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ON THE SULFATE PARTICLES IN THE SUBMICRON SIZE RANGE COLLECTED AT MIZUHO STATION AND IN EAST QUEEN MAUD LAND, ANTARCTICA: PRELIMINARY RESULTS

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Abstract: Aerosol particles were sampled at Mizuho Station (70°42′S, 44°20′E) and in East Queen Maud Land (73°06′–74°50′S, 39°45′–34°56′E), Antarctica from April to November in 1984. The vapor-deposited $BaCl_2$ thin film method was used to identify sulfate-containing particles. Morphological identification of the individual particles was also made in order to determine their actual molecular state.

It was confirmed from the morphology of particles that particles containing sulfuric acid were predominant in East Queen Maud Land in summer, whereas ammonium sulfate particles were predominant in winter at Mizuho Station. These results are similar to the results at Syowa Station (T. ITO, Pap. Meteorol. Geophys., **34**, 151, 1983). An interesting finding is that sulfuric acid particles existed as a minor component at Mizuho Station even in winter when photochemical production of sulfuric acid particles was not dominant.

1. Introduction

The nature of Antarctic aerosol particles reflects a background condition of global atmosphere. Antarctica is isolated from other continents and areas of human activities. As pointed out by many investigators, the information on Antarctic aerosols is interesting from the viewpoint of atmospheric environment, global pollution, and long-range transport of particles and related gases.

According to SHOW (1979), HOGAN (1982), and ITO (1983), the air mass exchange between the oceans and the plateau frequently affects the behavior of aerosol particles near the coastal region of Antarctica. Thus, the aerosol over inner Antarctic continent is very interesting for the studies of transport of particles and effect of the air mass exchange on the atmospheric condition of inner continent.

It is well known that sulfate-containing particles are the major component of aerosol particles in Antarctica (MAENHAUT *et al.*, 1979). However, the origin of sulfate particles in the Antarctic atmosphere is not fully understood. It is important to understand the nature of these particles including their actual molecular state in the atmosphere at a single particle level in order to study the origin of these particle.

Sulfur contained in aerosol particles at the South Pole Station was identified with X-ray energy spectrometry (PARUNGO *et al.*, 1979, 1981). Previously the molecular state of sulfate particles in the Antarctic atmosphere has been studied by CADLE *et al.* (1968), BIGG (1980), ITO (1983) and IWASAKA *et al.* (1985) based on particle morphology. Morphological identification of particles is an ordinary method. However, as pointed out by HAYES *et al.* (1980), collected sulfuric acid particles are easily converted into ammonium sulfate particles by the absorption of ambient ammonia in the laboratory air. Thus, the morphological identification does not always reflect the actual molecular state of sulfate particles in the atmosphere.

In order to avoid possible contamination by ammonia, the vapor-deposited calcium thin film method was useful. Previously this method was used for the identification of the chemical composition of aerosol particles in the remote Everest highland (ONO *et al.*, 1983). In the present study, in addition to morphological identification of particles, this method was applied to the aerosol particles in the Antarctic atmosphere. We report the preliminary results about the molecular state of sulfate particles collected at Mizuho Station (M/S) and in East Queen Maud Land (EQML) in Antarctica.

2. Aerosol Sampling and Chemical Test

Aerosol particles were collected on a carbon-coated nitrocellulose film sustained on the electron microscope grid (EM grids) with an impactor. The impactor used here is shown in Fig. 1. A nozzle shape of the impactor was rectangle of 10×0.5 mm size. Sampling volume of air was about 20 *l* for one sampling. Air was introduced into the impactor directly without removal of water vapor.

A transmission electron microscope was used to measure the morphology of particles, the morphology of reaction rings and the size of collected particles. The radius of particles was measured with a digitizer from the photograph of TEM. Sulfate-containing particles are identified with a vapor-deposited $BaCl_2$ thin film technique (BIGG *et al.*, 1974). Particles collected on a carbon film were coated with $BaCl_2$ by vacuum vapor deposition. Later the EM grids were placed in the atmosphere saturated with octanol vapor for about one day. Particles containing sulfate react with $BaCl_2$

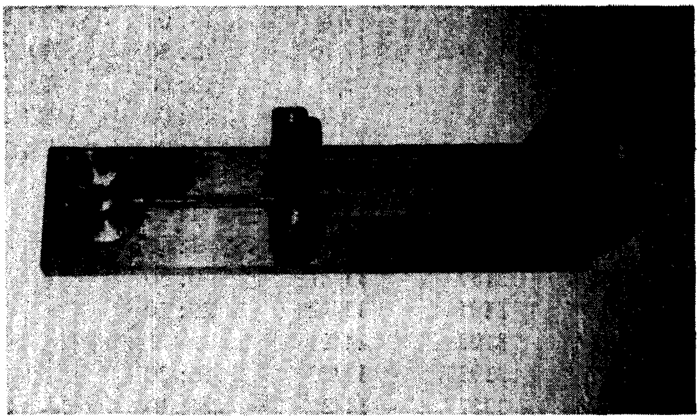

Fig. 1. An impactor used in aerosol sampling.

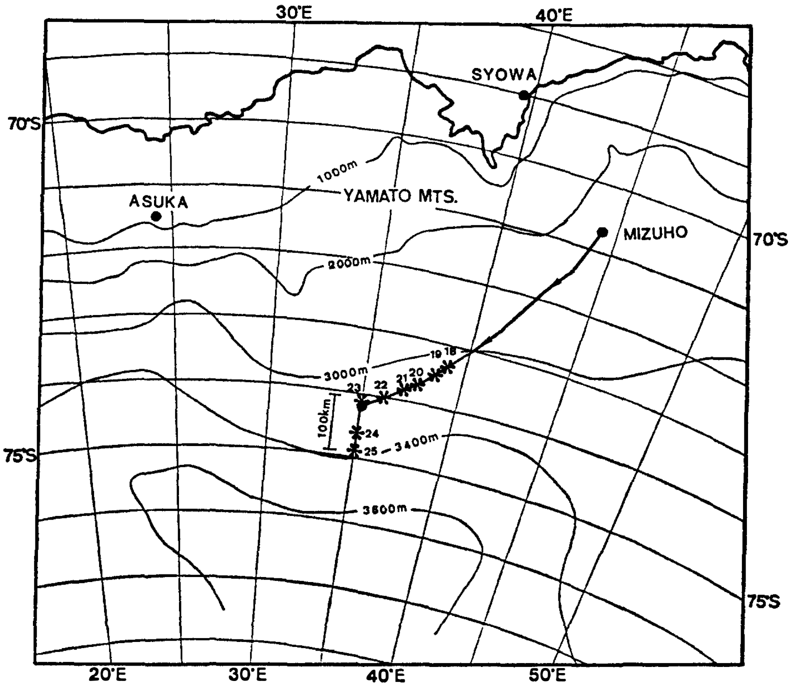

Fig. 2. Aerosol sampling sites along the oversnow traverse routes in East Queen Maud Land, indicated by "". Samplings from No. 1 to No. 17 were carried out at Mizuho Station, and samplings from No. 18 to No. 25 were performed on this traverse.*

Table 1. Aerosol sampling sites, its height, time, and meteorological parameters.

No.	Location	Height (m)	Date	Time	Pressure (mb)	Temperature (°C)
1	Mizuho Station	2200	4/22	17: 00	723.1	−42.8
2	〃		4/25	15: 40	734.0	−49.0
3	〃		5/9	14: 20	754.3	−25.7
4	〃		5/13	15: 30	748.0	−36.7
5	〃		5/18	17: 30	734.9	−31.0
6	〃		5/25	13: 00	721.3	−42.1
7	〃		5/30	13: 00	721.3	−49.6
8	〃		6/10	14: 00	733.1	−38.5
9	〃		6/17	13: 20	727.4	−48.7
10	〃		6/21	13: 30	716	−51.2
11	〃		6/27	13: 30	737	−51.0
12	〃		7/8	13: 00	727.4	−42.8
13	〃		7/15	12: 30	731.7	−44.6
14	〃		8/2	13: 00	725.0	−35.0
15	〃		8/7	14: 00	723.8	−34.0
16	〃		8/13	14: 00	734.8	−38.0
17	IM 157 (G6)	3006	11/8	22: 00		−38.5
18	IM 174	3098	11/9	1: 00		−41.6
19	IM 188	3154	11/10	1: 00		−43.7
20	IM 205	3187	11/11	0: 30		−42.0
21	IM 215	3191	11/12	20: 20		−36.1
22	IM 232	3198	11/13			−39.0
23	IM 252	3193	11/20	16: 20		−30.9
24	ID 16	3227	11/21	24: 30		−37.3
25	ID 34	3371	11/22	21: 50		−34.3

and form a Liesegang ring composed of $BaSO_4$.

The vapor-deposited calcium thin film was used as a reactive particle collecting surface for the detection of sulfuric acid particles. When sulfuric acid particles impact on the calcium thin film (thickness 3–6 nm), they react with calcium rapidly and form Liesegang rings composed of $CaSO_4$. On the other hand, ammonium sulfate particles do not react with calcium under dry condition, since they are solid particles. The morphology of the reaction spots indicates the *in situ* reactivity of particles with calcium in the atmosphere. A noticeable merit of this method is that the reactivity (acidity) of sulfate particles is determined at the same time when the particles impact onto the calcium surface. Thus, any contamination with ammonia can't take place after sampling. The morphology of the reaction ring on the calcium thin film indicates the *in situ* molecular state of individual sulfate particles.

Aerosol particles were sampled at M/S from April to August and at several sites along the traverse routes in EQML in November 1984. Figure 2 shows the sampling sites. Table 1 shows the sampling location, time, data and meteorological parameters.

3. Results

The morphology and the reactivity of particles with $BaCl_2$ and calcium were measured with TEM. Most calcium thin films used (22 sheets in total 25 sheets) were damaged with humidity. The results presented here are based on the three samples which escaped damage.

3.1. Aerosol particles at Mizuho Station during the winter season

Ammonium sulfate particles were often observed at M/S in the winter season of 1984. Figure 3a shows the typical electron micrograph of aerosol particles collected on the calcium thin film (sample No. 12, see Table 1) at Mizuho Station. Most of the particles (about 95% of the total number), especially in the smaller size range, did not react with calcium. "A" in the figure indicates ammonium sulfate particles, which were identified on account of their electron-dense spherical morphology.

However, a few sulfuric acid particles (about 1% of the total number of particles) were present. These particles reacted with calcium and formed Liesegang rings composed of $CaSO_4$. "S" in Fig. 3a indicates the reaction ring of sulfuric acid particles. The morphology of the reaction ring is the same as that of pure sulfuric acid particles. This fact that sulfuric acid particles were present even in winter is a new result which has not been reported previously by other investigators.

Particles of intermediate chemical composition between sulfuric acid and ammonium sulfate were also present. These particles (about 4% of the total number of particles) reacted partially with calcium, and were composed of two parts; a non-reacted electron-dense central particle and surrounding reaction ring ("SA" in Fig. 3a). "SA" represents the internally mixed particles composed of sulfuric acid and ammonium sulfate. These particles were speculated to be ammonium sulfate particles containing a little sulfuric acid. Other two samples, No. 4 (5/13) and No. 13 (7/15) collected on calcium thin film at M/S show similar feature to sample No. 12 (7/8).

Figure 3b shows the morphology of particles collected at M/S (No. 15) on 7 August.

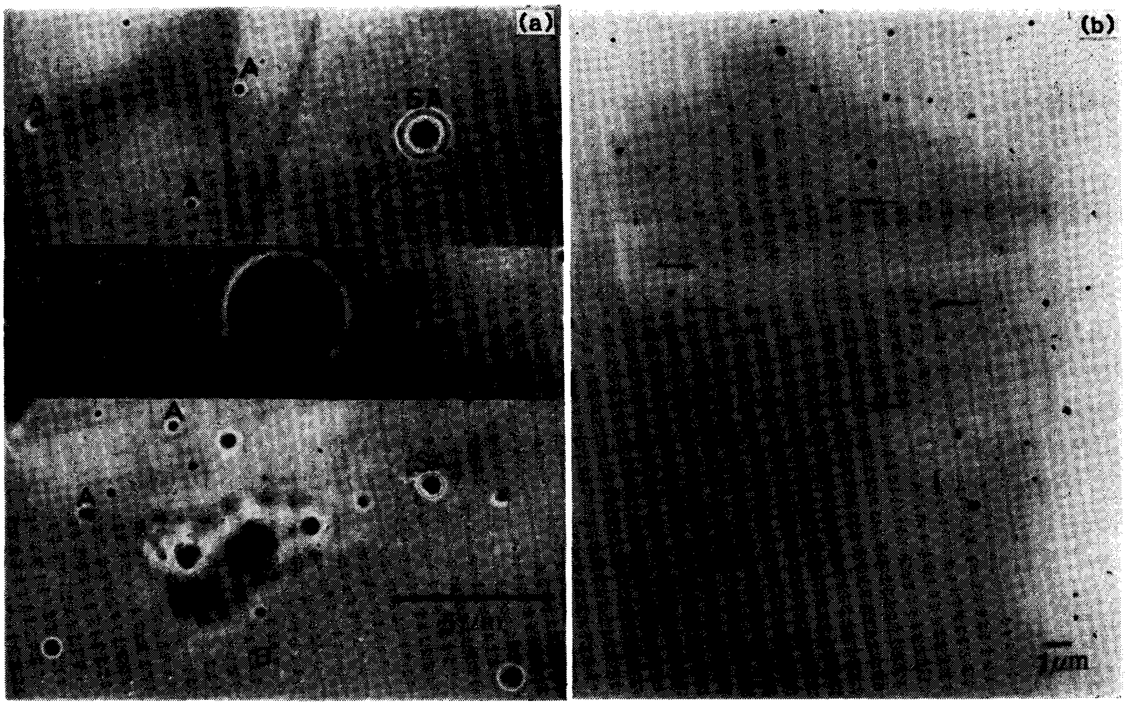

Fig. 3. Aerosol particles collected at Mizuho Station in winter of 1984.
(a) Aerosol particles collected on the calcium thin film, on 8 July (sample No. 12).
(b) Aerosol particles collected on the carbon film, on 7 August (sample No. 15).

Each mother particle has several small satellite particles, which suggests that the particles contain sulfuric acid (indicated by "→" in the figure). Since the number of satellite droplets of these particles is much smaller than pure sulfuric acid droplets, the mixing ratio of sulfuric acid (acidity) in individual particles is probably smaller than pure sulfuric acid particles. The maximum radius of the collected sulfuric acid-containing particles is 0.18 μm, with the average radius 0.08 μm. The number fraction of large particles is about 27%. Most of the collected particles are Aitken particles.

Summarizing the reaction of the calcium thin film and the satellite structure of the sampled particles, we can suggest that even in winter sulfuric acid particles were present, although they were not the major aerosol component.

3.2. Aerosol particles in East Queen Maud Land during the summer season

The particles collected during the traverse over the plateau in EQML on 9 November (No. 18) are shown in Fig. 4. Fig. 4a shows the sulfate test with $BaCl_2$. All particles reacted with $BaCl_2$ and formed Liesegang rings composed of $BaSO_4$. This indicates the predominancy of sulfate-containing particles in submicron size range.

The typical morphology of particles collected on the carbon film on the plateau is shown in Fig. 4b. Around each mother particle, many fine satellite droplets surround. Pure aqueous sulfuric acid particles have more widely distributed satellite rings around central mother particles. Thus the acidity of these particles is probably smaller than pure aqueous sulfuric acid particles.

The radius of the particles collected in EQML on 20 November (sample No. 23)

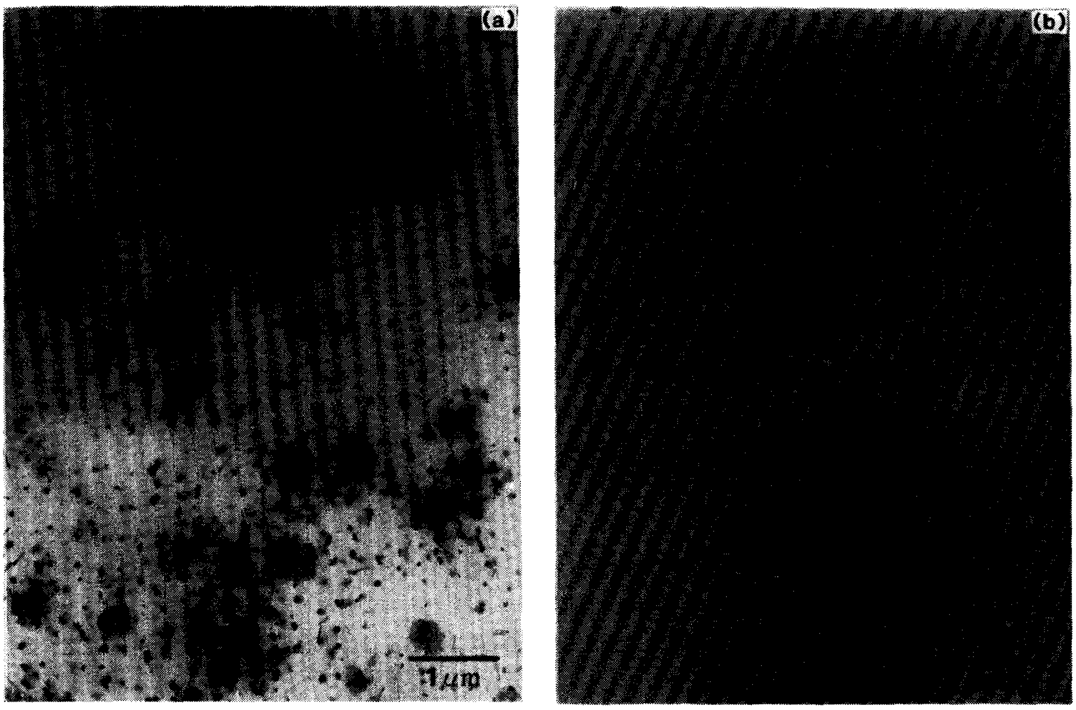

Fig. 4. Aerosol particles sampled in East Queen Maud Land on 9 November 1984.
(a) $BaCl_2$ thin film test for sulfate-containing particles (sample No. 18).
(b) Morphology of particles collected on the carbon thin film (sample No. 18).

was measured. Coarse particles were not found and the large particles occupied only 5% of the total number of particles. Most particles were Aitken particles ($r<0.1$ μm). The minimum radius of collected particles was 0.01 μm. On the other hand, at Asuka Camp in the summer of 1985, a representative particle radius in large particle size range was 0.2 μm (YAMATO *et al.*, 1987). The particles collected in EQML in the summer of 1984 were much smaller than the particles at Syowa Station and Asuka Camp in the summer of 1985 and 1986.

4. Discussions

4.1. Molecular state of sulfate particles

The predominancy of sulfuric acid particles in the summer season (Fig. 4b) reflects the dominancy of the photochemical production of these particles as pointed out by many authors (*e.g.*, ITO, 1983).

Aerosol particles in submicron size range collected at Asuka Camp (A/C) and Syowa Station (S/S) in summer were sulfuric acid particles (YAMATO *et al.*, 1987). Since the particles have more widely dispersed satellite structure at S/S and at A/C than that in EQML, these sulfuric acid particles are more acidic than the particles collected in EQML. It is worth to point out that the particles at S/S were composed of almost pure aqueous sulfuric acid solution, whereas particles collected in EQML in the summer season were possibly composed of aqueous solution of sulfuric acid containing a little ammonium sulfate. The difference is possibly due to the difference of sunlight intensity between two periods and/or concentration of gaseous precursors between two locations.

Ammonium sulfate particles were the predominant component of submicron sulfate particles in winter at Syowa Station (Ito, 1983). However, our present finding is that particles containing sulfuric acid existed even in the winter season when photochemical production of sulfate particles is not dominant. Only a few sulfuric acid particles were externally mixed with ammonium sulfate particles (sample No. 12). Particles containing sulfuric acid in small fraction were found at M/S (No. 15) and most of these particles were Aitken particles. Thus, it is not likely that these sulfuric acid particles were of stratospheric origin, since stratospheric aerosol is dominated with large particles. One possible explanation for the presence of sulfuric acid particles in the winter season is that these particles were transported from the surrounding areas where photochemical production of particles takes place.

4.2. Particle radius

The size distribution of sulfate particles collected at M/S and EQML was monomodal. The typical particle radius and acidity of particles collected in EQML in early summer of 1984 were rather smaller than those of the particles collected at S/S

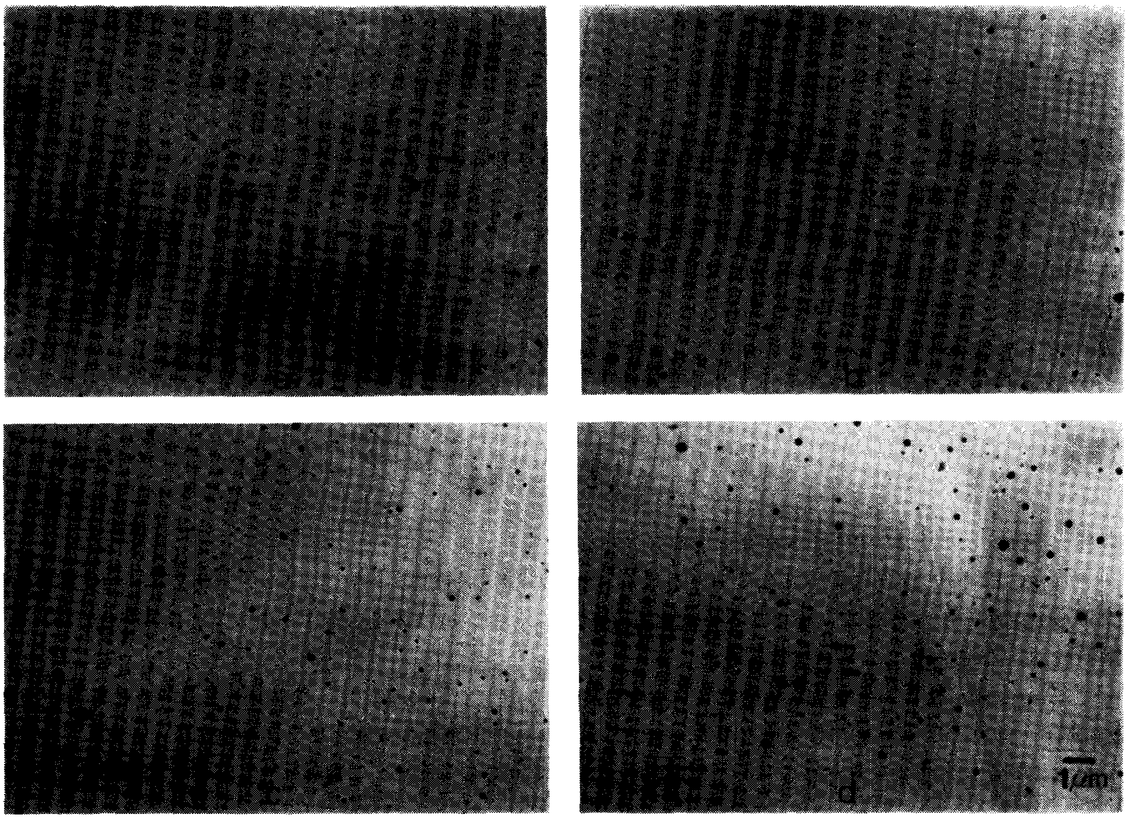

Fig. 5. Aerosol particles collected on the carbon thin film in East Queen Maud Land, November 1984.
(a) November 9 (sample No. 18).
(b) November 10 (sample No. 19).
(c) November 20 (sample No. 23).
(d) November 22 (sample No. 25).

and A/C in midsummer. The implication is that the photochemical production rate of sulfuric acid vapor in EQML was smaller than that at S/S and A/C. This reflects the geographical and/or seasonal difference of the light intensity and concentration of sulfur-bearing gasses.

4.3. *Uniformity of particle shape*

In Fig. 5a to 5d the aerosol particles collected on the carbon thin film on 9, 10, 20 and 22 November are shown. The morphology of the particles collected in EQML has well-marked uniformity. All particles have an electron-dense spherical cap shape. Any other sorts of particles were not found in these samples. The uniformity of particle shape was reported for the particles at S/S and A/C in summer (YAMATO *et al.*, 1987).

We suggest that well-marked uniformity of particle shape and the monomodality of size distribution of submicron particles are the characters of the Antarctic aerosol particles which are not affected by local air pollution.

4.4. *Damage of the calcium thin film with humidity*

Aerosol particles were collected with an impactor without a diffusion drier which is used to remove water vapor from the sampled air. Most calcium thin films used (22 sheets in total 25 sheets) were damaged by humidity and did not work well. A diffusion drier is indispensable when we use the calcium thin film in Antarctica.

5. Conclusion

Aerosol particles were collected and analyzed with the calcium thin film method, along with morphological identification.

It should be noticed that sulfuric acid particles were present at M/S even in winter when photochemical production of particles does not take place. In the EQML summer, sulfuric acid-containing particles are predominant, and the particle size was much smaller than that at S/S and A/C. This difference reflects the difference of particle production rate according to location and/or season. The chemical composition of sulfate particles was uniform and constant and the size distribution in EQML was monomodal irrespective of geographical locations and time. The monomodality of particle size and well-marked uniformity of chemical composition of the Antarctic aerosol particles are the characters of background aerosol particles in the atmosphere remote from polluted areas.

Further observations and examination are needed to measure the seasonal and geographical trends of size distribution and molecular state (acidity) of aerosol particles in order to clarify the origin of sulfate particle. In addition to measurements of particles, measurements of the concentrations of gaseous species (*e.g.*, sulfur dioxide and ammonia) are needed to evaluate the production rate of particles and the neutralization speed of sulfuric acid particles with ammonia.

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