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Micro-PIXE as a Technique for Multi-elemental Detection and Localization in Various Atmospheric Environmental Samples

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Abstract

Microbeam PIXE, often called micro-PIXE, is one of powerful tools for analyzing a wide range of elements for various samples. Moreover, it has important applications of interest to the atmospheric science. In the present study, a qualitative elemental imagination for various atmospheric environmental species was attempted using micro-PIXE. Especially, in combination with a novel individual droplet collection method and the micro-PIXE analytical technique, the chemical specification of various individual atmospheric samples could be carried out. Here, we briefly introduce 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 ($1\sim2\,\mu m$) accelerated by 3 MeV single-end accelerator.

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

1. INTRODUCTION

It is well known 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 characteristics of the PIXE analysis are non-destructiveness, rapidity, easy preparation of the samples, and determination of multielement with a good accuracy and precision. 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 (Ma *et al.*, 2004; Ma *et al.*, 2001b; Park *et al.*, 2001; Kasahara *et al.*, 1996; Cornille and Maenhaut, 1990; Scheff and Valiozis, 1990). 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 $10^{-15}\sim10^{-16}$ g.

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

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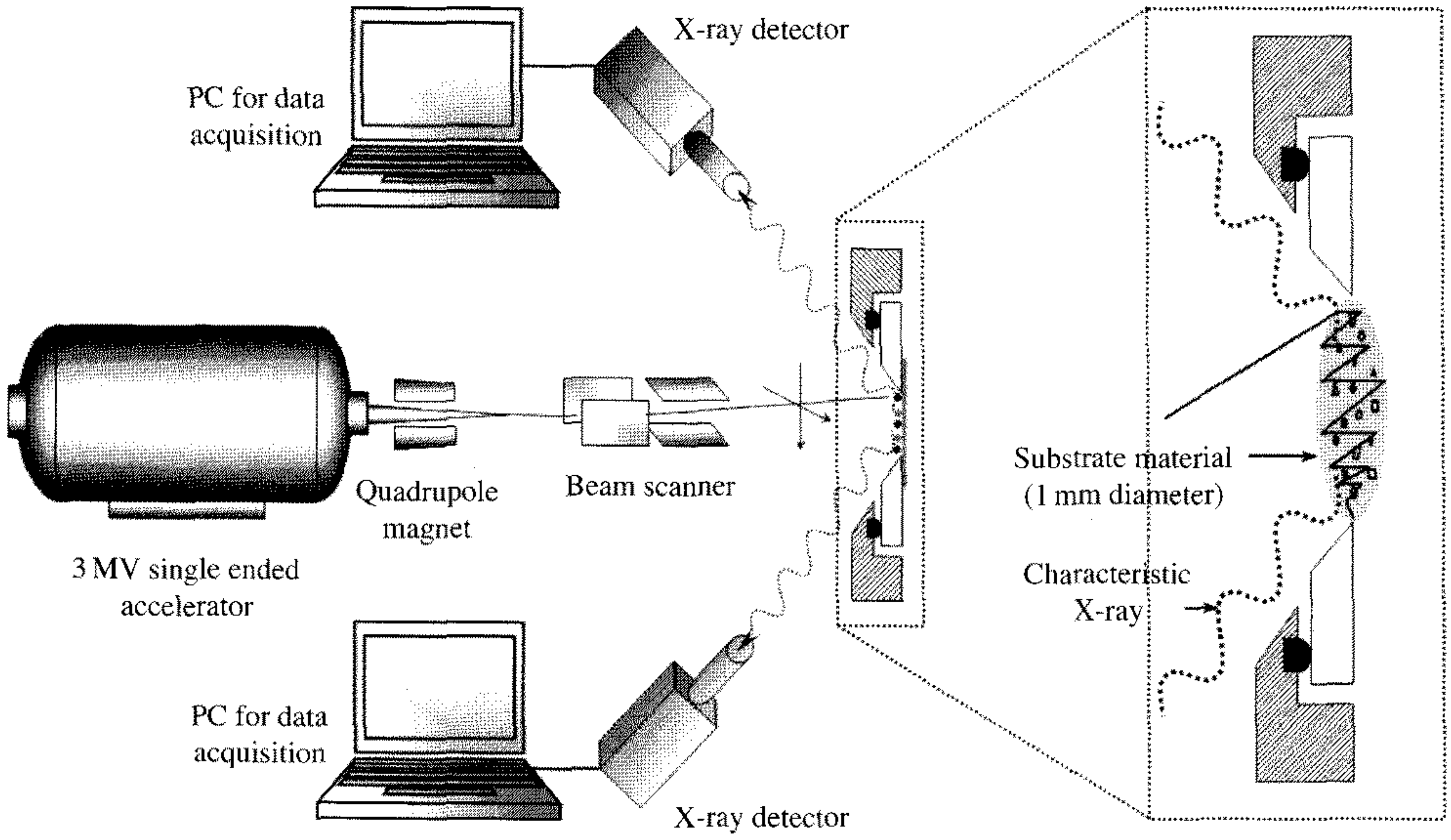

Fig. 1. Schematic diagram of the beam scanning and data acquisition system of micro-PIXE.

cially individual particles and droplets.

2. MATERIALS AND METHODS

2. 1 Micro-PIXE set-up

Micro-PIXE analysis was performed at the division of Takasaki Ion Accelerator for Advanced Radiation Application (TIARA) in Japan Atomic Energy Research Institute (JAERI). Figs. 1 and 2 show the schematic diagram of micro-PIXE and its window screen for data analysis, respectively. 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 (Ma *et al.*, 2001a; Sakai *et al.*, 1998).

2. 2 Replication of individual drops and ice-crystals

The determination of chemical composition of single drops and ice-crystals is expected to give a new and interesting information about washout of pollutants and drop (or crystal) formation processes in and below the cloud. However, it is possible to obtain a great amount of information by analysis of individual drops and ice-crystals, there is difficulty in their sampling and handling processes.

In this study, for the purpose of collecting and subsequent chemical analysis of individual drops and ice-crystals, the replication method was applied. Replica formation process of individual liquid drop-

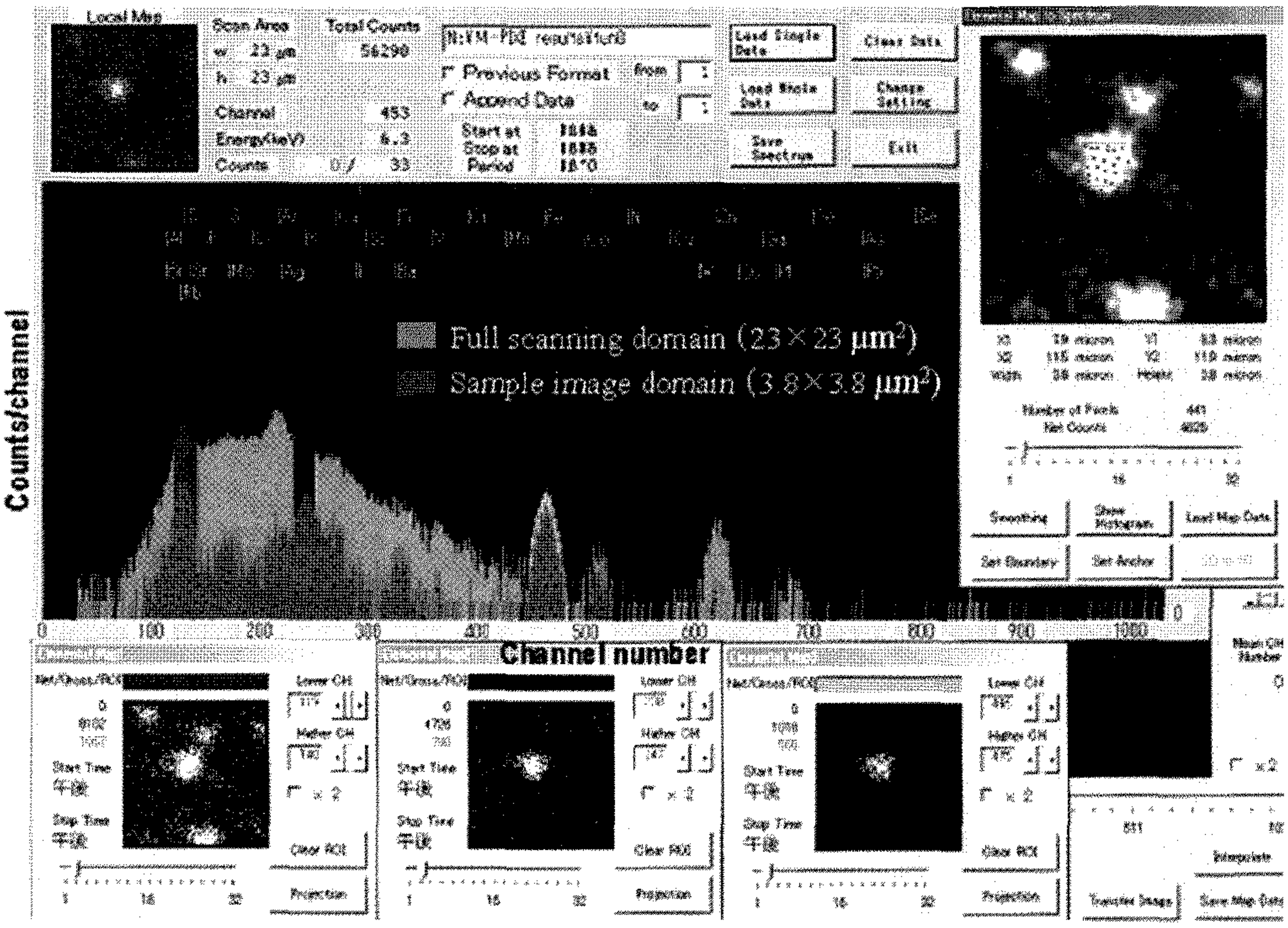

Fig. 2. Window screen of Micro-PIXE data analysis program.

lets and snow crystals on the Collodion film was illustrated in Fig. 3. The Collodion solution was mounted onto a polycarbonate filter just before collection. When drops and ice-crystals fall onto the thin layer of Collodion film, they gently settled without deformation and bounce-off. Allowing the ethyl alcohol, which plays a role in dissolving nitrocellulose in the Collodion solution, to evaporate, finally a thin film containing the replication of individual raindrops was left.

Before the sampling of snow crystal, the set of Collodion replication was set-up outside and preconditioned to the ambient outdoor temperature. After selecting process of ideal portion by microscopic measurement, samples were attached on the sample holder of micro-PIXE. And then the sample without any sample pretreatment, containing the replicas of raindrop and snow crystal, was directly irradiated by micro-beam. Finally, the non-volatile insoluble particles and residues existent on individual replicas of raindrop and snow crystal were de-

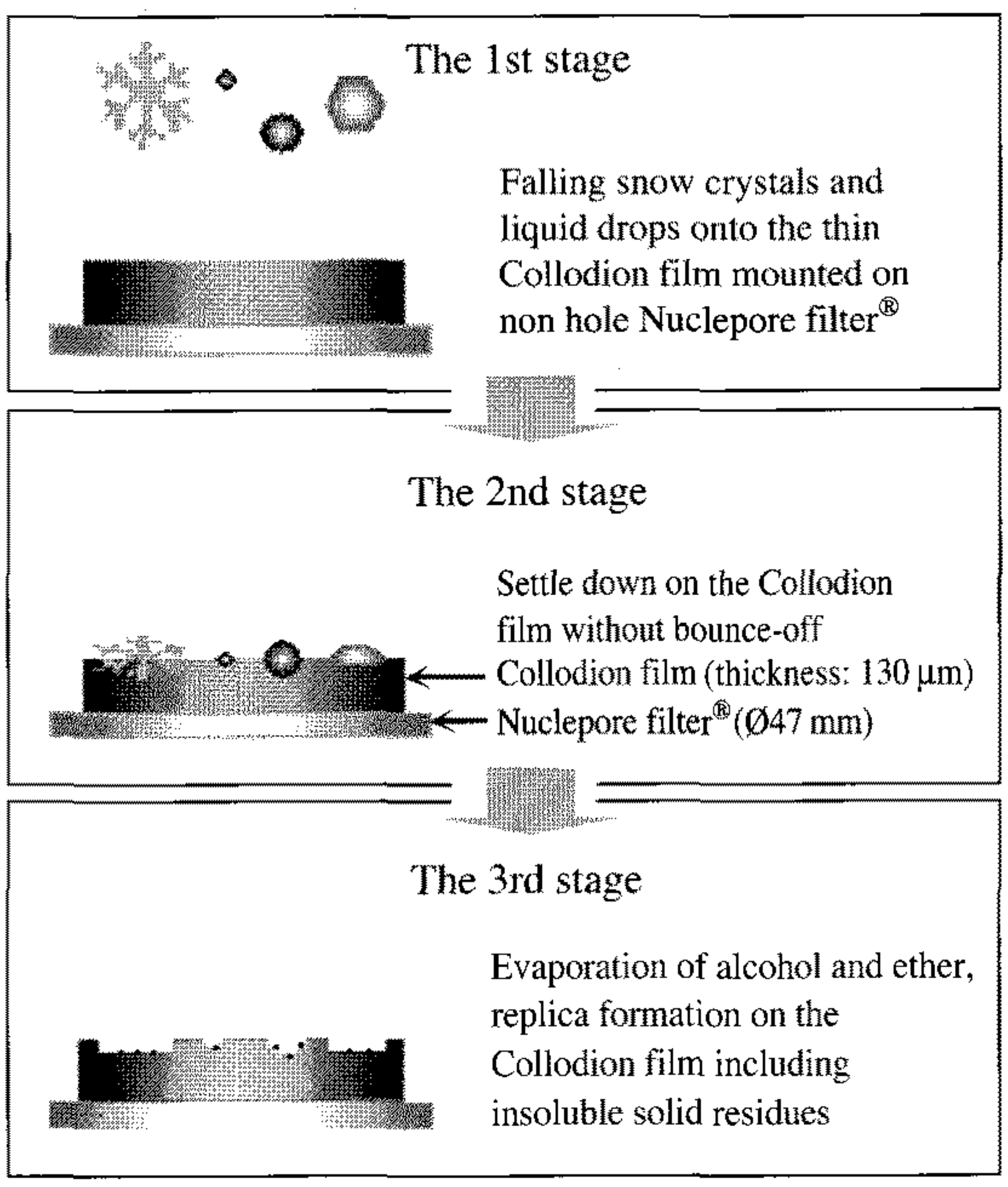

Fig. 3. Replica formation process of individual liquid droplets and snow crystals on the collodion film.

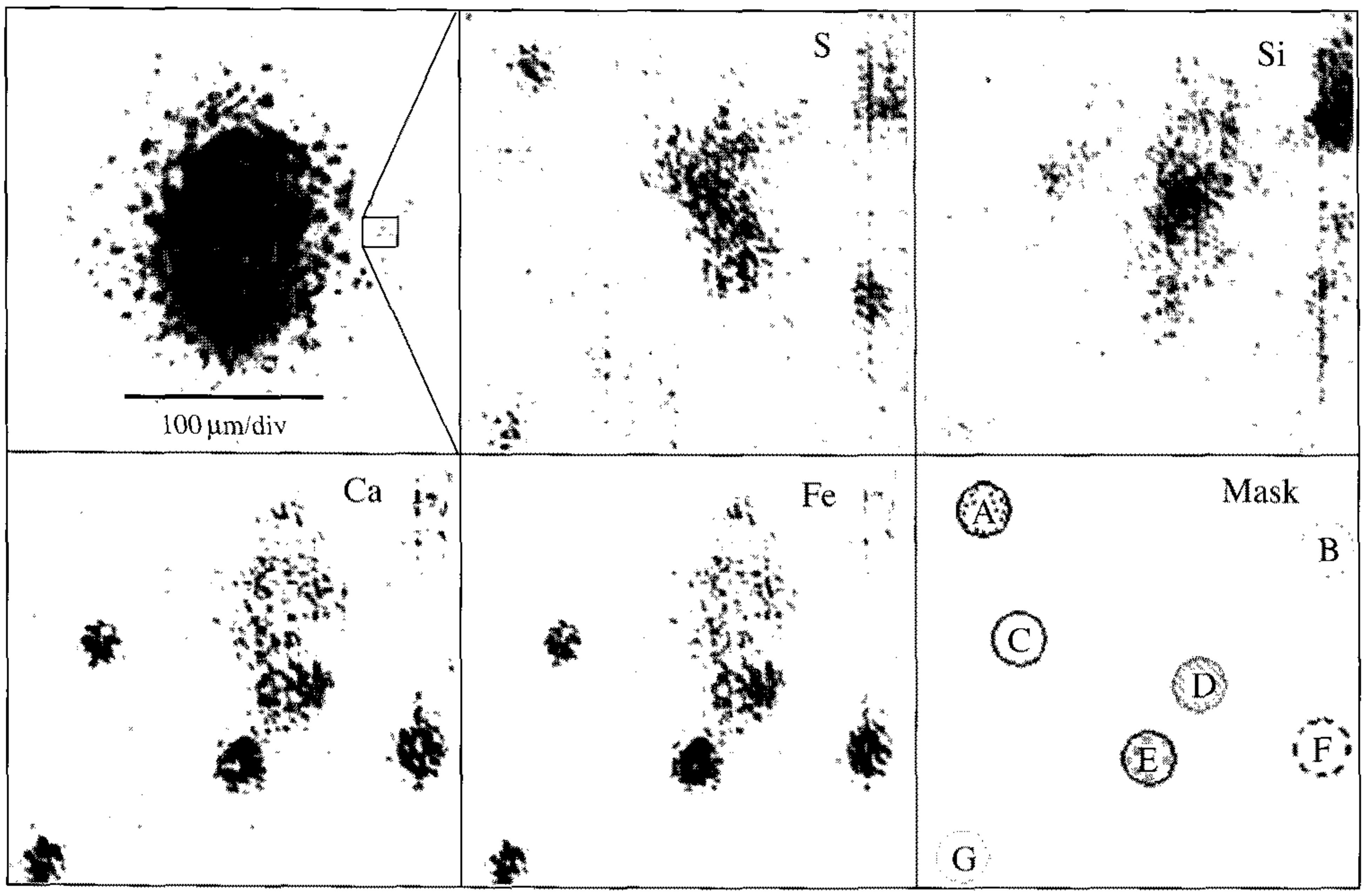

Fig. 4. A particle cluster forming a spot onto impactor particle sampler (left upper) and the elemental maps of several individual particles. Elemental masks are drawn at right down. Measurement time is 12 minutes. Scan area of micro beam is $20 \times 20\,\mu m^2$. Image resolution is 128×128 pixels.

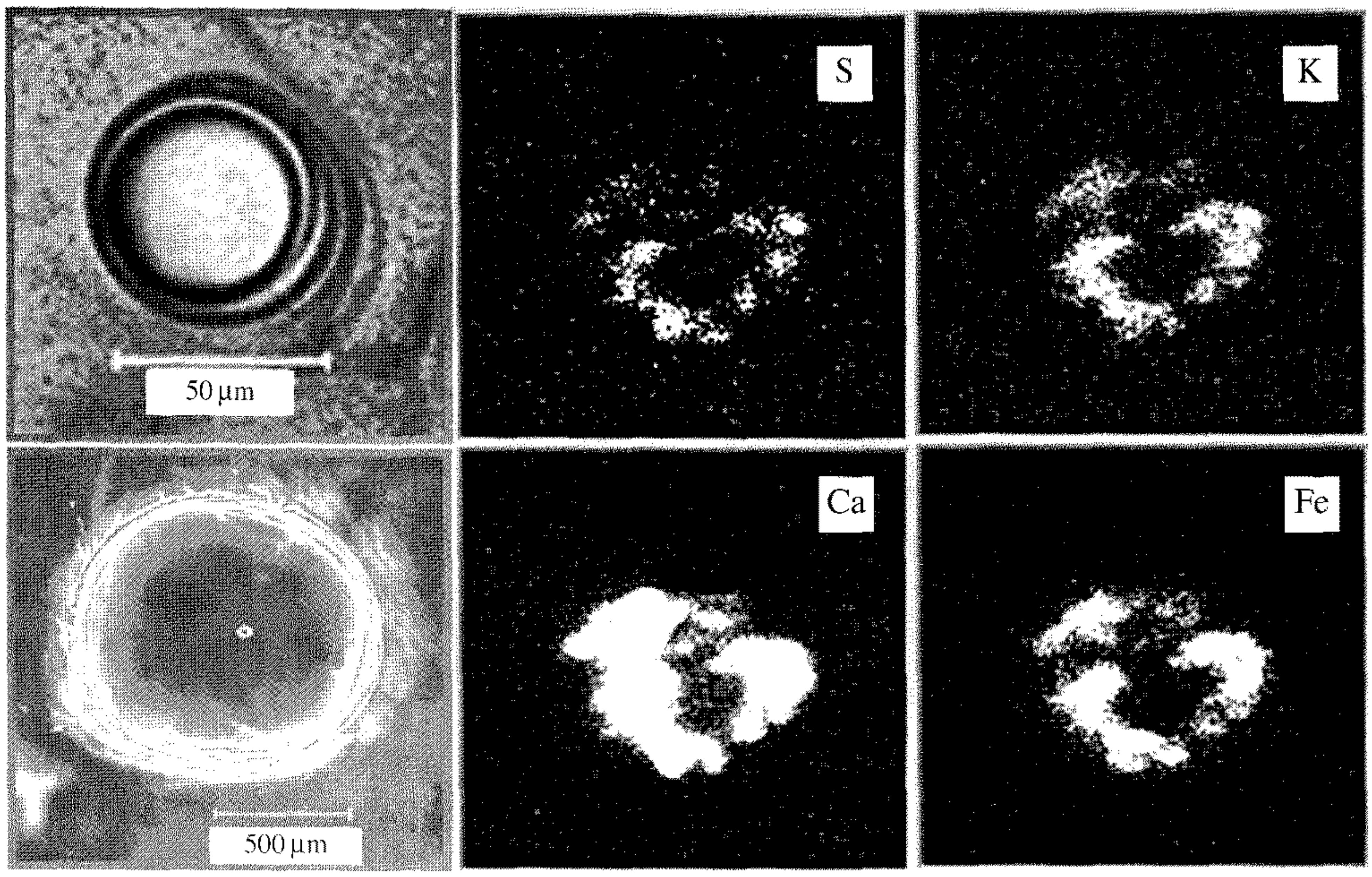

Fig. 5. An example of a drizzle droplet replica (top left) and a raindrop replica (bottom left). Four kinds elemental maps on a whole drizzle droplet. Measurement time is 21 minutes. Scan area of micro beam is $100 \times 100\,\mu m^2$.

tected by an electron beam of micro-PIXE.

3. RESULTS AND DISCUSSION

3.1 Single particle

The detailed information on composition of single particles is essential to fully 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 ones (Kasahara *et al.*, 2000).

The particles individually collected by various types of sampling devices can be the target of micro-PIXE analysis. In the present study, a low pressure Andersen impactor (LPAI) was used for aerosol sampling. Since the particles often overlap and form clusters, the edge portion of a spot (as a conglomeration of individual particles) formed on the each stage of LPAI is desirable for single particle analysis. In this study, a whole individual particles separately distributed on the fringe of an aerosol spot were irradiated by micro-beam.

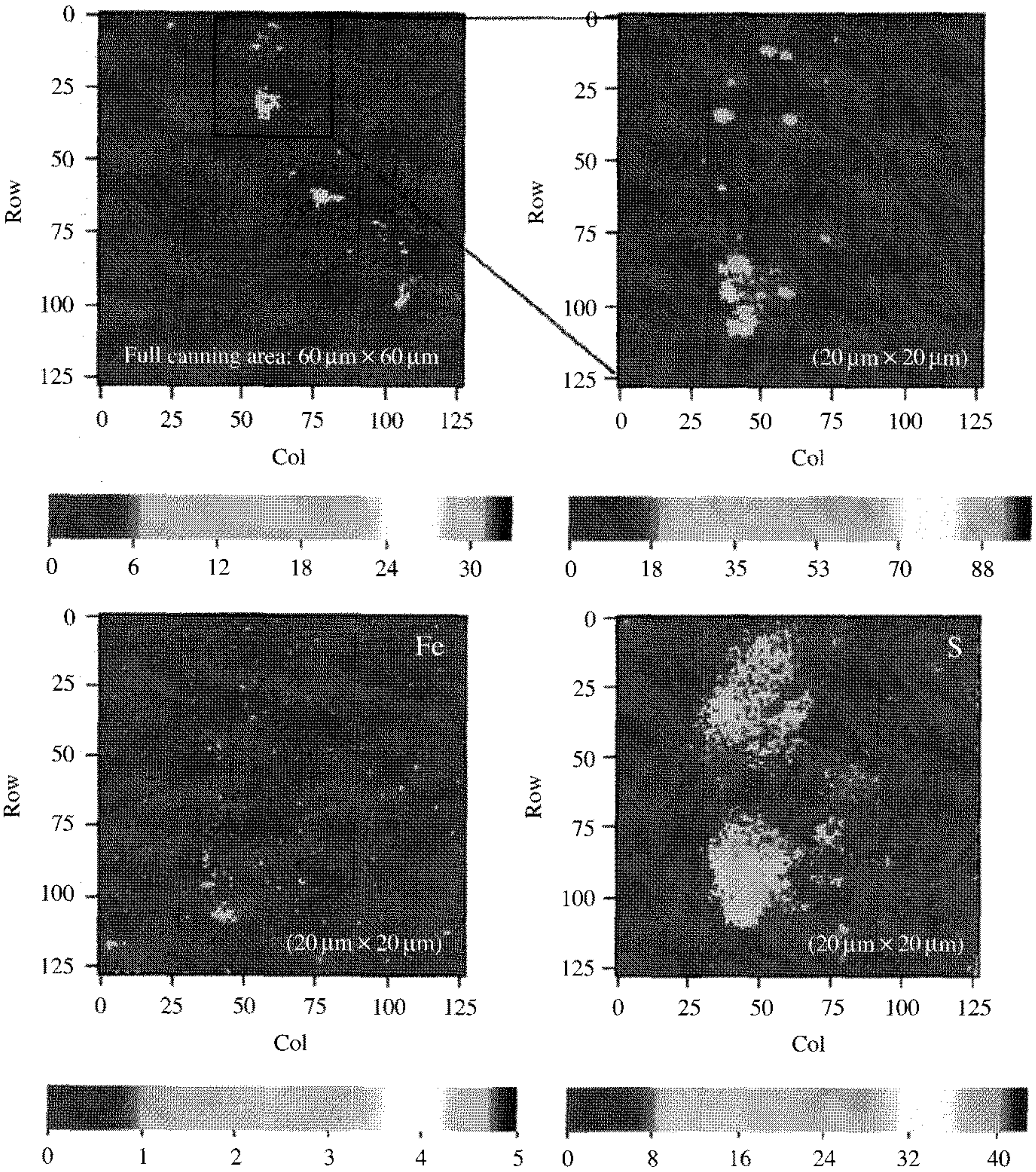

Fig. 6. Micro-PIXE elemental maps taken on the residue retained at a portion of a single raindrop collected on Collodion film. Measurement time is 15 minutes. Final scan area of micro beam is 20 × 20 µm².

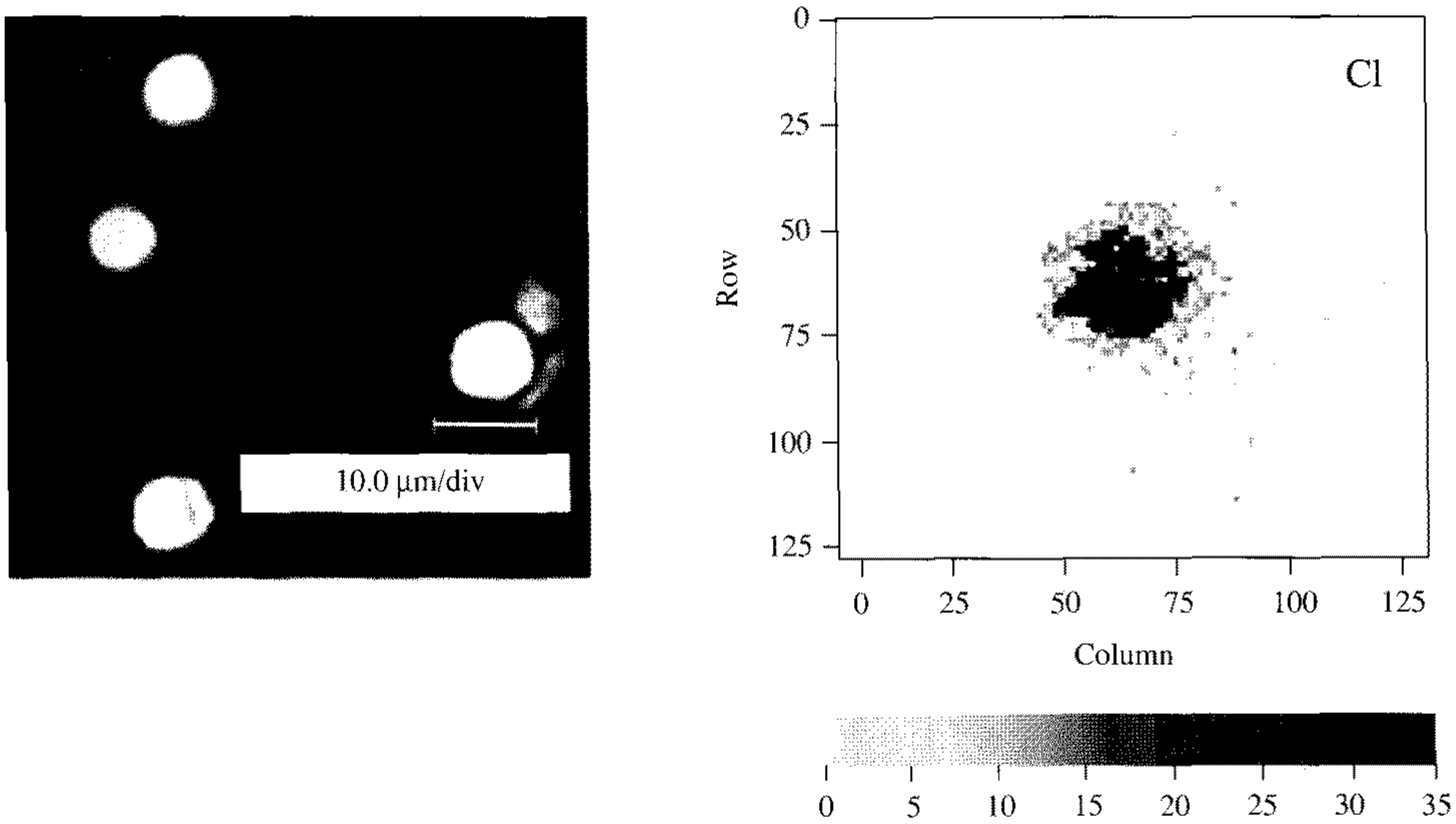

Fig. 7. Replicas of individual fog droplets successfully formed on collodion film (left) and Cl map drawn on a single fog droplet. Measurement time is 35 minutes. Scan area of micro beam is $23 \times 23\,\mu m^2$.

An example of elemental maps for the urban individual particles arrested onto the 5th stage (1.17 μm cutoff diameter) of LPAI is shown in Fig. 4. 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 are principally detected in and/or on several individual particles and their localizations are varied in each particle. For instance, sulfur is clearly distributed in mask number A, while silicon shows 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.

Though, in the present study, we do not practice the point analysis on a single particle, the point-to-point variation of elemental distribution on a particle can be considered.

3. 2 Single raindrop

Example of the replicas of a drizzle and a rain drop and four kinds elemental maps on a whole drizzle droplet are shown in Fig. 5. And elemental maps taken on the residue retained at a portion of a raindrop were also drawn in Fig. 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 abundant components in 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 also 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 Fig. 7. Also

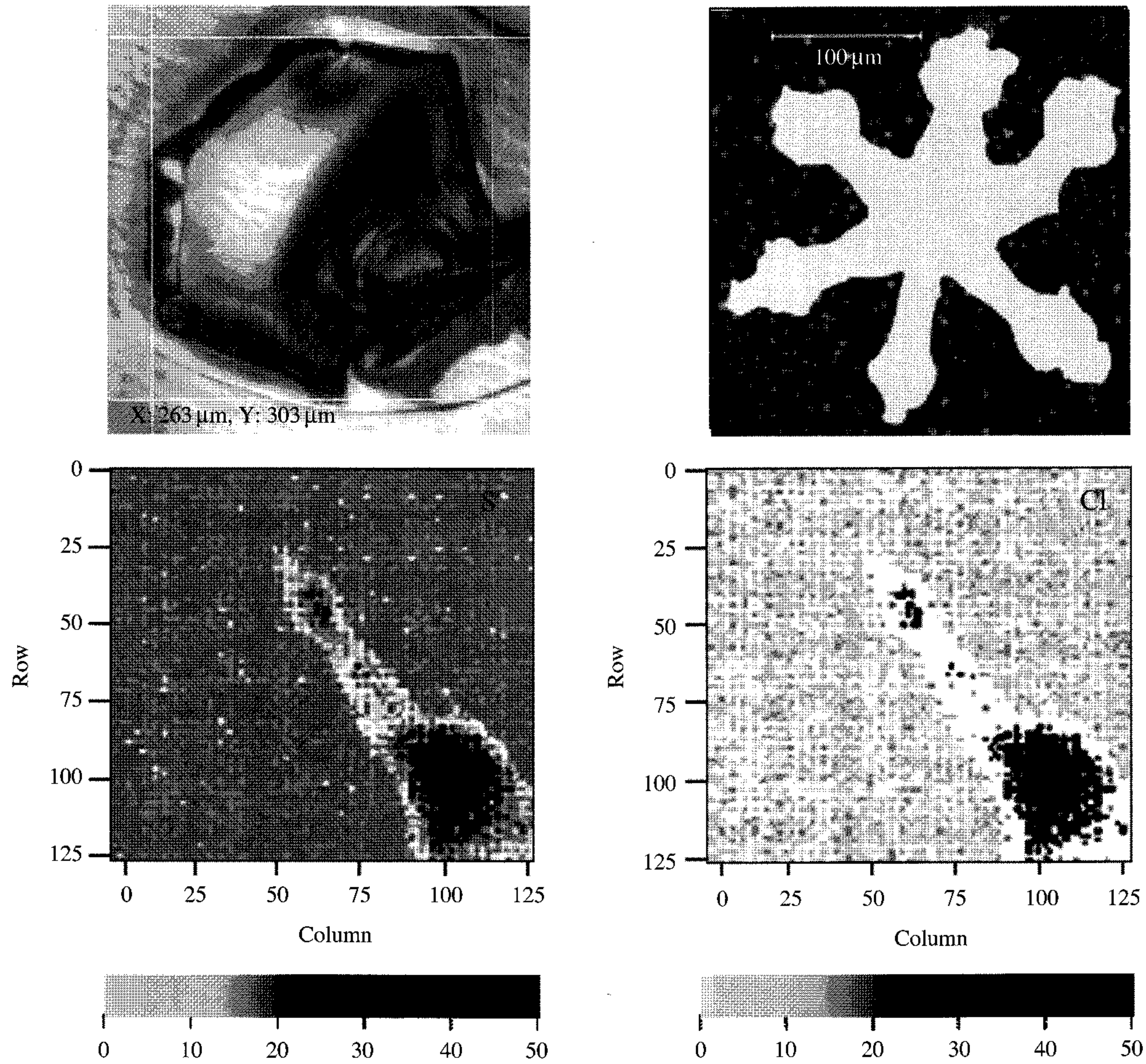

Fig. 8. Replicas of hexagonal and dendritic form snow crystals (upper) and elemental maps of sulfur and chloride taken on an arm of dendritic snow crystal (down). Measurement time is 24 minutes. Scan area of micro beam is 200 × 200 µm².

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 period.

3.4 Single snow crystal

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 (Mitra *et al.*, 1990; Murakami *et al.*, 1981; Knutson *et al.*, 1975) 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 Fig. 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.

4. SUMMARY

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.

Even though this micro-PIXE has certain advantage over alternative sensitive individual particles measurement methods, e.g., laser microprobe mass spectrometry (LAMMS) and secondary ion mass spectrometry (SIMS), as one of the defective points of this micro-PIXE, the quantitative elemental analysis is not generalized. Thus, it is to be desired that the subsequently attempt to quantitative analysis of trace elements in a single ambient sample will be done.

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