

A NOTE ON THE ORIGIN AND NATURE OF THE ANTARCTIC AEROSOL

Akira ONO,

Water Research Institute, Nagoya University, Chikusa-ku, Nagoya 464

Tomoyuki ITO

Meteorological Research Institute, Yatabe-machi, Tsukuba-gun, Ibaraki 305

and

Kunimoto IWAI

*Department of Earth Science, Faculty of Education, Shinshu University,
Nishinagano, Nagano 380*

Abstract: In order to obtain a better understanding of the character of the aerosol in "clean" air, a series of continuous aerosol measurements was carried out at Syowa Station, Antarctica for two consecutive years (February 1977–January 1979) with emphasis on the chemistry of individual aerosols.

From the annual and meteorological variations in the concentration and size distribution of size-fractionated aerosols together with the physical and chemical properties of individual aerosols, it is found that the antarctic aerosol is characterized by the presence of newborn sulfuric acid aerosols, and that aged ammonium sulfate aerosols coexist with sea salt aerosols.

Some of the implications of the present findings in relation to the origin of the antarctic aerosol are discussed.

1. Introduction

It is conceivable that mankind may have the capability of producing enough pollutants to compete with those occurring in nature, and may have the potential of altering the climate. Although this is open to question at present, it is urgent to establish long-term trends in global background pollutants and to make measurements in an area remote from the source of man-made pollutants. Antarctica is particularly interesting in this respect.

In order to provide a better understanding on the concentration and properties of the antarctic aerosol, a series of systematic aerosol measurements with emphasis on aerosol chemistry was undertaken at Syowa Station (69.0°S, 39.6°E), Antarctica, for two consecutive years from February 1977 to January 1979 by the members of the 18th Japanese Antarctic Research Expedition (JARE-18) (K. IWAI) and JARE-19 (T. ITO) wintering parties.

In this note, an attempt is made to deduce the nature and origin of the antarctic aerosol by combining the results obtained from a series of systematic aerosol measurements.

2. Instrumentation for Aerosol Measurements

The aerosol measurements at Syowa Station were as follows:

Continuous measurements of the concentration and size of the aerosol over the size range larger than $0.002 \mu\text{m}$ in radius were carried out using an automatic Pollak expansion-type photoelectric nucleus counter constructed by one of the authors (T. ITO, 1976) in conjunction with a diffusion battery and an optical particle counter (Dan Co. Ltd., Japan) similar in principle to that of a Royco light scattering particle counter for "large" particles ($r > 0.15 \mu\text{m}$).

These methods of counting and sizing the aerosol are well-established and give very reproducible results but give no information on the chemical nature of the aerosol.

In our interpretation of the origin and environmental effects of the atmospheric aerosol, we depend heavily on the knowledge of its physical and chemical properties as well as its concentration and size distribution.

For this reason, besides the continuous measurements of the aerosol described above, sequential sampling of the aerosol by impaction and/or electrostatic precipitation was made, and the aerosol was subjected later to physical and chemical investigation of individual particles by means of electron microscopy. In addition, the volatility of the aerosol was measured by passing the sample through a heated silica tube prior to counting with a Pollak nucleus counter, similar in principle to that of TWOMEY (1971). We believe that the parameters measured constitute significant body of representative data at Syowa Station. Our studies have incorporated some new measurements of the antarctic aerosol which have not been described before, such as by HOGAN and BARNARD (1978) and VOSKRESENSKII (1968) for example.

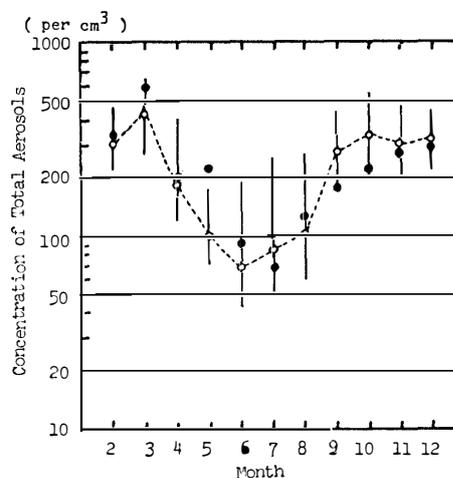
3. Results and Discussion

3.1. *The annual variation in the total aerosol concentration*

From the continuous record of the total aerosol concentration made with the automatic Pollak nucleus counter (at intervals of 6 minutes), three values, N_{20} , N_{50} and N_{80} , are calculated from the cumulative frequency distribution curve of observations in each month. N_{20} stands for the concentration below which lay only 20% of observations; N_{50} , the median; and N_{80} , the concentration above which only 20% of observations lay. The number of observations in each month is more than 7000.

Figure 1 shows the annual variation of the monthly median concentration of the total aerosol concentration for the calendar year 1977 and 1978. In the figure,

Fig. 1. The annual variation in the median concentration (N_{50}) of total aerosols for the calendar year 1977 (●) and 1978 (○) observed at Syowa Station, Antarctica. In the figure, N_{80} and N_{20} values are plotted with a vertical line for the calendar year 1978 (based on IWAI, 1979; ITO, 1980).



the range of concentrations observed in each month is indicated with the monthly N_{20} and N_{80} for the calendar year 1978 (IWAI, 1979; ITO, 1980).

As can be seen, there is a clear trend in the total aerosol concentration, revealing a pronounced annual variation: The median concentration during the summer months is about 200 to 300 cm^{-3} and less than 100 cm^{-3} during the winter months. A gradual decrease in the concentration begins around the time of the astronomical sunset and remains at low values throughout the winter months. A rather rapid increase in the concentration begins just before the astronomical sunrise and reached the maximum in March.

Since the similar annual variation in the total aerosol concentration was observed at Mirnii Station by VOSKRESENSKII (1968) and at South Pole Station by HOGAN and BARNARD (1978), the observed annual variation seems to be a common feature of the antarctic aerosol in the near-surface air over Antarctica.

3.2. Meteorological variation in the aerosol concentration

To gain additional useful information in the continuous aerosol data, we assessed other atmospheric variables, such as surface temperature, relative humidity, wind speed and surface ozone content.

Figure 2 gives a composite presentation of the annual variation of hourly averages of surface temperature, wind speed, median concentration of total and "large" (Mie) particles, and surface ozone content observed at Syowa Station for the period of 1 February through 31 December 1978. In the figure, each curve is obtained by smoothing out the hourly averages with a five days moving average technique.

It is significant to note that the annual variation of the total aerosol concentration is quite different from that of the "large" particle. Although the total aerosol concentration is low in winter and relatively high in summer, the "large" particle

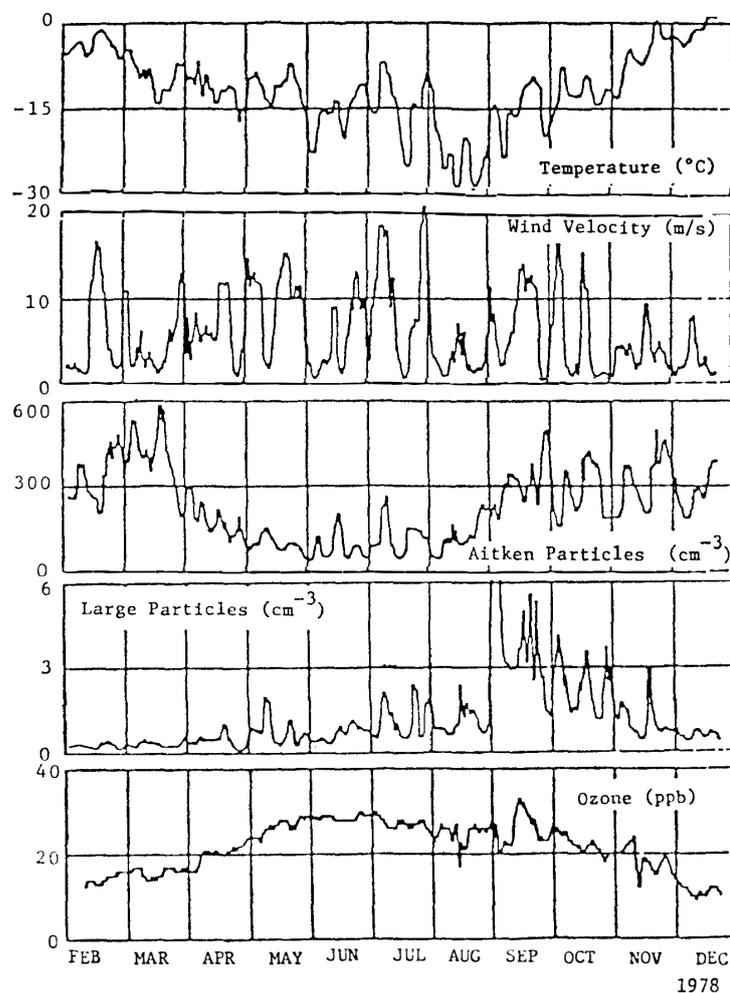


Fig. 2. Meteorological variation in the concentration of total aerosols ($r > 0.002 \mu\text{m}$) and "large" aerosols ($r > 0.15 \mu\text{m}$) plotted together with meteorological variables observed at Syowa Station, Antarctica in 1978.

concentration is noticeably low in summer and higher in September. In general, instruments that measure the total aerosol concentration respond to the aerosol in the size range of $0.002 \mu\text{m} < r < 0.1 \mu\text{m}$ and that measure the "large" particle respond in the size range of $r > 0.15 \mu\text{m}$, so that the observed significant difference in the annual variation of the concentration between the total aerosol and the "large" particle would indicate the difference in their origin, but the rapid increase in the "large" particle concentration observed in September cannot be explained at present.

The data compiled in Fig. 2 give some indications of the origin of the antarctic aerosol: Peak values in the variation of the "large" particle concentration are always accompanied with strong winds and advection of warm air. And during the winter months (June to September), peak values in the variation of the total aerosol con-

centration are also accompanied with strong winds and advection of warm air. These results suggest that those aerosols observed in the winter months at Syowa Station would have been the aerosols contained in the maritime air transported from oceanic regions to Antarctica by moving cyclonic storms.

On the other hand, during the summer months, peak values in the variation of the total aerosol concentration are not always accompanied with cyclonic storms and the "large" particle concentration is quite low. These results, considered together, suggest that the aerosols in the summer months are not of the maritime air origin. It is also interesting to note that the high concentration of the total aerosol is not associated with the high surface ozone values. In general, in Antarctica, the high surface ozone values are thought to be associated with subsidence of the stratospheric air. Therefore, the aerosol in summer months does not seem to be attributed to stratospheric sources, and photochemical generation of the aerosol in the antarctic atmosphere itself would have been possible.

3.3. *Nature of the aerosol associated with the event of increased aerosol concentrations*

As mentioned above, the results obtained from the analysis of the continuous data of the aerosol measurements indicate clearly that the aerosol found in the near-surface air at Syowa Station can be classified into two types according to their different behaviors in the annual and meteorological variations of concentration.

As a further aid in deducing a better understanding of the nature and origin of the antarctic aerosol, it is useful to refer to the results of systematic studies of the event of increased aerosol concentration as discussed fully by ITO and IWAI (1981).

Figure 3 gives a composite presentation of two typical events of increased aerosol concentration observed at Syowa Station on 25 November and 1 December 1978. In the figure, size-fractionated concentrations are plotted together with relevant meteorological variables (weather, wind speed and direction, relative humidity, and surface temperature). The heavy dotted line in the figure stands for the concentrations of aerosol particles larger than $0.002 \mu\text{m}$ in radius; the thin dotted line, the concentrations of aerosol particles larger than $0.01 \mu\text{m}$ in radius; and the full line, the concentrations of "large" particles (Mie particles) larger than $0.15 \mu\text{m}$ in radius.

The event of increased aerosol concentration observed on 25 November 1978 ("type-2" event) was accompanied with strong winds and advection of warm air as shown in Fig. 3. The most significant feature of the "type-2" event is that the increase in the aerosol concentration takes place simultaneously over the wide size range and the aerosol consists of volatile and non-volatile particles. In the "type-2" event, a relatively large portion of the aerosol (more than 70%) is composed of non-volatiles surviving as aerosol particles even at a temperature of 600°C , which indicates that they are of sea salt origin (TWOMEY, 1971). From the morphological examination of individual aerosol particles by means of electron microscopy, it is found

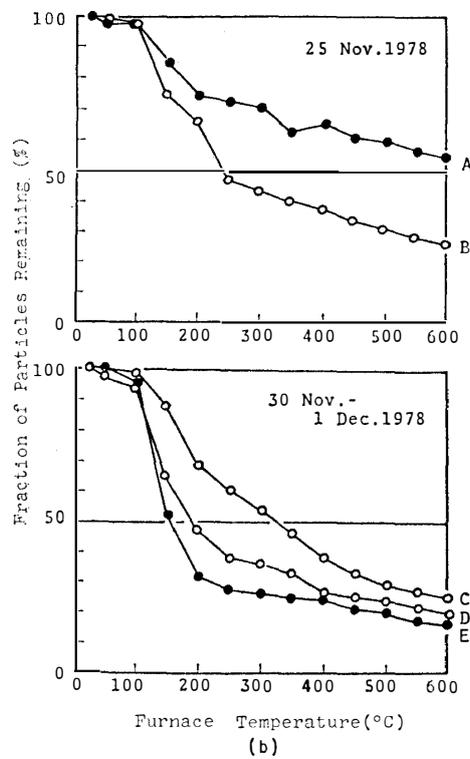
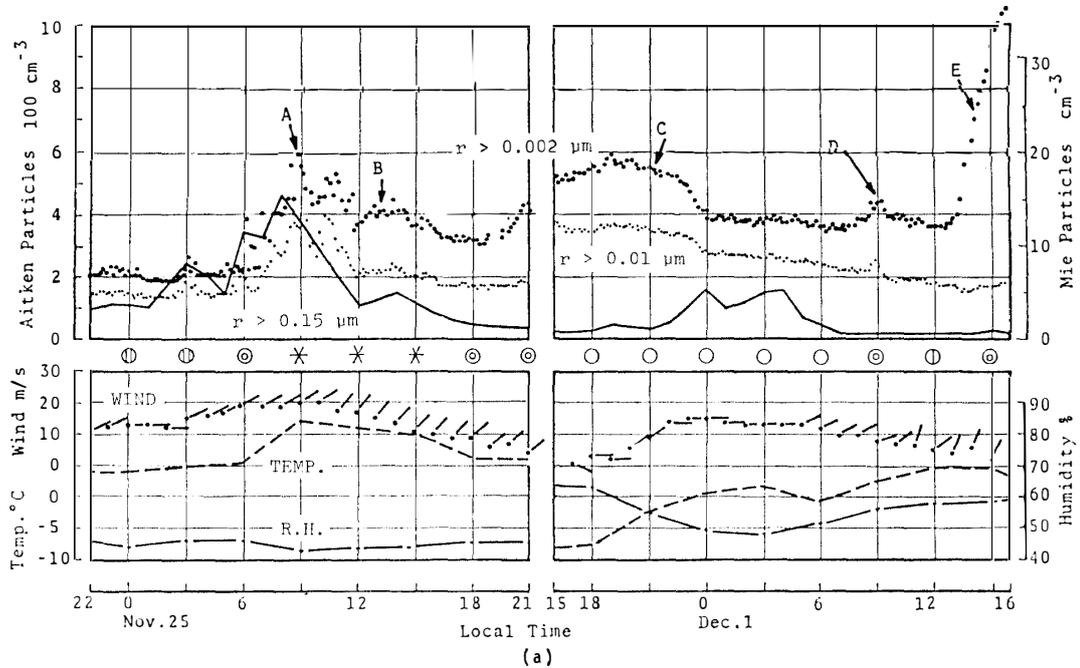


Fig. 3. Events of increases of aerosol concentrations (a) and the volatility of the aerosol (b) observed at Syowa Station, Antarctica (after ITO and IWAI, 1981).

that aerosol particles collected during a storm consisted of sea salt particles and sulfate particles as shown in Fig. 4a, similar to the aerosol particles collected over the sub-antarctic ocean from the research vessel FUJI (ONO *et al.*, 1979). Sulfate particles of the “type-2” event seem to be aged aerosols consisting of ammonium sulfate as discussed in the following section. Therefore, it is strongly suggested that the aerosol associated with the “type-2” event is the maritime aerosol contained in the air over the sub-antarctic ocean and was transported to Syowa Station by moving cyclonic storms.

The “type-1” event of increased aerosol concentration observed on 1 December 1978 is not accompanied with any storms and quite contrasted with the “type-2” event in many points. The most interesting feature of the “type-1” event is that the increase in the aerosol concentration takes place only in the smallest size class ($0.002 \mu\text{m} < r < 0.03 \mu\text{m}$) and the concentration of larger aerosol particles more than $0.03 \mu\text{m}$ in radius and of the “large” particle more than $0.15 \mu\text{m}$ in radius remains almost constant throughout the event period as shown in Fig. 3. From the volatility measurements of the aerosol during the “type-1” event, it is found that the aerosol is very volatile and the greater part of it is evaporated/decomposed at a temperature of 200°C . By means of electron microscopy, the morphological examination of individual particles collected by electrostatic precipitation during the summer months indicates that the size of the aerosol is confined in the size range smaller than $0.1 \mu\text{m}$ in radius. The majority of aerosol particles have discrete widespread concentric rings of satellites of graded size surrounding a central particle as shown in Fig. 4b, indicating they are sulfuric acid aerosols (ITO, 1980).

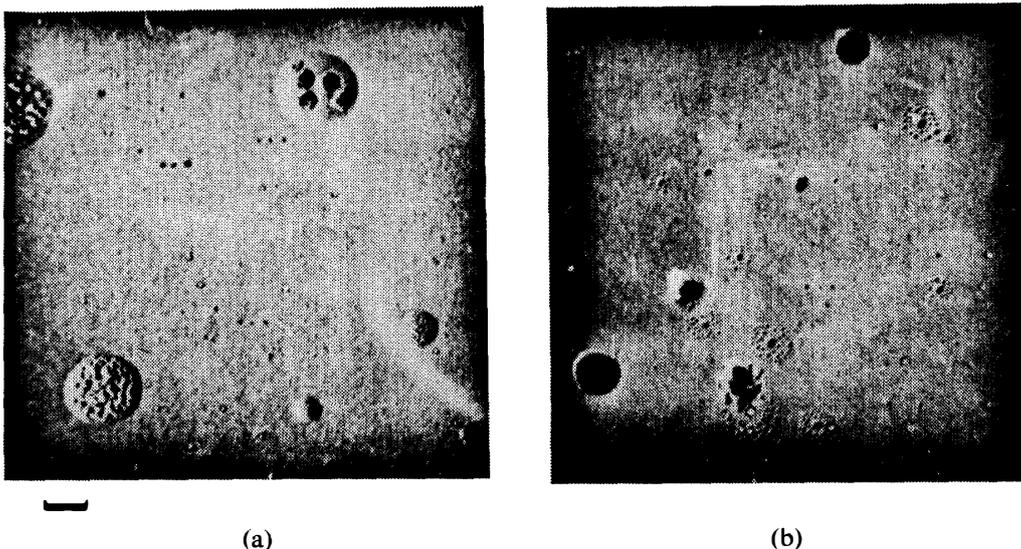


Fig. 4. Electron micrograph of the aerosol observed at Syowa Station, Antarctica in the winter months (a), and in the summer months (b) of 1978 (after ITO, 1980). (Scale: $1 \mu\text{m}$).

Since the “type-1” event is not observed during the polar night season as described by ITO and IWAI (1981), it is suggested that the solar radiation could be an important factor for the occurrence of the “type-1” event. It should be noted, however, that the peak concentration of the aerosol in the “type-1” event did not show any diurnal variations and the duration of the event varied from several to tens of hours as pointed out by ITO and IWAI (1981). These facts, considered together, suggest that the dominant aerosol in the “type-1” event is not formed directly in the near-surface air by photochemical processes. It would have been formed aloft in the atmosphere by photochemical processes (gas-to-particle conversion) and would have been transported down into the atmospheric surface boundary layer under certain circumstances by meteorological processes, such as frontal passages at a lower level and subsidence of the upper air as discussed by HOGAN and BARNARD (1978) and SHAW (1979).

3.4. *Aerosols containing sulfate in air over Antarctica and sub-antarctic oceans*

As discussed above, it is found that the most common aerosol at Syowa Station consists of sulfuric acid aerosols and other sulfate-bearing aerosols. However, there is a distinct difference between them not only in the appearance but also in the size of aerosols. In general, sulfuric acid aerosols (observed only during the summer months) are in the smallest size range in the Aitken size range ($r < 0.1 \mu\text{m}$) compared with the size of sulfate aerosols.

Most of the aerosols in the summer months are present in the form of sulfuric acid droplets, similar in nature to those observed at the summit of Mt. Fuji (3776 m) in the subsiding upper air by ONO (1978) as shown in Fig. 5. In addition, the size distribution of these summer aerosols is bimodal in the Aitken size range, with enhancements in the aerosol concentration occurring at $0.005 \mu\text{m}$ and at $0.02\text{--}0.03 \mu\text{m}$ in radius as observed by ITO (1981). Therefore, it is very likely that they are of recent photochemical generation in the sunlit antarctic troposphere. In fact, HOGAN



Fig. 5. *Electron micrograph of the aerosol in subsiding air at the summit of Mt. Fuji (3776 m) during nighttime of 24–25 August 1975 (based on ONO, 1978). (Scale: $1 \mu\text{m}$).*

and BARNARD (1978) observed in summer the higher concentration of the Aitken-sized aerosol in the antarctic upper layer compared with that at the surface.

On the other hand, during the intrusion of maritime air accompanied with cyclonic storms, the aerosol consists of sea-salt particles and sulfate aerosols, similar to those observed in the "clean" maritime air.

In December 1977, in order to study the aerosol in the "clean" maritime air, sampling of the aerosol by electrostatic precipitation was carried out by JARE-19 over the sub-antarctic ocean on board the research vessel FUJI. As shown in Fig. 6, from the electron microscopy, the aerosol consists of sea salt particles accompanied with a crystalline particle and hemispherical particles, but no sulfuric acid aerosols are observed. By an application of a thin film technique of BaCl_2 described by BIGG *et al.* (1974), those hemispherical particles are identified as "ammonium sulfate" through a combination of the heat-sensitive nature and the reaction with a vapor-deposited thin film of BaCl_2 of the particles to be tested as shown in Fig. 6 (ONO *et al.*, 1979). In the figure, those containing sulfate change completely in appearance because a characteristic ring of very insoluble BaSO_4 is precipitated around the particle and indicates the presence of sulfate ion in the particle (ONO *et al.*, 1981).

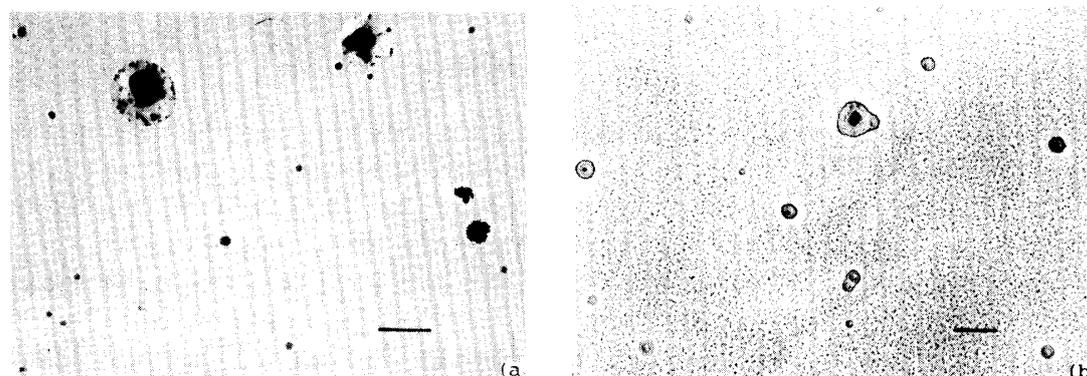


Fig. 6. Electron micrograph of the aerosol observed off the coast of Enderby Land, Antarctica in December 1977 (a), and it reacted later with BaCl_2 thin film (b). (Scale: $1 \mu\text{m}$).

Although the origin of the sulfate aerosols in the "clean" maritime air requires further study, they are not the remnants of originally continental aerosol and are formed independent of light (TWOMEY and WOJCIECHOWSKI, 1969). It has been postulated that the aqueous oxidation processes of gaseous sulfur compounds in water droplets involve the formation of sulfate by the oxidation of SO_2 to SO_4^- in the presence of trace amount of ammonia, and when the droplets evaporate, sulfate aerosols remain (*e. g.*, HOBBS, 1971). Evidence to support the mechanism postulated above is provided by the recent field experiments in which individual residues of evaporated cloud droplets were investigated by applying a thin film technique of BaCl_2 . It is suggested that the chemical reaction occurring within cloud droplets in

the presence of trace amount of ammonia could be an important source of background sulfate aerosols in the "large particle" size range (ONO and AKAEI, 1981).

4. Concluding Remarks

Even though the findings discussed above are still somewhat preliminary in nature, they are adequate to provide a reasonable framework for making a few broad generalizations regarding the origin of the antarctic aerosol.

In the antarctic atmosphere, two types of the aerosol originated from different sources are present.

With the intrusion of the maritime air by cyclonic storms, mostly in the winter months, the aerosol composed of sea salt particles and ammonium sulfate aerosols contained originally in the "clean" maritime air is dominant.

Whereas in the summer months, the aerosol in the chemical form of sulfuric acid droplets is predominant. Those sulfuric acid aerosols are formed by photochemical oxidation of sulfur-bearing gases in the sunlit troposphere and are transported down into the surface boundary layer under certain circumstances by meteorological processes.

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