

EVIDENCE FOR THE PRESENCE OF SUBMICRON SULFURIC ACID PARTICLES IN SUMMER ANTARCTIC ATMOSPHERE: PRELIMINARY RESULTS

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Abstract: Direct samplings of aerosol particles in the summer Antarctic atmosphere were carried out at Syowa Station (69°00'S, 39°35'E) and Asuka Camp (71°31'S, 24°07'E) in 1985 and 1986. To determine the molecular state of sub-micron sulfate particles, a vapor-deposited calcium thin film method was used. It was proved directly that sulfuric acid particles predominantly existed at Syowa Station and Asuka Camp in the summer Antarctic atmosphere.

1. Introduction

Antarctica is a suitable place for the observation of "background" aerosols, since it is remote from other continents and mostly covered with ice and snow which suppress the emission of gases and primary aerosols. Additionally, a large difference of sunlight condition between winter and summer is very interesting to the study of photochemical processes including particle production and particle growth from sulfur bearing gases. Chemical composition and physical properties of the Antarctic aerosols, as well as their sources, sinks and transportations, have been studied by many investigators (*e.g.*, SHOW, 1979; PARUNGO *et al.*, 1981; HOGAN, 1982). PARUNGO *et al.* (1981, 1979) analyzed individual particles at the South Pole with an electron microscope equipped with an X-ray energy spectrometer. The percent of sulfur-containing aerosol particles varied seasonally, maximum in summer and minimum in winter.

Analysis of the molecular state of individual particles in the Antarctic atmosphere has been limited so far. According to ITO (1983) Aitken nucleus concentration at Syowa Station (69°00'S, 39°35'E) shows typical seasonal variation. He also showed by morphological analysis that sulfuric acid particles were predominant in summer, while ammonium sulfate particles were major in winter. IWASAKA *et al.* (1985) showed by morphological identification of particles directly sampled with aircraft that sulfuric acid particles actually existed in the summer Antarctic atmosphere up to an 8 km height.

However, the molecular state of individual particles was not determined exactly

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in those previous studies. HAYES *et al.* (1980) pointed out that sulfuric acid particles collected in the stratosphere are easy to be converted to ammonium sulfate particles by absorption of ammonia in the laboratory. The morphological identification of sulfate particles is less reliable.

In order to identify directly the actual molecular state of individual sulfate particles, a vapor-deposited calcium thin film method is useful. In the previous study, aerosol in the remote Everest highland was examined with this method (ONO *et al.*, 1983). In the Antarctic atmosphere, aerosol particles were also examined with this method (YAMATO *et al.*, 1987). However, most of the calcium thin films used in Antarctica were damaged by the humidity of sampling air, because the particles were not dried before sampling on the calcium thin film surface. Thus, it can be said that the presence of sulfuric acid particles in the summer Antarctic atmosphere has not been confirmed yet directly with the calcium thin film method.

When we want to confirm perfectly the presence of sulfuric acid particles, it is essential to dry the particles before their impaction on the calcium thin film. In this using a diffusion drier, we examine the actual molecular state of individual sulfate particles collected at Syowa Station on 24 January 1986 and at Asuka Camp on 27 December 1985 with the improved calcium thin film method by the members of the 27th Japanese Antarctic Research Expedition (JARE-27) (F. NISHIO and M. FUKABORI).

2. Observational Procedure

2.1. Chemical test

Electron microscope grids (EM grids) covered with a nitrocellulose film were prepared to collect aerosol particles. Carbon was evaporated onto the nitrocellulose surface in a vacuum evaporator. Aerosol particles are collected on the EM grids with an impactor. First, morphology of collected particles is observed with a transmission electron microscope (TEM). Second, the direct chemical test using a vapor-deposited calcium thin film as a reactive particle collecting surfate (ONO *et al.*, 1983) is applied for the detection of sulfuric acid component in individual particles.

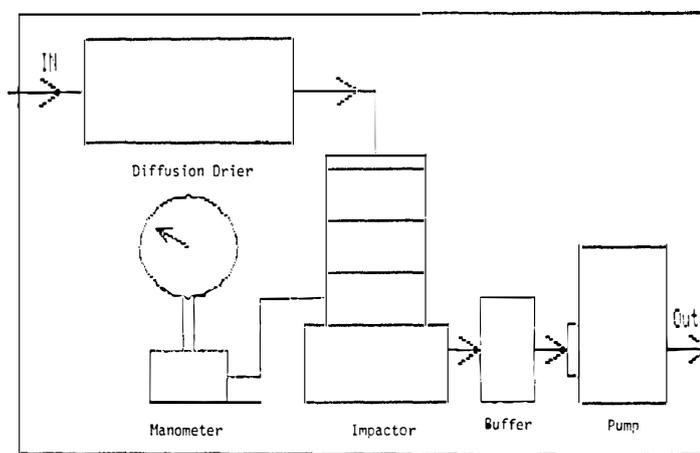
A metal calcium ingot of 0.7 mg was evaporated in a vacuum evaporator. The EM grids covered with a carbon thin film were set 14 cm apart from the tungsten boat with an angle of depression of 45 degrees. Under the low pressure about 10^{-5} torr, the metal calcium ingot is evaporated. Then a calcium thin film with thickness about 3.6 nm is formed on the EM grids. This thickness is calculated after HOLLAND (1963).

The previous study (YAMATO *et al.*, 1987) showed that the calcium thin film was frequently damaged by humidity. Thus, the aerosol particles must be collected on a calcium thin film under a low relative humidity. Solid ammonium sulfate particles deliquesce at about 80% relative humidity for increasing the relative humidity. However, for decreasing the relative humidity, ammonium sulfate aqueous droplets are dried below 28% relative humidity (TANG *et al.*, 1981). If the sampling air is dried sufficiently to keep ammonium sulfate particles solid and prevent the reaction with calcium, we can easily distinguish sulfuric acid droplets from ammonium sulfate particles. With the diffusion drier used here, the sampling air can be dried below

10% relative humidity. Sulfuric acid particles are still liquid even under such low relative humidity and are highly reactive with calcium. When they are collected on the calcium thin film, Liesegang rings composed of CaSO_4 are formed. The morphology of the Liesegang ring is observed with TEM.

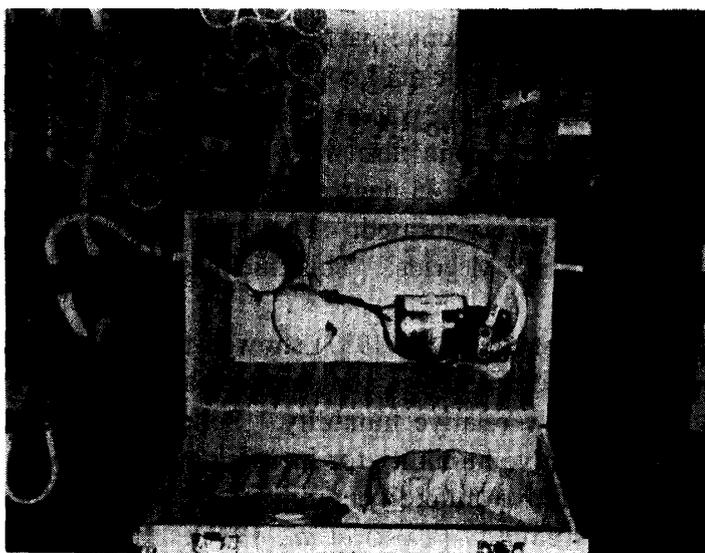
2.2. Sampling equipment

Aerosol particles were collected with a two-stage low-pressure impactor. The first stage of the impactor collected larger particles, while the second stage collected smaller one, involving Aitken particles. Pressure decrement at the second stage was set to be 50 cmHg, which was measured with a manometer. Flow rate of this impactor is 1.2 l/min and one sampling time was 60 min at Syowa Station and 80 min



Aerosol Sampling System

(a)



(b)

Fig. 1. Schematic diagram of the compact aerosol sampling equipment (a) and photograph of the sampling set (b).

at Asuka Camp. Sampling volume of aerosol particles was 72 l at Syowa Station and 96 l at Asuka Camp, respectively.

To remove humidity in sucked air before impaction, air was passed through a diffusion drier. Silicagel was put in a tube of the diffusion drier. The terminal relative humidity was below 10%. This compact sampling set is shown in Fig. 1.

Aerosol particles were collected on 27 December 1985 and 24 January 1986 at Asuka Camp and Syowa Station, respectively. Temperatures at Syowa Station were between -5 to -8°C . Relative humidity was 58%. Collected particles were kept in a dry closed package.

3. Results

The particles collected on the calcium thin film at Syowa Station on 24 January 1986 are shown in Fig. 2. Before impaction on the calcium thin film, aerosol particles were sufficiently dried with the diffusion drier. If ammonium sulfate particles were collected, they were dried and could not react with calcium. Most of the collected particles react well with calcium. This reaction occurred even under dry condition and the morphology of the Liesegang ring is closely similar to that of sulfuric acid particles. It is clear that these particles were sulfuric acid particles.

Figure 3 shows the morphology of particles collected on a carbon thin film at the

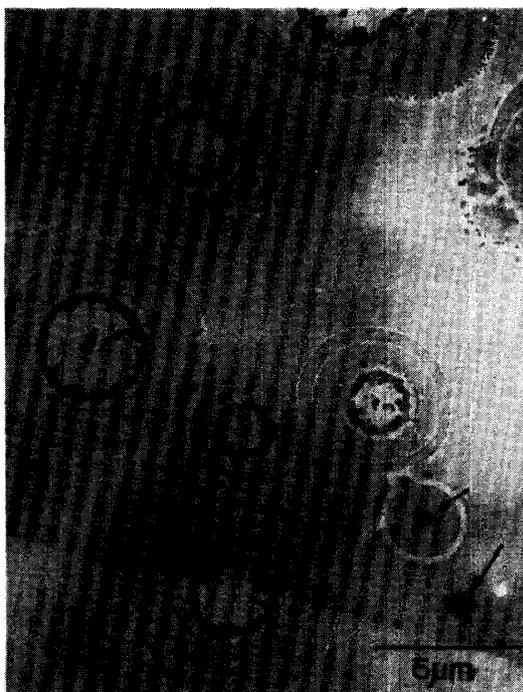


Fig. 2. Aerosol particles collected on the calcium thin film at Syowa Station ($69^{\circ}00'S$, $39^{\circ}35'E$) on 24 January 1986. Arrow " \rightarrow " indicates the typical example of non-reacted particle or electron dense core.



Fig. 3. Aerosol particles collected on the carbon thin film at Syowa Station ($69^{\circ}00'S$, $39^{\circ}35'E$) on 24 January 1986.



Fig. 4. Aerosol particles collected on the carbon thin film at Asuka Camp ($71^{\circ}31'S$, $24^{\circ}08'E$) on 27 December 1985.

same time as the collection of particles in Fig. 2. Most of the particles have many small droplets surrounding central mother particles. This is called "satellite structure" characterizing sulfuric acid particles. All sulfuric acid particles collected with the first stage of the impactor were large particles ($0.1 \mu\text{m} < r < 1 \mu\text{m}$). All particles collected with the second stage of the impactor had the satellite structure, which suggests that these smaller particles were also sulfuric acid particles.

At Syowa Station, sea salt particles in the coarse particle size range were collected (Fig. 5 see " \rightarrow "), but they were not a major component. The dominant aerosol particles were sulfuric acid particles.

The calcium thin film method was not applied at Asuka Camp on 27 December 1985. Figure 4 shows the aerosol particles collected on a carbon thin film at Asuka Camp on 27 December 1985. All particles have the satellite structure which indicates a possible evidence for the presence of sulfuric acid particles. The size of the particles ranges from $0.2 \mu\text{m}$ (large particles) to $0.04 \mu\text{m}$ (Aitken particles). Sea salt particles were not found within the size range including Aitken, large, and giant particles at Asuka Camp.

4. Discussion

Some remarks on the method of aerosol sampling and on the features of aerosol particles in the Antarctic atmosphere are listed below.

(1) Diffusion drier of aerosol sampler

In 1983–1984 (JARE-25) aerosol particles were collected with an impactor without a diffusion drier (YAMATO *et al.*, 1987). Most of the prepared calcium thin films (22

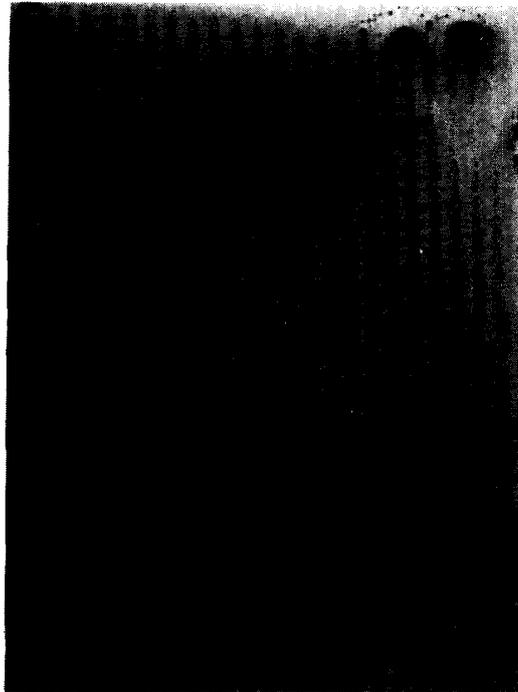


Fig. 5. Aerosol particles collected on the carbon thin film at Syowa Station ($69^{\circ}00'S$, $39^{\circ}35'E$) on 24 January 1986. Arrow " \rightarrow " indicates the typical example of sea salt particles.

sheets in total 25 sheets) were damaged by humidity and did not work well. Calcium is unstable against the humidity of sampling air, so that the removal of humidity of the sampling air is necessary before impaction of particles.

(2) Ammonium sulfate particles

Several particles did not react with the calcium thin film in the samples collected at Syowa Station on 24 January 1986, although such particles were few. These non-reacted electron-dense particles were probably ammonium sulfate particles. An electron-dense core was sometimes found at the center of the Liesegang ring of CaSO_4 (for example, see " \rightarrow " in Fig. 2). These particles may be ammonium sulfate dissolved in sulfuric acid aqueous droplets. The results obtained here indicate that a small number of ammonium containing sulfate particles were present even in the summer season in the Antarctic atmosphere.

(3) Sea salt particles

In addition to sulfate particles, sea salt particles are also present at Syowa Station (in Fig. 5 see " \rightarrow "). The particle radius is larger than $1 \mu\text{m}$ and classified as coarse particle. In the samples collected at Asuka Camp, any sea salt particles were not found. Syowa Station is situated on an island close to the continental shore, while Asuka Camp is about 60 km away from the ocean. This difference reflects the difference of the distance of the path from the ocean to the sampling site.

(4) Uniformity of particle size and composition

The particles collected at Asuka Camp closely resemble each other in morphology (Fig. 4). All particles have similar satellite structures, with the same degree of dispersion of many small droplets around the central mother particles. The morphological uniformity is characteristic of the aerosol particles collected in the East

Queen Maud Land (YAMATO *et al.*, 1987). It is worthy to note that the size distribution of the particles collected at Asuka Camp is monomodal which is not found in the polluted air.

(5) Production process of sulfuric acid particles

Sulfuric acid particles in the summer Antarctic atmosphere are thought to be produced through gas to particle conversion processes including photochemical oxidation of sulfur-bearing gas such as SO₂. Produced sulfuric acid particles retain their acidity without suffering neutralization by ammonia in the summer season when photo-chemical oxidation is active. Ammonia gas concentration in the Antarctic atmosphere may be too low to neutralize sulfuric acid particles in the summer season.

5. Conclusion

Vapor-deposited calcium thin films were used at Syowa Station as a specific method for determining sulfuric acid component in individual aerosol particles. The result shows that the calcium thin film method used here was the first success for Antarctic aerosol research, and confirmed, even with the limited samples, that sulfuric acid particles were a dominant aerosol component in the summer coastal atmosphere at Syowa Station. A few ammonium sulfate particles were present even in the summer season.

A systematic observation using the calcium thin film method is under way to clarify the seasonal and geographical variation of the molecular state of sulfate particles.

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