Measurement of Insoluble Mineral Particles in a Saturated Atmosphere

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Abstract

This study was undertaken to measure the properties of individual mineral particles in an artificially saturated atmosphere at a vertical extinct mine with 430 m height. By synchrotron radiation X-ray fluorescence (SR-XRF) microprobe analysis, it was possible to determine the elemental composition of residual insoluble particles on individual cloud droplet replicas formed on the Collodion film. The XRF visualized elemental maps enabled us not only to presume the chemical mixing state of particles retained in cloud droplet, but also to estimate their source. Details about the individual mineral particles captured by artificial cloud droplets should be helpful to understand about the removal characteristics of dust particles such as interaction with clouds. Nearly all individual particles captured in cloud droplets are strongly enriched in Fe. Mass of Fe is ranged between 41 fg and 360 fg with average 112 fg. There is a good agreement between single particle analysis by SR-XRF and bulk particle analysis by PIXE.

Key words : Mineral particle, Artificial cloud, Droplets, SR-XRF

1. INTRODUCTION

Atmospheric particles are classed according to their affinity for water: hygroscopic, neutral, and hydrophobic. Some water-attracting particles become wetted at relative humidity less than 100%, and then they grow to cloud droplet size. Water vapor will stick to, and condense on, particles to form clouds; hence the particles are termed CCN. There are many different types of condensation nuclei in the atmosphere. CCN can be formed from a byproduct of any combustion process like motor vehicles emissions, industrial activity, and controlled fires. CCN also occur naturally in the atmosphere. Major natural sources of CCN are volcanic activities, sea salts, sulfate particles formed by gases given off by phytoplankton, natural fires, and dust storm.

Though some atmospheric aerosols are insoluble in water, they begin to serve as centers upon which water vapor can condense. For example, though crustal aerosols are less soluble than marine and anthropogenic aerosols, their solubility weathered by condensation-evaporation cycles can be increased (Desboeusf *et al.*, 2001; Vong *et al.*, 1997; Cachier *et al.*, 1989). Also the in-cloud scavenging of dust particles originated from the massive sandstorm blowing off the widespread distribution of loess and desert in China and northwest African desert areas have been expected. To get the detailed information

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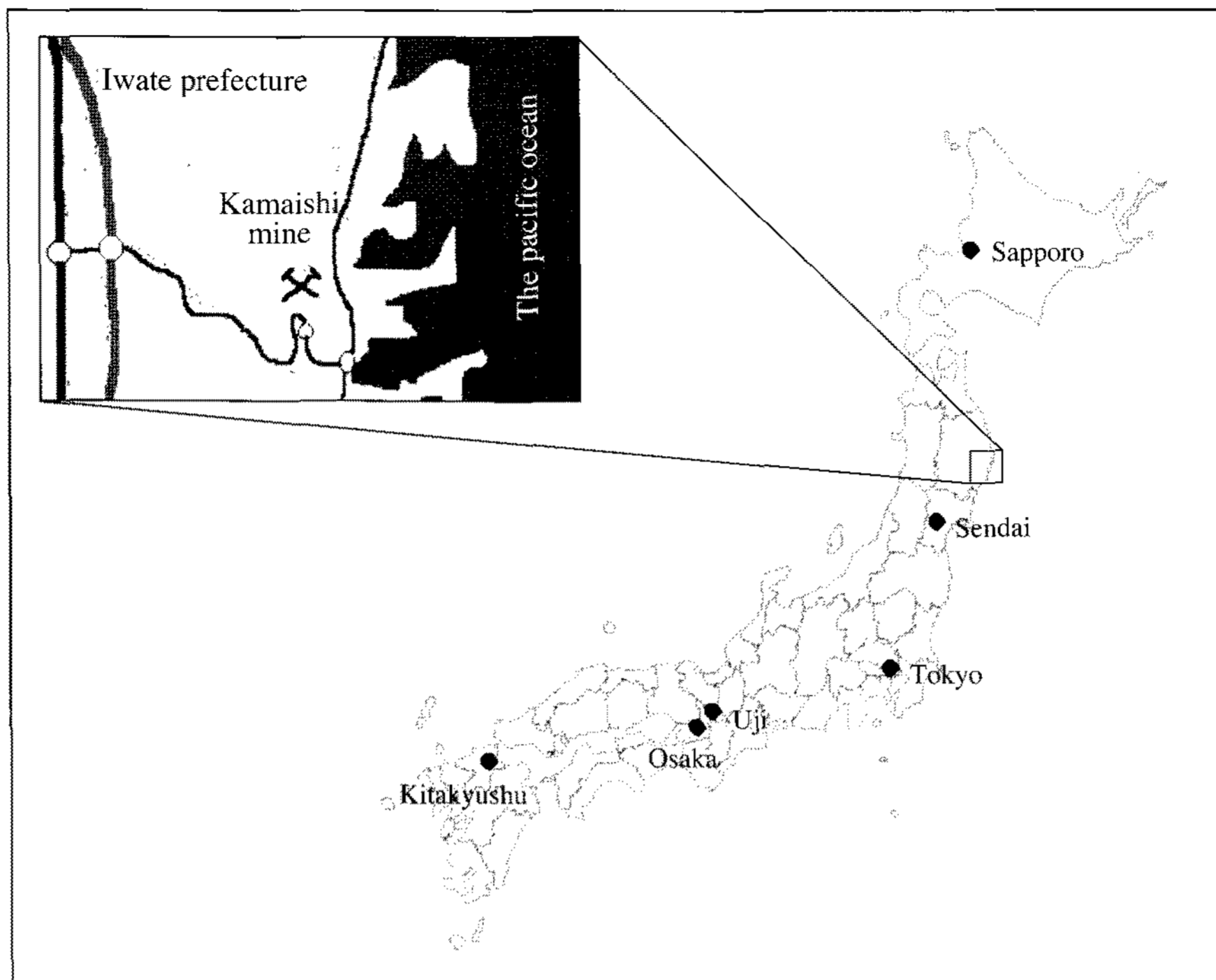Tel : +81-92-661-2411 (ext.373), E-mail : ma@fwu.ac.jp

Fig. 1. Map showing the Kamaishi mine, which is an abandoned mine at present, applied in a quasi-real scale cloud generation.

about the removal characteristics of dust particles by interaction with clouds, the behavior of dust mineral particles as CCN has to be studied in view of individual cloud droplets. However no experimental study on individual dust particles captured by cloud droplets has not been reported.

In the present study, for the purpose of estimating the behavior of mineral particles we made an attempt to generate artificial clouds using a huge vertical pit. Moreover, the chemical properties of individual mineral particles captured by cloud droplets were determined by SR-XRF microprobe analyzer.

2. EXPERIMENTAL

2.1 The shaft of semi-real scale cloud chamber

By the common procedures of cloud generation in the laboratorial experiment, which are usually per-

formed on a small scale at most several tens of meters, it is not enough for thorough assessment of micro-physicochemical characteristics of the cloud scavenging (e.g. rainout) of hydrophobic mineral particles.

Accordingly, for the experimental study on the behavior of dust mineral particles in a saturated atmosphere, a quasi-real scale artificial clouds generation was attempted using a huge vertical pit with 430 m height. We had the happiness to find this Kamaishi mine (Fig. 1) which is an abandoned mine at present. Since the geological advantage of Kamaishi mine was described already in elsewhere (Ma, 2006), we make mention of its merit here briefly. This mine, which is one of the extinct iron-copper mines, has the very stable four-side walls without any entrance of artificial particles. Also due to the subterranean water, the atmosphere of vertical mine is always wetted with relative humidity near 100%. Thus a thin background cloud is always forming. Conse-
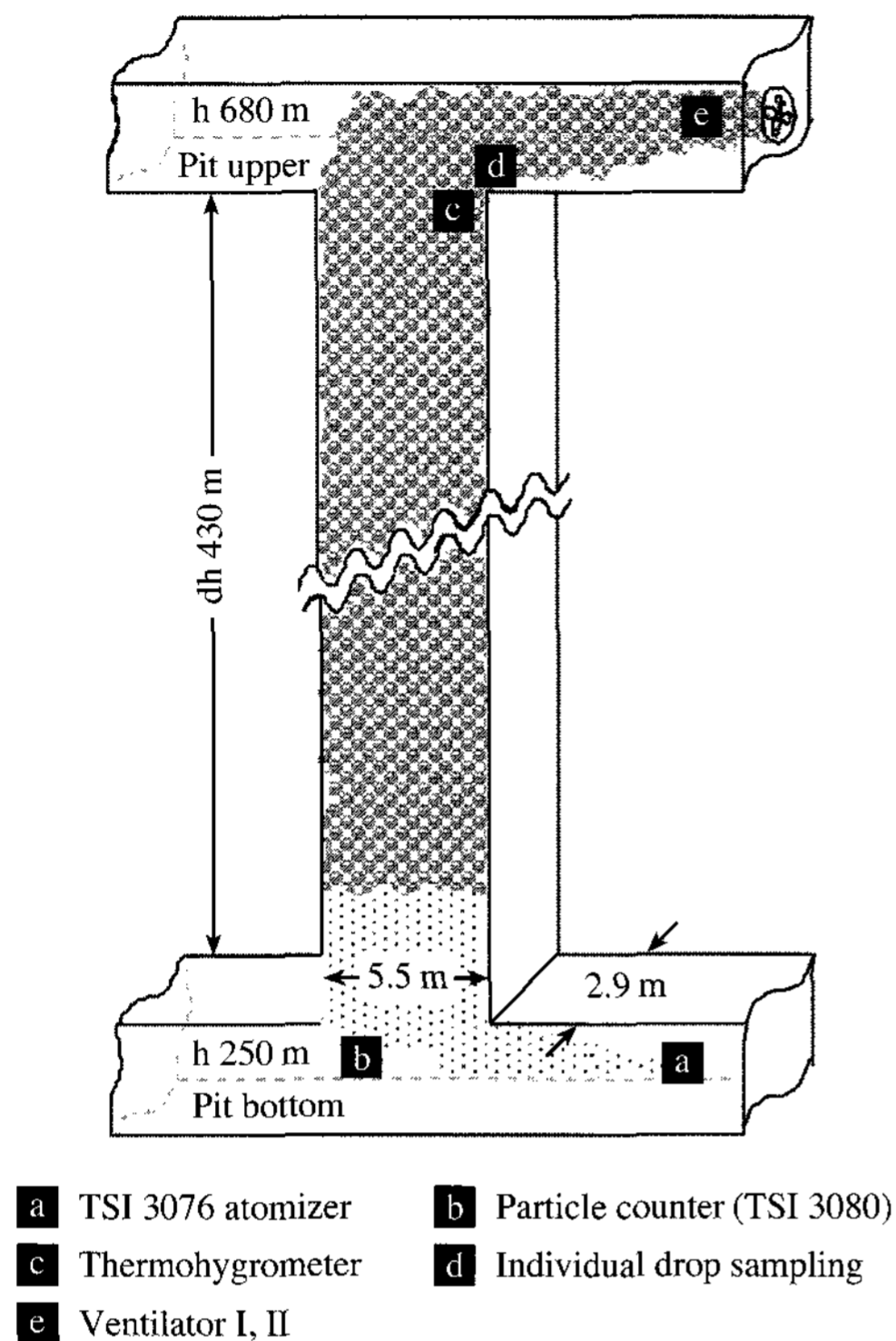
h 680 m
Pit upper

dh 430 m

←5.5 m→   2.9 m

h 250 m
Pit bottom

	TSI 3076 atomizer		Particle counter (TSI 3080)
	Thermohygrometer		Individual drop sampling
	Ventilator I, II		

Fig. 2. Schematic illustration of cloud generation at a vertical pit formed in a disused mine.

quently, it certainly is the natural bounty for the accomplishment of our experimental objective.

2. 2 Artificial cloud formation

As mentioned above, though background cloud was always forming, to make a successful estimation of the scavenging of mineral particles into droplet an artificial cloud formation is needed. Fig. 2 shows the schematic illustration of a trial for the activation of thin background cloud to thick one. The ascension of damp air stream is an essential prerequisite for cloud formation. To make an ascending air parcel, two huge ventilators were installed at the top of pit (see Fig. 2) and the wind speed was controlled. To increase the number of cloud droplets, the hydrophilic dry particles were dispersed into the bottom entrance of a shaft (see Fig. 2). The dry particles were generated from 1 g/L NaCl aqueous solution by using an atomizer (TSI 3076) with a diffu-

sion silica gel dryer. As the aerosol goes through the inner cylinder of the cartridge, the water vapor diffuses into the silica gel through the mesh screen.

2. 3 Cloud collection

For the purpose of effective discussion on the wet removal characteristics of mineral particles, cloud droplets have to be analyzed not bulkily but individually, because the bulkily collected cloud water can easily contain the interstitial particles which could not work on cloud formation.

In order to collect individual cloud droplets, the Collodion replication method introduced from Ma *et al.* (2003a) was applied. As already described in former studies (Ma *et al.*, 2004; Ma *et al.*, 2003a, b; Ma *et al.*, 2001), about 0.2 mL of Collodion solution (3%) being sold was mounted onto the Mylar ($C_{10}H_8O_4$) film with a thickness of 10 μm on the brink of sampling. When cloud droplets adhere freely onto the thin layer of collodion film (130 ± 10 μm) they gently settled without bounce-off. This procedure not only allows us to get information about the physical properties of droplets but also enable us to analyze the retained components in and/or on cloud droplet. Added to this individual cloud droplet sampling, bulk cloud water was simultaneously collected by a cloud water collector (see Fig. 3) consisting of a fan, a Teflon impaction mesh, and the storage bottles controlled by a timer.

2. 4 Analysis of chemical composition

After natural evaporation of the liquid water and the solved volatile substances, the non-volatile components as dry residual particles, which captured by droplets, are released. These residual particles probably captured by Brownian collision were the target of the SR-XRF microprobe analytical system equipped at SPring-8, BL-37XU of the Japan Synchrotron Radiation Research Institute (JASRI). This micro-beamline can be successfully used to carry out the reconstruction of elemental map and the quantification analysis for multiple elements with fg level sensitivity (Hayakawa *et al.*, 2001). By scanning the microbeam on the surface of droplet replica, it is possible to obtain spatial distribution of trace
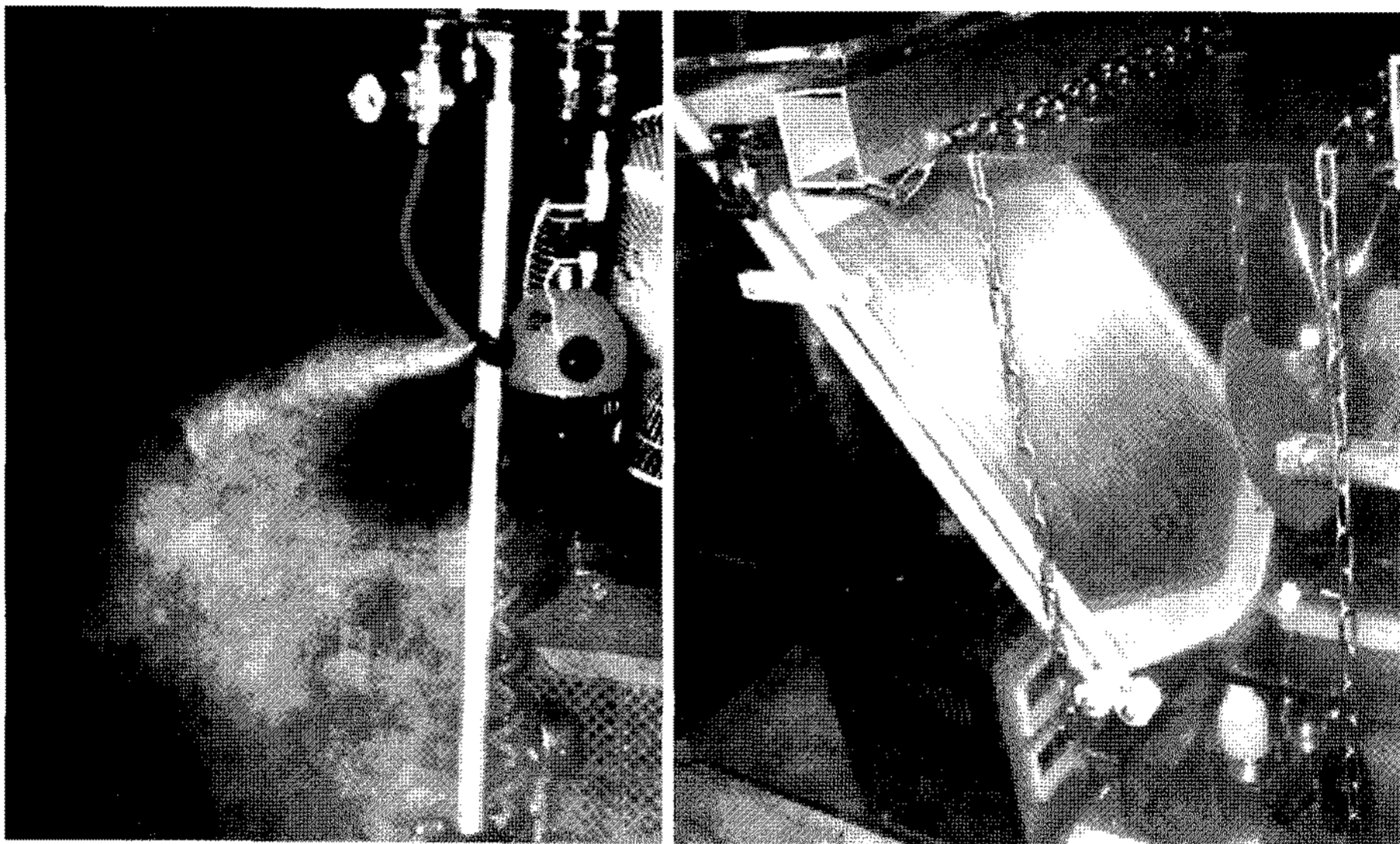
Fig. 3. An atomizer (TSI 3076) used in nebulizing mist spray (left) and a cloud water collector consisting of a fan and a Teflon impaction mesh (right).

elements in scanning area $300 \times 300\ \mu m^2$. The intensity of the incident X-rays was monitored by an ionization chamber. The fluorescence X-rays were recorded with a Si (Li) detector placed in the electron orbit plane of the storage ring and mounted at $90°$ to the incident X-rays to minimize background caused by the scattering. To realize elemental quantification, we measured XRF spectra of the selected portions and the blank of backing material (Mylar film) with the data acquisition time of 200 s.

Moreover the chemical composition of bulk particles contained in cloud water was determined by Particle Induced X-ray Emission (PIXE). To separate the solid particles from cloud water, cloud water was centrifuged under the condition of 4,000 rpm (maximum centrifugal force: 2,670 g) for 10 minutes. And then the solid particles were deposited on $10\ \mu m$ thickness Mylar film. Subsequently they were analyzed by PIXE. PIXE analysis was performed by exposing the homogeneous deposited particles on polycarbonate filter to a 2 MeV proton beam from a tandem accelerator. The protons hitting the sample cause the atoms to emit X-rays, which are detected with a Si(Li) detector. The emitted X-radiation permits the determination of the chemical element in

the sample. The more detailed analytical procedures and experimental set-up used for SR-XRF and PIXE analyses were described elsewhere (Hayakawa *et al.*, 2001; Kasahara *et al.*, 1993).

3. RESULTS AND DISCUSSION

The individual artificial cloud droplets formed as replicas on the Collodion film and insoluble particles retained in bulk cloud water formed, when the 1 g/L NaCl solution was nebulized, are shown in Fig. 4. As ascertained in Fig. 4, cloud droplets are successively reappeared as their replicas which are containing mineral particles. Particle activation depends not only on particle number concentration, updraft velocity, and mean radius of aerosol, but also on aerosol composition. The processing of cloud formation by insoluble mineral particle is schematically illustrated in Fig. 5. Although fresh mineral particles are not water-soluble, if mineral particles are aged by surface reactions and mixing processes, they become more hydrophilic. This enables the transfer of mineral particles into cloud droplets via nucleation scavenging. However, in general, the original
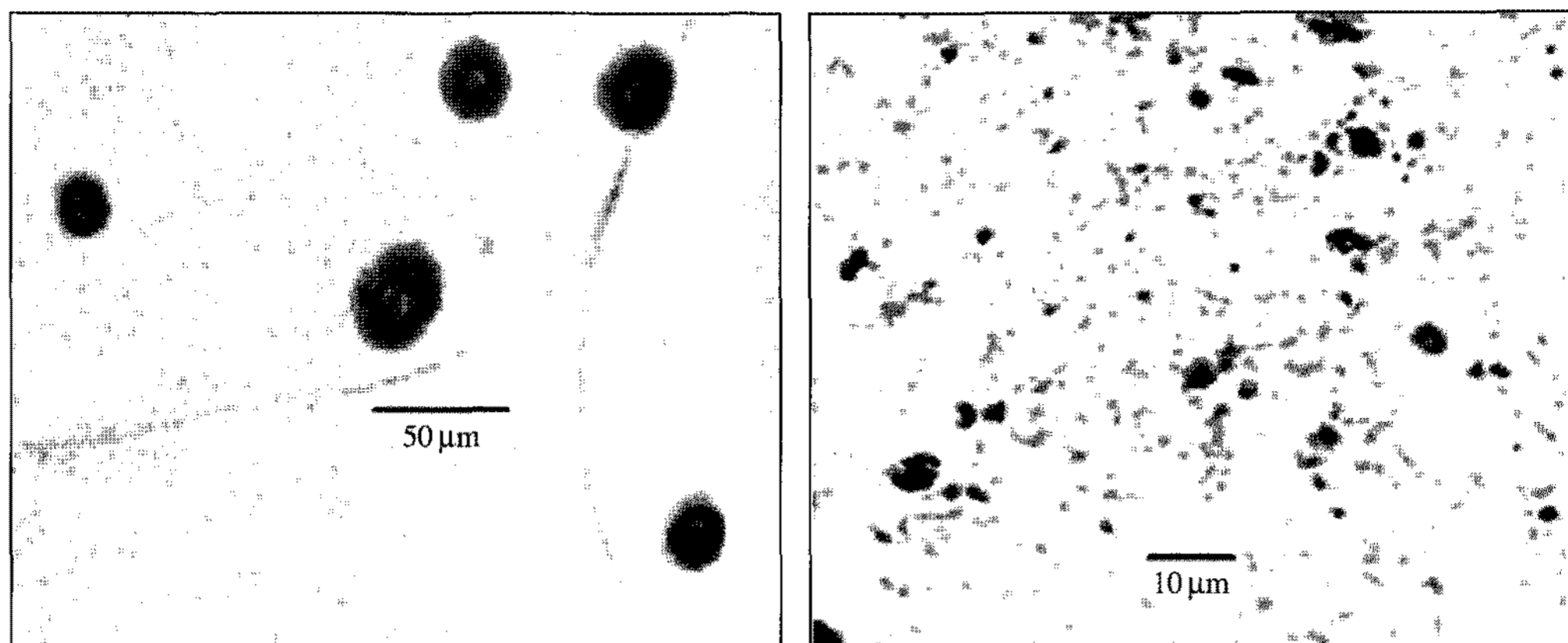
Fig. 4. Individual artificial cloud droplets formed as replicas on the Collodion film (left) and insoluble particles (individual or lumps of particles) retained in bulk cloud water formed when the NaCl 1 g/L was nebulized.
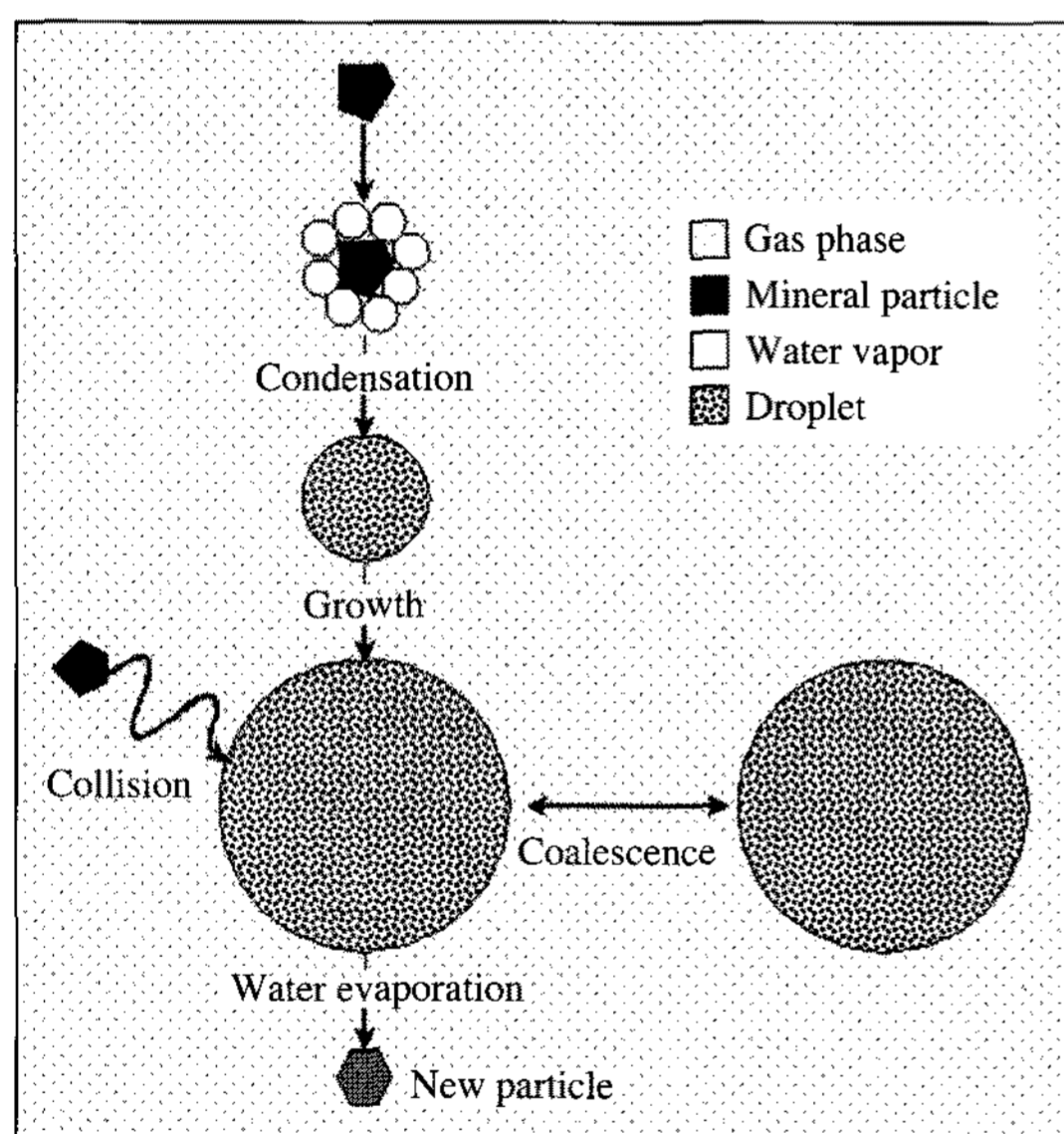

Fig. 5. Predicted particle-cloud-particle cycle during cloud processing in the shaft of semi-real scale cloud chamber.

mineral particles have no affinity for water. They cannot be easily dissolved in cloud droplet by itself and do not take up any water. According to this property of mineral particles, the background particles in the vertical pit may exist as the interstitial particles, which have not been activated to droplets within the cloud. Regretfully, in the present study, the

synchronous collection and analysis of interstitial particles were not performed. From this point of view, it is necessary to discuss interstitial particles and their lifetime in detail.

A portion of interstitial mineral particles collides with cloud droplets and is removed from cloud interstitial air. The Brownian coagulation theory introduced by Seinfeld and Pandis (Seinfeldand Pandis, 1998) can be used to quantify the rate and effects of interstitial particle removal. If $n(D_p, t)$ is the particle number distribution and $n_d(D_p, t)$ is the droplet size distribution at time $t(s)$, the loss rate of particles per unit volume of air due to scavenging by cloud drops is given by

$$-\frac{\partial n(D_p, t)}{\partial t} = n(D_p, t) \int_0^\infty K(D_p, x) n_d(x, t) dx \qquad (1)$$

where $K(D_p, x)$ is the collection coefficient $(\text{cm}^{-3}\,\text{s}^{-1})$ for collisions between an interstitial aerosol particle of diameter D_p (μm) and a droplet of diameter x (μm). One can define the scavenging coefficient $\Lambda(D_p, t)$ for the full droplet population.

$$\Lambda(D_p, t) = -\frac{1}{n(D_p, t)} \frac{\partial n(D_p, t)}{\partial t}$$

$$= \int_0^\infty K(D_p, x) n_d(x, t) dx \qquad (2)$$

If the scavenging coefficient did not vary with time

and were equal to $\Lambda(D_p)$, then the evolution of the number distribution would be given by

$$n(D_p, t)=n(D_p, 0)\,exp[-\Lambda(D_p)t] \qquad (3)$$

If cloud droplets are stationary, then particles are captured by Brownian diffusion, on the assumption that the cloud has a liquid water content (W_L) of 0.5 g m^{-3} and that all drops have diameters of 10 μm, resulting in a number concentration of $N_d=955$ cm^{-3}, the lifetime of interstitial particles can be estimated (Seinfeld and Pandis, 1998). For such a monodisperse droplet population (Eq. 2) simplifies to

$$\Lambda(D_p)=N_d K(D_p, 10\,\mu m) \qquad (4)$$

and $K(D_p, 10\,\mu m)$ can be calculated from Fuchs's coagulation coefficient (Fuchs, 1964). When inter-

stitial particle size (D_p) is 0.05 μm, collection coefficient $K(D_p, 10\,\mu m)$ (cm^{-3} s^{-1}) is 1.1×10^{-7} and scavenging coefficient $\Lambda(D_p)$ (s^{-1}) is 1×10^{-4}, the lifetime of interstitial particles $(1/\Lambda)$ can be calculated to be approximately 2.8 h.

As mentioned earlier, the wind speed of ascending air parcel could be controlled. By using a large ventilator, every blank mineral particle might be elevated to the top of pit with 0.8 m s^{-1} wind speed. The particle elevating time through the vertical pit could be calculated as to be approximately 9 min. If so, most of background mineral particles will be left as the interstitial particles in the vertical chamber.

As stated already, it is possible to maintain residual insoluble particle on individual cloud droplet replicas formed on collodion film. These retained
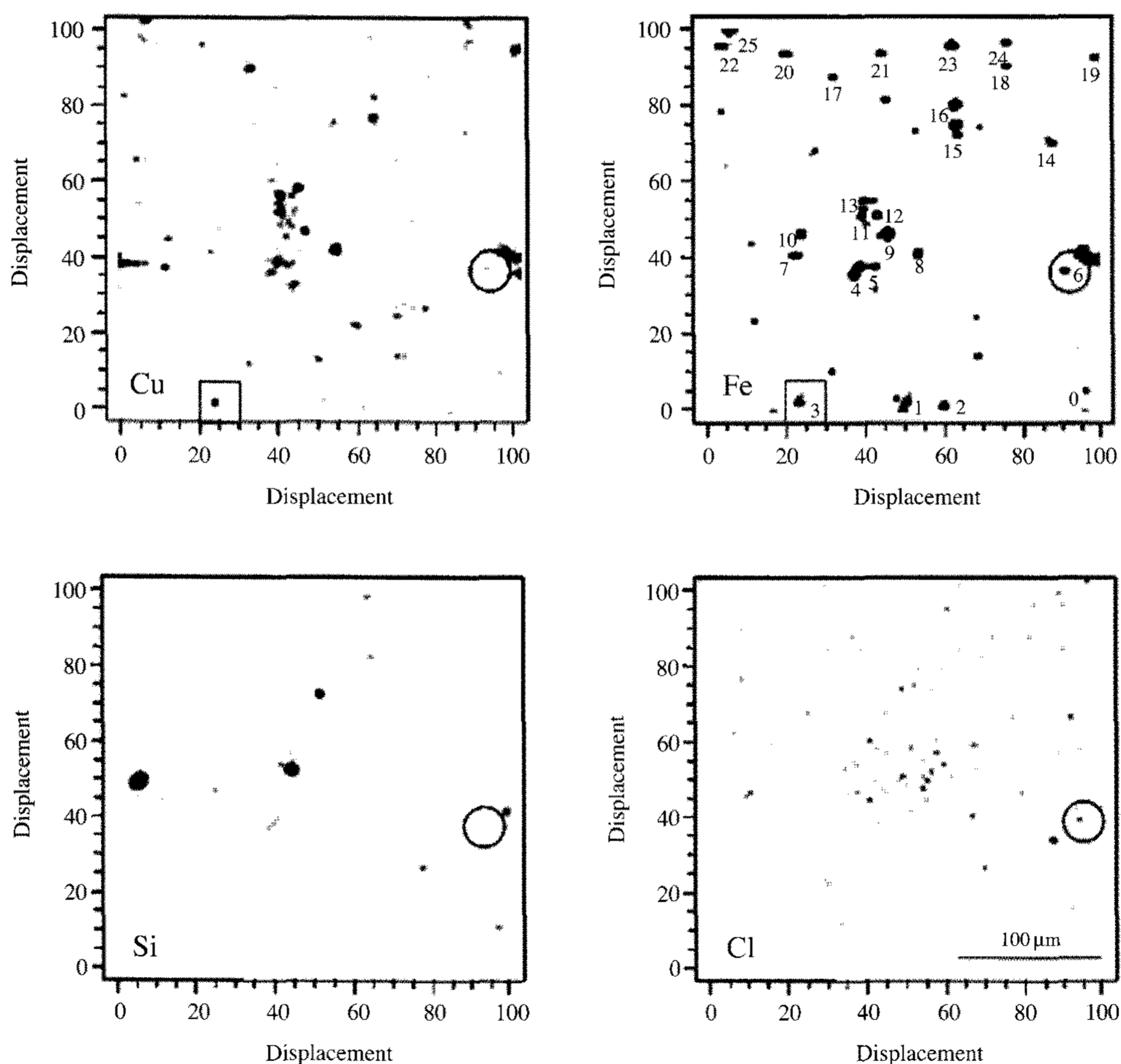

Fig. 6. XRF elemental maps of residual particles in cloud droplets. Full scanning area for each map is 300 × 300 μm².
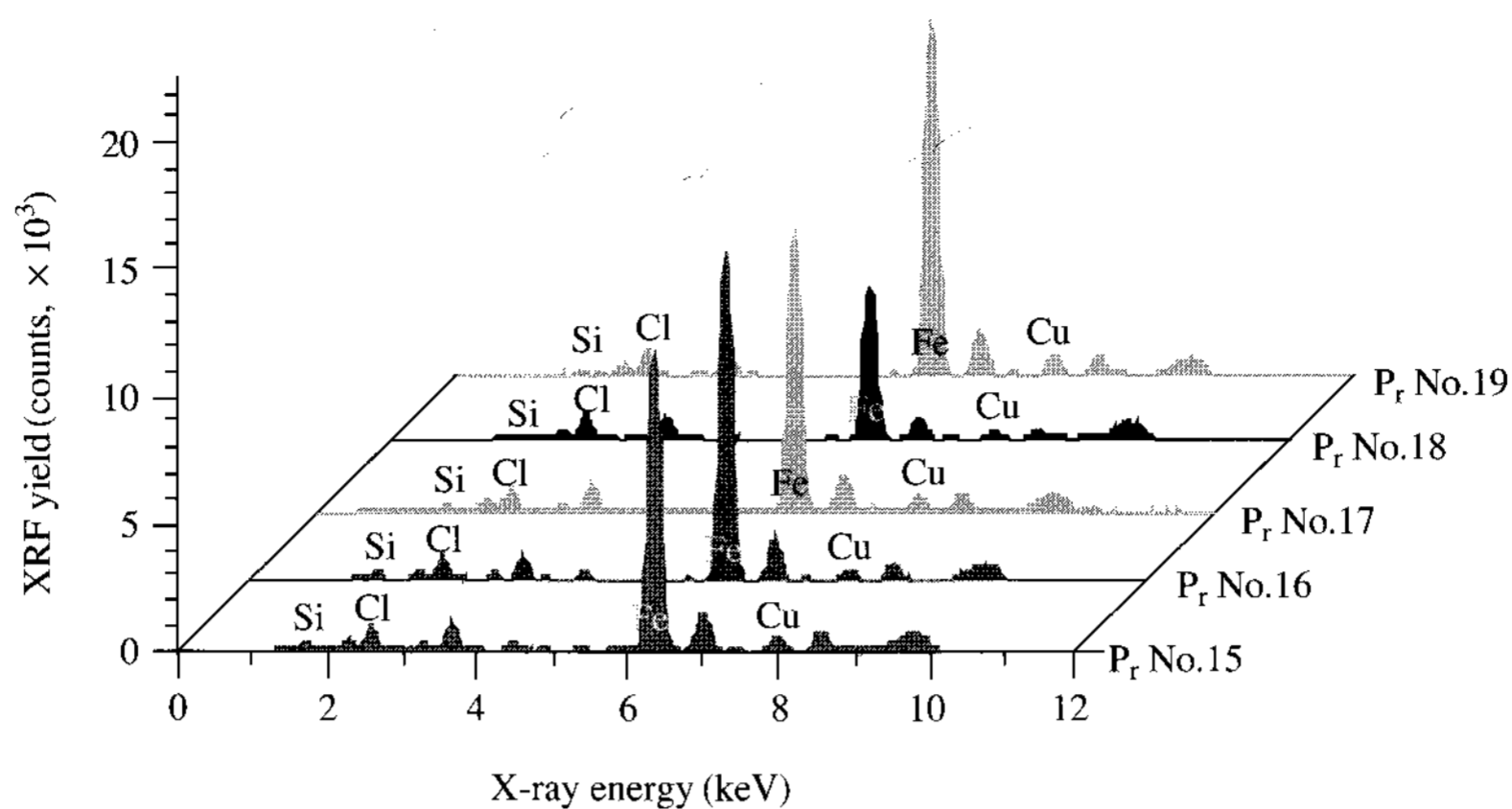
Fig. 7. XRF spectra of five individual residue particles in the Fe XRF mapping image of Fig. 4. A beam of 10 keV x-rays were applied for excitation. The P$_r$No means the number of retained individual particle.

matters could be the targets of SR-XRF microprobe analysis. Fig. 6 draws the XRF images for Cu, Fe, Si, and Cl in individual solid particles retained in individual cloud droplets which were generated during NaCl (1 g/L) nebulizing. These four-kind visualized elemental maps enable us not only to presume the chemical mixing state of residual particles, but also to estimate their source. For example, the residual particle marked number 6 (circles in Fig. 6) indicates the chemical mixing state with soil derived components and Cl. Whereas, particle number 3 (squares in Fig. 6) consists of only Fe and Cu. Consequently, from these four kinds of XRF images replayed corresponding to a single residual particle in individual cloud droplets, it is suggested that internal mixture of mineral particle with NaCl particle was produced by several mechanisms, such as Brownian impaction between mineral particle and cloud droplet formed by NaCl CCN and coalescence of cloud droplets containing minerals with those containing NaCl.

In addition, the XRF spectra for five individual residual particles in the Fe XRF mapping image of Fig. 6 are drawn in Fig. 7. As might be expected, Fe shows the highest XRF count for every five residual particle. Also as the minor peaks, Si, Cl and Cu are forming small peaks. From these XRF spectra for five residues, it can be undoubtedly said that mine-

ral components were coexisted with Cl. Though the peak of Cu was resolved, Cu XRF count might be overestimated because the sample holder of XRF microprobe analytical system contained Cu.

It has been reported that water droplets would nucleate on quartz and samples of surface dust only under high supersaturation not observed in the atmosphere (Pruppacher and Klett, 1997). However, an earlier study indicated that clay-sized particles ($<4\,\mu m$) may be hydrophilic and removed by cloud nucleation (McDonald, 1964).

Not only particle number concentration but also droplet number concentration and liquid water content under same experimental condition were already reported in previous study (Ma, 2006). As described in previous study (Ma, 2006), the initial background particles measured by Scanning Mobility Particle Sizer (SMPS) at the entrance of vertical pit showed a monomodal size distribution showing the maximum size 65 nm. However, the vertical profile of relative humidity in the vertical pit ranges from 95% (at bottom) to 100% (at top). Thus, droplets can not be easily formed in our vertical semi-real scale cloud chamber by heterogeneous nucleation of condensation.

But, since the heterogeneous nucleation processes can be heteromolecular (involving two or more species which are partially wettable), mineral particles

Table 1. Elemental components of the individual particles retained in cloud droplet replicas and bulk insoluble particles in cloud water generated when the NaCl 1 g/L was nebulized.

Elements	Individual particles in cloud droplets				Bulk particles in cloud water	
	n	Mean mass $\pm$ S.D.[a] (fg)	Mass range (fg)	Z_{mass}/Fe_{mass}[b]	Concentration ($\mu g\ L^{-1}$)	$Z_{conc.}/Fe_{conc.}$[b]
Si	126	70.1 $\pm$ 60.4	28.9 ~ 286.7	0.63	355.6	0.71
S	126	21.2 $\pm$ 7.5	16.8 ~ 50.5	0.19	67.8	0.14
Cl	126	67.3 $\pm$ 10.1	52.7 ~ 102.3	0.60	16.2	0.03
K	126	17.6 $\pm$ 22.2	7.7 ~ 121.6	0.16	60.4	0.12
Ca	126	38.4 $\pm$ 12.0	29.1 ~ 73.2	0.34	137.1	0.27
V	126	1.9 $\pm$ 2.8	0.6 ~ 15.3	0.02	5.1	0.01
Cr	126	1.6 $\pm$ 0.9	0.8 ~ 4.2	0.01	5.7	0.01
Mn	126	1.9 $\pm$ 1.3	0.8 ~ 5.5	0.02	12.9	0.03
Fe	126	111.8 $\pm$ 80.3	41.0 ~ 359.6	1.00	501.3	1.00
Cu	126	2.2 $\pm$ 1.9	0.9 ~ 9.2	0.02	14.1	0.03
Zn	126	1.9 $\pm$ 1.5	0.8 ~ 6.5	0.02	6.9	0.01

n = Number of particles
[a] Standard deviation of mass
[b] Ratio of elemental mass (concentration) to Fe mass (concentration)

coagulated with NaCl are likely to activated as CCN in the vertical pit. However, we can not clearly prove this possibility in the present experimental step.

Table 1 summarizes the elemental components of the individual particles retained in cloud droplet replicas and bulk insoluble particles in cloud water generated when the 1 g/L NaCl solution was nebulized. Nearly all individual particles captured in cloud droplets are strongly enriched in Fe. Mass of Fe is ranged between 41 fg and 360 fg with average 112 fg. Also the elemental concentrations for bulk cloud water show the maximum value for Fe (501 μg /L) and followed by Si and Ca.

Though single particle analysis has a lot of merit, as one of disadvantages of single particle study, it can not fully estimate the property of whole particle since generally only a portion of particles is the target of analysis. Hence, it is necessary to confirm that the result of single particle analysis will be representative of whole particle.

The chemical compositions of individual particles in cloud droplets are comparable to those of bulk particles in cloud water. With the exception of Cl, the coefficient of determination (R^2) of the ratio of each element to Fe (Z/Fe) between individual particles and bulk particles is found to be 0.97 (Fig. 8). This result suggests that there is a good agreement between single particle analysis by SR-XRF and bulk
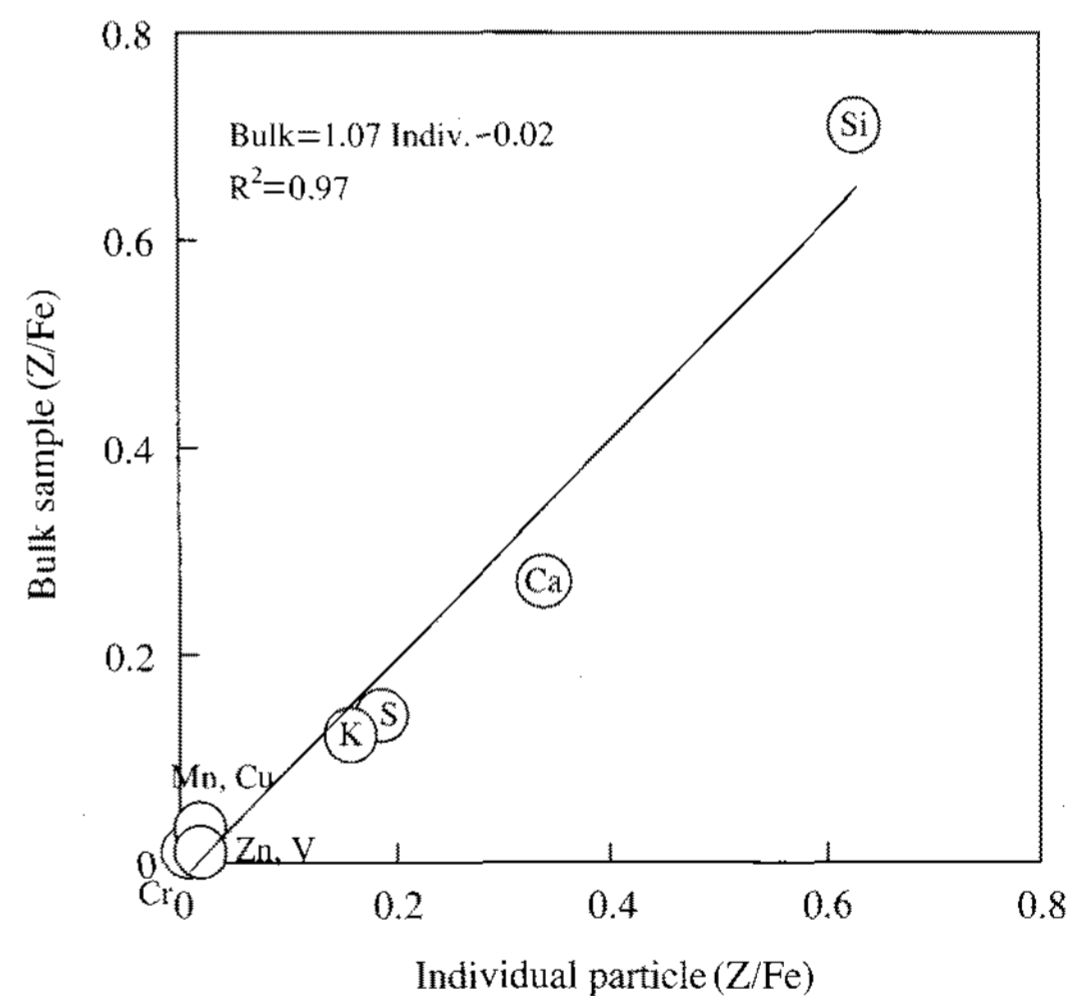

Fig. 8. Correlationship of Z/Fe between the individual particles in droplets and the bulk particles in cloud water.

particle analysis by PIXE.

4. SUMMARY

Though the cloud scavenging of soluble aerosols is relatively well established, the behavior of insoluble mineral particles is still not completely understood. Thus, in this study, to understand the be-

havior of insoluble mineral particles in the saturated atmosphere, an attempt was made to generate artificial cloud using a huge vertical pit. It was possible to make the replicas of individual cloud droplets by the Collodion film replication technique. Also the SR-XRF microprobe system installed at the Spring-8 was newly applied to the chemical analysis of individual particles contained cloud droplet replicas. By means of SR-XRF microprobe analytical system, the chemical properties of individual particles retained in cloud droplets could be satisfactorily determined. The analytical results indicate that not only water-soluble particles but also non-hygroscopic particles play a considerable part in droplet formation. The analytical data could be also used for the identification of individual particles contained in cloud droplets as well as the estimation of their behavior in cloud formation processes.

ACKNOWLEDGEMENTS

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