1A5) Application of Microbeam Technique to Atmospheric Science

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Abstract

Microbeam PIXE, often called micro-PIXE, is a powerful tool for analyzing a wide range of elements for various samples, as well as, it has important applications of interest to the atmospheric science. In this study, qualitative elemental imagination for various atmospheric environmental species was attempted using micro-PIXE. Here, we present the results of an application of micro-PIXE to the study of atmospheric environment. The detailed spatial resolution of multiple elements for various samples like individual ambient particles, individual raindrops, individual fog droplets, and individual snow crystals could be successfully achieved by scanning 2.6 MeV H+ micro beam (1-2 μm) accelerated by 3 MV single-end accelerator.

Key words: Micro-PIXE, Individual particles, Individual raindrop, Individual fog droplet, Individual snow crystals, Replication, Trace element

1. INTRODUCTION

It is well know that PIXE is now one of key instruments of the analytical chemistry. PIXE has been applied to the various fields of research like biomedicine, materials science, atmospheric science, geology, and archaeology ever since it was introduced. The principle of PIXE method consists in an ionization of the levels near the atomic nucleus. The detailed principle of PIXE Analysis can be summarized as the following:

1. Samples are bombarded with the protons.
2. An electron in inner shell jumps with the interaction with a particle beam.
3. Anoter electron in outer shell moves to an inner orbit.
4. A characteristic X-ray which has particular energy is emitted.
5. Quantity of an element in a sample can be measured by counting the number of characteristic X-rays.

The characteristics of the method are the following:

1. Non-destructiveness (Specimens can be repeatedly analyzed.)
2. Rapidity (±15 minutes for thin targets)
3. Easy preparation of the samples
4. Determination of multielement (Z>12) with a good accuracy (about ±5%) and precision (about ± 2%)

Respected for its practical accuracy and detection range of parts per million, application of PIXE to the field of atmospheric science, especially in the compositional analysis of atmospheric aerosols has been described by numerous researchers (Cornille and Maenhaut, 1990; Scheff and Valiozis, 1990; Kasahara *et al*, 1996; Ma *et al*, 2001c). However, this is not the case with micro-PIXE technology, which is still relatively new and untested. By making a beam spot size smaller than a few micrometers and scanning this micro beam on a species, it is possible to obtain spatial distribution of trace elements in various samples. With a spatial resolution of a few micrometers, the absolute detection limits are of the order of 10^{-15}-10^{-16}g.

The principal objective of this study is to introduce the application of micro-PIXE technique to analysis of various atmospheric environmental species.

2. MICRO-PIXE ANALYSIS

Micro-PIXE analysis was performed at the division of Takasaki Ion Accelerator for Advanced Radiation Application (TIARA) in Japan Atomic Energy Research Institute (JAERI). Figures. 1 and 2 show the schematic diagram of micro-PIXEand its window screen for data analysis, respectively.

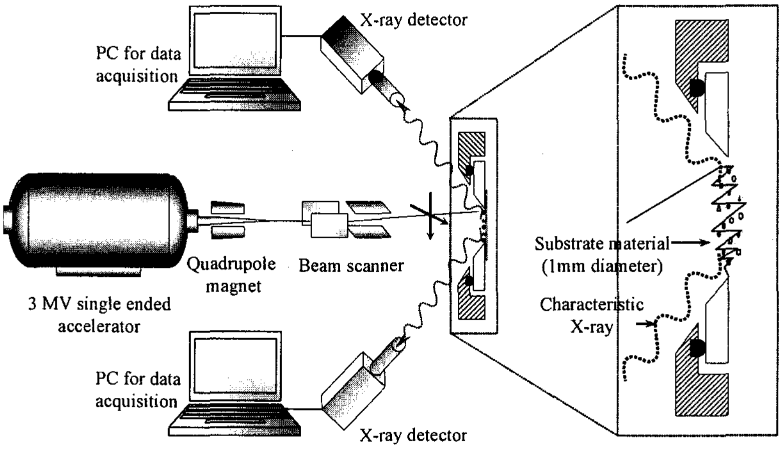

Fig. 1. Schematic diagram of the beam scanning and data acquisition system of micro-PIXE.

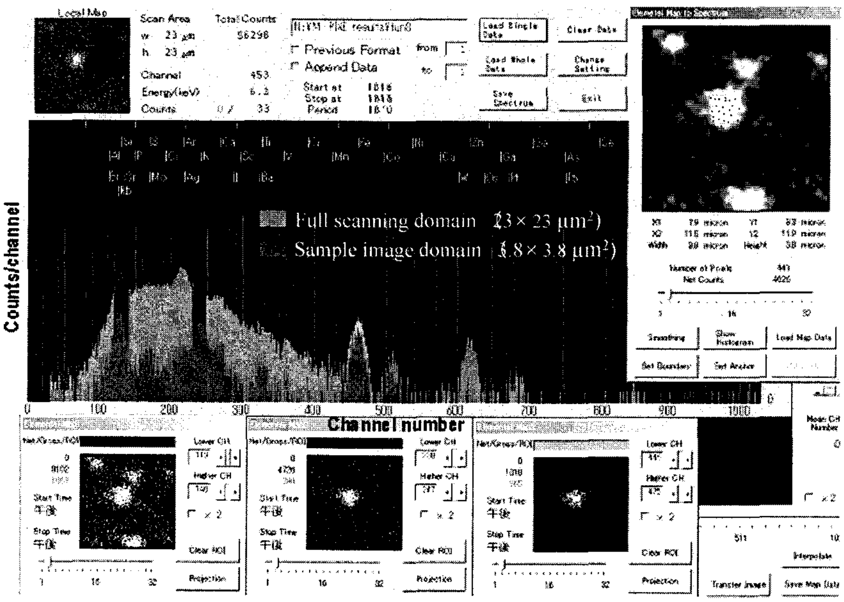

Fig. 2. Window screen of Micro-PIXE data analysis program.

Beam scanning, data acquisition, evaluation and the drawing 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 3 D matrices in the memory space, that consist of 1024 channels for the energy spectra and 128×128 pixels for corresponding the beam scan area. After selecting process of ideal portion by digital microscope, sample was attached to 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. Micro-PIXE measurements were performed with a scanning 2.6 MeV H^{+} micro beam accelerated by 3 MV single-end accelerator. Beam diameter and beam current were 1-2 μm and <100 pA, respectively. Beam collection time was about 10-40 min. More details about micro-PIXE were described in other publications (Sakai *et al.*, 1998; Ma *et al.*, 2001a).

3. RESULTS AND DISCUSSION

3.1 Singleparticle analysis

The detailed information on composition of single particles is needed to assess their environmental impact. Also the chemical inner-structure and mixing state of individual particles especially can be used for "finger printing" of diverse aerosols, natural as well as anthropogenic (Kasahara *et al.*, 2000; Ma *et al.*, 2001a).

The separated individual particles collected by various types of sampling devices can be the target of micro-PIXE analysis. In the present study, low pressure Andersen impactor (LPAI) was used for the sampling of size-classified aerosols. Since the particles often overlap and form clusters, the edge portion of a spot formed on the each stage of LPAI is desirable for single particle analysis. An example of elemental maps for the urban individual particles arrested onto the 5th stage (1.17 μm cutoff diameter) of LPAI was shown in Figure 3. Corresponding to micro-PIXE imaging with scanning transmission ion microscopy, it enables us to obtain the distributions of trace elements of individual particles. Sulfur, Silicon, calcium, and iron were mainly detected in and/or on several Individual particles and their localizations were varied in each particle. For instance, sulfur was higher in mask number A, while silicon showed relative abundance in mask number B. In contrast, calcium and iron were detected in nearly all of particles. These results suggest that micro-PIXE analysis is a promising technique for investigation of chemical mixing state of individual particles. From the analytical result of individual particles, it is possible to know the particle-to-particle variation in composition.

3.2 Single raindrop analysis

The analysis of single raindrops is expected to give new and interesting information about washout of pollutants and drop formation processes in the atmosphere. Although it is possible to obtain a great amount of information by analysis of individual raindrops, there is difficulty in samplingand handling processes of individual raindrops.

In this. work, for the purpose of collecting and subsequent chemical analysis of individual raindrops, the collodion film method, which was introduced by Ma *et al.* (2001b); was applied. Replica formation process of individual liquid droplets and snow crystals on the collodion film was illustrated in Figure 4. The detailed replica formation process of individual raindrops on the collodion film was described in elsewhere (Ma *et al.*, 2003a; Ma *et al.*, 2003b) and was noted here briefly.

The collodion solution was mounted onto polycarbonate filter just before sampling. When raindrops fall onto the thin layer of collodion film they gently settled without sprit out and bounce-off. Allowing the alcohol and ether to evaporate, finally a thin film containing the replication of individual raindrops was left The non-volatile components existent on individual raindrop replicas were the target of micro-PIXE analysis.

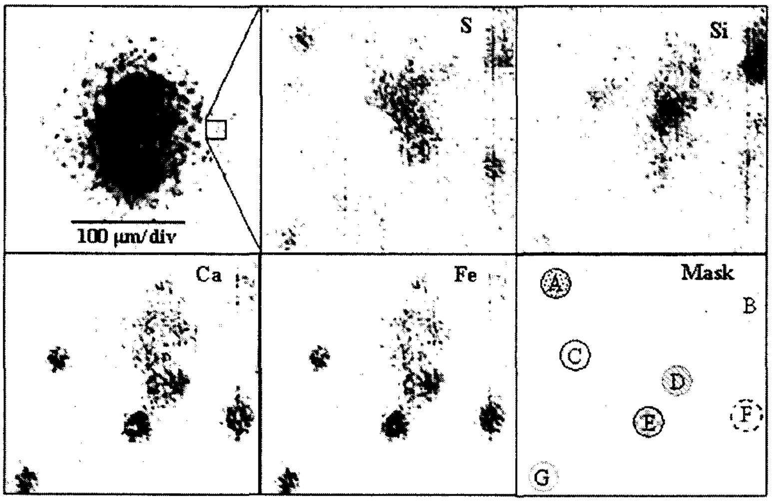

Fig. 3. A particle cluster forming a spot onto impactor particle sampler (left upper) and the elemental maps of several individual particles. Elemental masks are drawn at right down. Measurement time is 12 minutes. Scan area of micro beam is 20×20 μm^2. Image resolution is 128×128 pixels.

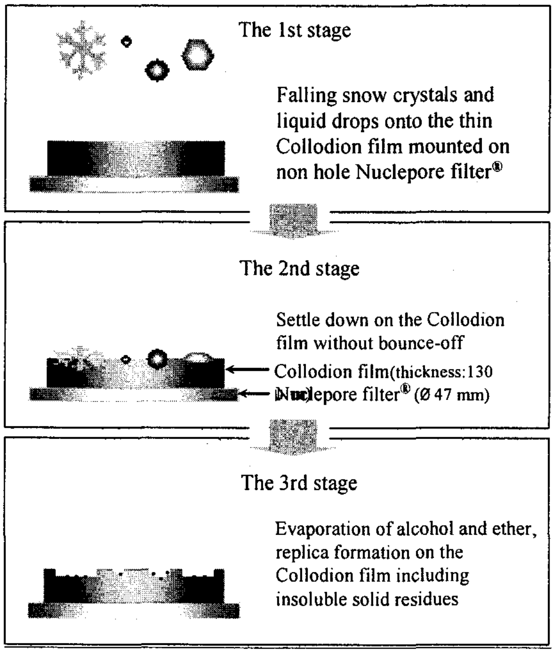

Fig. 4. Replica formation process of individual liquid droplets and snow crystals on the collodion film.

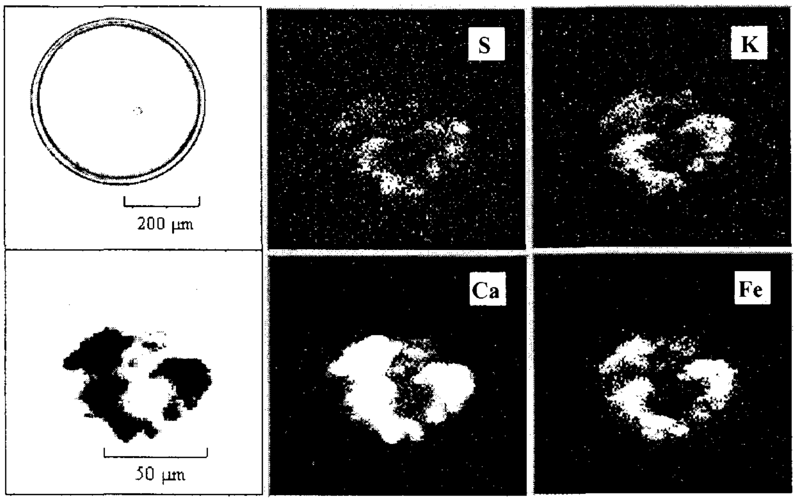

Fig. 5. An example of a raindrop replica (top left) and a drizzle droplet replica (top right). Four kinds elemental maps on a whole drizzle droplet. Measurement time is 21 minutes. Scan area of micro beam is 100×100 μm^2.

Example of single rain drop replicas and four kinds elemental maps on a whole drizzle droplet are shown in Figure 5. And elemental maps taken on the residue retained at the center of a raindrop were drawn in Figure 6. Row and col are pixels corresponding beam scan area and the scale bar is the peak count of characteristic X-ray. Soil originated components with S were found to be the most abundant componentin both a drizzle droplet and the residue of a raindrop.From these results, we can assume the washout processes of pollutants in the atmosphere and initial particle which acts as the cloud condensation nucleation.

3.3 Single fog droplet analysis

The characterization of individual fog droplets is of primary importance for both the explanation of fog formation processes and the modeling of acid deposition processes (Pandis and Seinfeld, 1989). The collodion film method was employed to the sampling of individual fog droplets. Since fog droplets do not really strike the ground by free falling, it is required to adjust the direction of collodion film toward wind.

Replicas of individual fog droplets are successfully formed on collodion film as shown in Figure 7. Also as the major component, Cl map was drawn on a single fog droplet. Thus sea-slat particles might have been incorporated into fog droplets during our sampling periods.

3.4 Single snow crystal analysis

Snow like rain is one of the most important natural processes in cleaning the particulate matter and aerosols that are present in the atmosphere. Previously reported data (Knutson *et al*, 1975; Mitra *et al*, 1990; Murakami *et al*, 1981) on aerosol scavenging by individual snow crystals or flakes indicates that snow scavenges aerosol much more efficiently than rain, when based on equal weights of precipitation. However, the snow scavenging has many unsolved problems because the shape of snow crystals is so complicated that it is very difficult compared with raindrops to deal with them experimentally and theoretically. As shown in Figure 8, the replication procedure not only allows us to get information about the physical property but also enable us to analyze the retained components on snow crystal replica. The elemental maps taken on an arm of dendritic snow crystal show fairly homogeneous distribution of S and Cl. The state of elemental distribution on individual snow crystals obtained from this study should be helpful to better understand the ice-nucleation and scavenging processes of pollutants by snow.

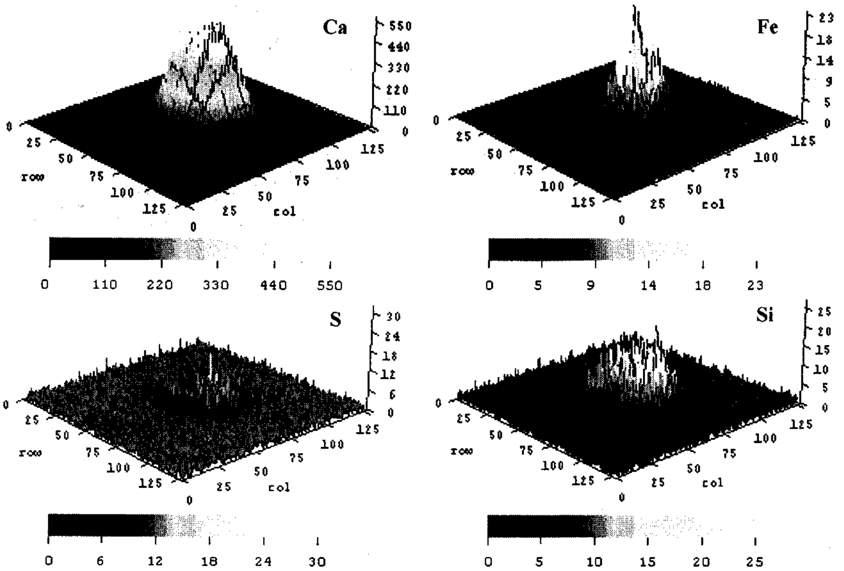

Fig. 6. Micro-PIXE elemental maps taken on the residue retained at the center of single raindrop collected on Collodion film. Measurement time is 15 minutes. Scan area of micro beam is 30×30 μm^2.

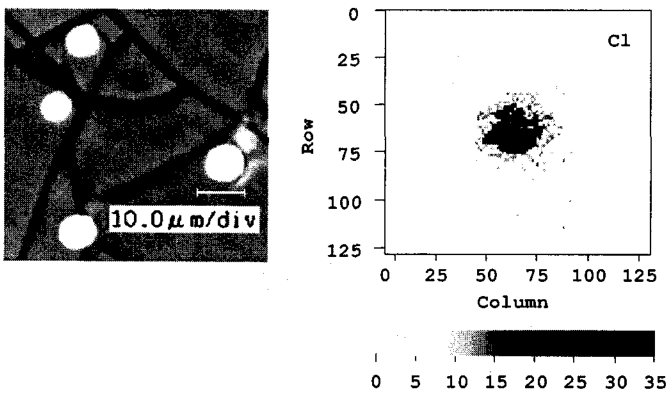

Fig. 7. Replicas of individual fog droplets successfully formed on collodion film (left) and Cl map drawn on a single fog droplet. Measurement time is 35 minutes. Scan area of micro beam is 23×23 μm^2.

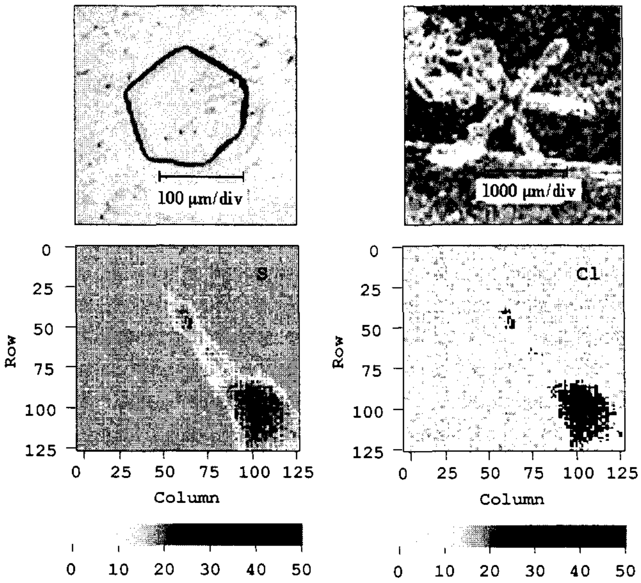

Fig. 8. Replicas of hexagonal and dendritic form snow crystals (upper) and elemental maps of sulfur and chloride taken on an arm of dendritic snow crystal (down). Measurement time is 24 minutes. Scan area of micro beam is $200 \times 200\ \mu m^2$.

4. CONCLUSIONS

In this study, we introduced the application of micro-PIXE to the various atmospheric samples. Up to recently, the elemental distribution of individual particles has been reported, while, the detailed distribution of the trace elements in a single fog droplet, a raindrop, a snow crystal has not been understood. In order to analyze individual liquid droplets (drizzle, fog, cloud) and snow crystals, their collection is a previous problem. In the present study, the replication technique was applied to the sampling of individual ambient liquid droplets and snow crystals. The ultra trace elements in residuals retained in individual liquid droplets and snow crystals can be the targets of micro-PIXE analysis. Elemental components of residuals, most of which became incorporated into liquid droplets and snow crystals by scavenging mechanisms of soluble and insoluble aerosol particles, should be helpful to better understand the nucleation and scavenging processes of pollutants by individual liquid droplets and snow crystals.

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