and powdered sample was ignited at 1000°C for 6 hr, and the ignited sample was washed in a 10-mL volume of 6 N hydrochloric acid for 20 min by ultrasonication. The residual particles were filtered off through a 0.45-μm PTFE membrane filter and washed with 3 mL of ultrapure water five times to remove any hydrochloric acid from the particles on the filter. After drying for 30 min at 110°C, the particles on the filters were detached by double-sided adhesive carbon tape and were fixed on the aluminum sample stands (15 mm in diameter, 5 mm in height) for

SEM (Hitachi S-3000N, Tokyo, Japan)-EDX (Horiba EMAX550, Kyoto, Japan). Thereafter, the particles were carbon coated (~200 Å) and the specimens were subjected to SEM-EDX analysis. Geological standard materials were also prepared in the same manner except for the ignition procedure.

Mineral particles, in size approximately from 1 to 10 μm, were used for analysis in this study. The SEM-EDX analysis was carried out under the condition of an accelerating voltage of 20 kV, using a probe current of 0.3 nA and a dead time of 20–30%. The takeoff angle for the EDX detector was fixed at 35°. These conditions were found to be suitable for good x-ray analysis and allowed reasonable secondary electron imaging. In the x-ray intensity measurements, an area analysis of individual particles was carried out as follows. The electron beam was usually irradiated at the central part of an individual particle to get the average composition, and the data were accumulated for 100 s. For the qualitative analysis, an element in the particle was determined when the characteristic x-ray intensity was three times standard deviation of the background intensity under the peak. For the semi-quantitative analysis, x-ray analysis data was processed by a standardless $\varphi(\rho z)$ correction program supplied by Horiba, and the results were normalized to 100% on the basis of oxide composition. SEM-EDX was used not for strict determination of elemental composition but for origin discrimination grain by grain. The current semiquantitaive SEM-EDX is a useful method for source apportionment study of atmospheric particles because it can deal with large number of particles rapidly.

RESULTS AND DISCUSSION

Single-Particle Analysis of Si-Poor Particles

A big problem in single-particle analysis using SEM-EDX is that mineral types of particles measured cannot be judged from only the SEM image. Therefore, mineral types were classified on the basis of SiO_2 contents measured by EDX. Particles having SiO_2 content over 80% were defined as the Si-rich particles like quartz.[18] Particles having SiO_2 contents of approximately 50–80% can be considered to be easily-weathering minerals like alkali feldspars, plagioclase, clay minerals, and volcanic glass,[18] so that the medium SiO_2 content particles are not suitable to Kosa particle identification or paleo-climate change analysis using sediments. Furthermore, because the medium SiO_2 content particles include many mineral types as described above, it is very difficult to understand the variation factor in the chemical composition measured. Particles having SiO_2 content under 50% were not detected in granite (JG-2) and andesite (JA-1, 2). Also, the minimum SiO_2 content detected in igneous rocks used was about 30%. Therefore, particles having SiO_2 contents of 30–50% were defined as the "Si-poor particles" in

this study. Figure 2 shows the contents (particle number frequency) of Si-poor particles in some Japanese igneous rocks and two Kosa aerosol source materials measured by SEM-EDX. Mafic minerals like olivine or pyroxene, which have low SiO_2 contents and high chemical stability, are a typical component of volcanic rocks like basalts,[20] and the geological feature is well reflected in Fig. 2. Therefore, Si-poor particles were examined as an indicator of the Kosa aerosol in this study. Although geological properties of the Kosa aerosol source materials can be considered to be plutonics type like granitics due to low volcanic activities in the inland areas of China, the content of Si-poor particles in China loess (CJ-1) was considerably higher than the initial expectation.

For real atmospheric aerosol samples, ignition and HCl washing procedures were required to remove major matrix components like carbonaceous components or sulfates and nitrates and to obtain a contamination-free surface suitable for SEM-EDX. Therefore, for checking the reliability of SEM-EDX data and chemical stability of Si-poor particles, a powdered olivine sample (DH4908) was analyzed. The olivine particles were pretreated by the two methods of 6 N HCl washing (US for 20 min) after ignition (at 1000°C for 6 hr) or 6 N HCl washing (US for 20 min) only. Thereafter, 20 particles were measured for each sample by SEM-EDX. Because Si-poor particles are characterized by their high contents of Mg and Fe, analytical results were evaluated as the difference of distribution area in a correlation plot between MgO/Fe_2O_3 and MgO/SiO_2. Figure 3 shows a comparison among the distribution areas obtained by the two pretreatment methods. It was confirmed that the ignition procedure does not affect the chemical composition of individual Si-poor particles.

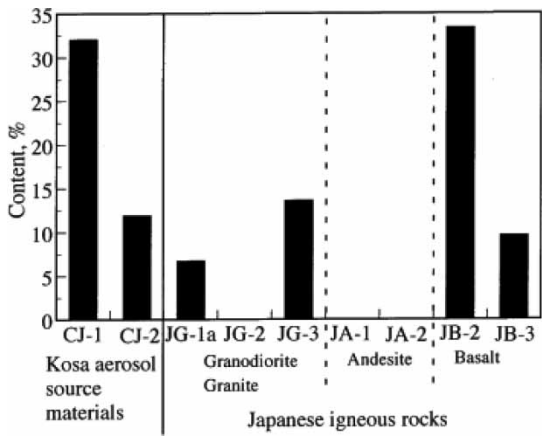

Figure 2. Number frequencies of Si-poor particles (SiO_2 content of 30–50%) detected in two Kosa aerosol source materials and several Japanese igneous rocks.

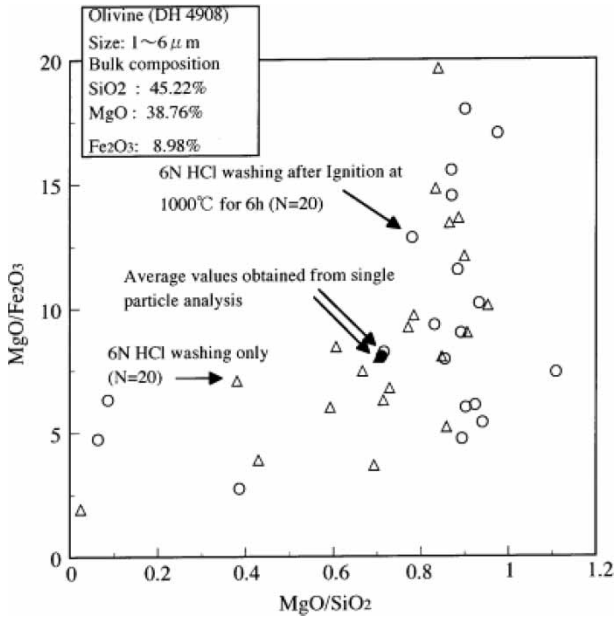

Figure 3. Effect of ignition procedure on the correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 in individual particles from powdered olivine sample. Each point expresses an individual particle.

Discrimination of Si-Poor Particles Between the Kosa Aerosol Source Materials and Japanese Igneous Rocks

As reference data to confirm the possibility of Si-poor particles as an indicator, Fig. 4 shows correlation plots between MgO/Fe_2O_3 and MgO/SiO_2 in individual Si-poor particles from the two Kosa aerosol source materials (CJ-1, CJ-2) and three Japanese igneous rocks (JB-2, JB-3, JG-1a). The distribution areas of the Kosa aerosol source materials clearly differed from those of Japanese igneous rocks, although number frequencies of Si-poor particles in Fig. 2 gave similar results for CJ and JB series. In the Kosa aerosol source materials, desert sand (CJ-2) showed relatively low values of MgO/Fe_2O_3 compared to loess (CJ-1). Consequently, these results indicate that the correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 obtained for individual Si-poor particles may be used as an indicator of the Kosa aerosol.

Identification of Kosa-Derived Si-Poor Particles in Real Atmospheric Aerosol

In the current sampling campaign, the Kosa phenomena were observed for three periods as shown in Fig. 5. Figure 5 shows a temporal variation of the

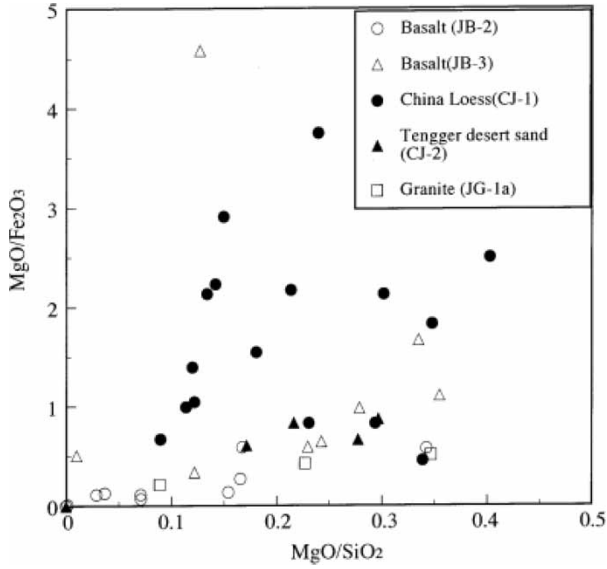

Figure 4. Correlation plots between MgO/Fe_2O_3 and MgO/SiO_2 in individual Si-poor particles (SiO_2 content of 30–50%) from the two Kosa aerosol source materials (CJ-1, 2) and three Japanese igneous rocks (JB-2, 3, and JG-1a). Each point expresses an individual particle.

distribution areas in the correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 obtained for individual Si-poor particles from atmospheric aerosol collected in the northern foot of Mt. Fuji, central Japan, March to May 2000. The distribution areas showed a clear temporal variation corresponding to transporting episodes of the Kosa aerosol from China. Furthermore, the distribution areas under the Kosa phenomena concentrated in the specific area, and the MgO/Fe_2O_3 values were much lower than those of non-Kosa aerosol (background aerosol). These results suggest that Si-poor particles are an indicator to identify the Kosa-derived particles grain by grain and to investigate transportation of the Kosa aerosol. However, the distribution areas of real Kosa aerosol in Fig. 5 did not coincide with those of the two Kosa aerosol source materials (CJ-1, 2) in Fig. 4. Besides the inconsistency, it may be a natural result that the distribution areas of non-Kosa aerosol in the current sampling site differed from those of JB-2, 3, and JG-1a, as Fig. 4 contains reference data showing only three Japanese igneous rocks and only two source materials. The most important result is a fact that the temporal variation corresponding to the Kosa events could be clearly observed for "real" atmospheric aerosol.

Although similar to the Si-poor particles in Fig. 5, a correlation plot between $(Na_2O + K_2O)$ and SiO_2 contents obtained for individual Si-rich particles from real atmospheric aerosol showed a sharp and clear seasonal variation.[18] Furthermore, the distribution of the Si-rich particles in

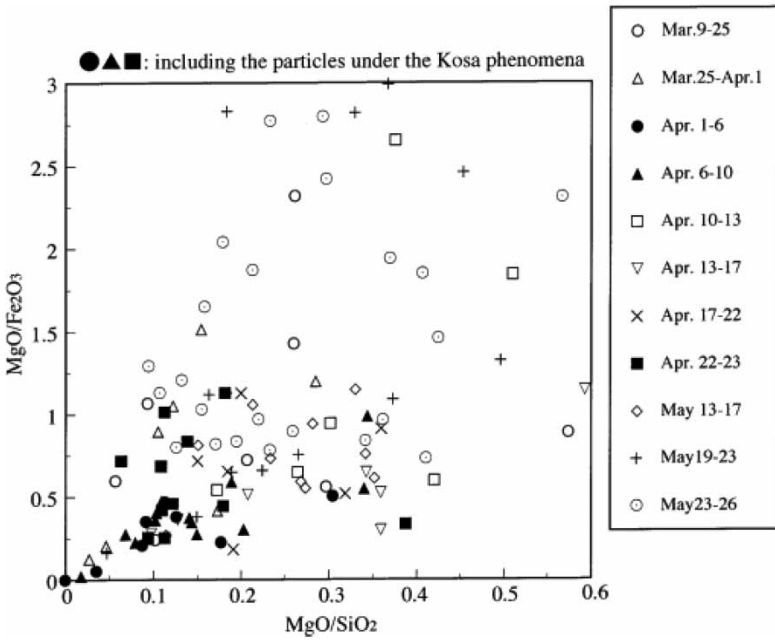

Figure 5. Temporal variation in the correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 in individual Si-poor particles (SiO_2 content of 30–50%) from atmospheric aerosol collected at the northern foot of Mt. Fuji, central Japan, March to May 2000. Each point expresses an individual particle.

springtime concentrated in the specific area and was closer to those in the China loess (CJ-1) and desert sand (CJ-2) compared to non-Kosa aerosol.[18] These results may suggest that the impurity compositions of Si-rich particles like quartz are fairly constant over China, but major element compositions of Si-poor particles like olivine or pyroxene vary widely corresponding to the source area. Thus, the variation of major elements like Mg and Fe in Si-poor particles is wide compared to trace impurities (Na and K)[18] in Si-rich particles like quartz. Such a big variation of Si-poor particles may be available to detailed source classification of the Kosa aerosol.

CONCLUSIONS

A correlation plot between MgO/Fe_2O_3 and MgO/SiO_2 in individual Si-poor particles obtained by a SEM-EDX showed a clear temporal variation corresponding to transporting episodes of the Kosa aerosol. Judging from the big variation in the correlation plot, Si-poor particles may be more useful than Si-rich particles. The current method based on single particle analysis can

be also used for the determination of Kosa contribution rate to aerosol or sediments, which is required for climate change analysis.

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