

SULFURIC ACID PARTICLES AND THEIR NEUTRALIZATION BY AMMONIA IN THE MARINE ATMOSPHERE: MEASUREMENTS DURING CRUISE FROM JAPAN TO ANTARCTICA

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Abstract: Samplings of marine boundary layer aerosol were made on board R/V "SHIRASE" during a cruise from Japan to Antarctica in 1986. Aerosols on land area were collected in Borneo in 1987. Particle morphology and their reactivity with vapor-deposited calcium thin film were observed by electron microscope. Sulfate or sulfuric acid aerosol were predominant in the fine particle size range. Sulfuric acid aerosol was predominant over the North Pacific Ocean, over the ocean near Antarctica and in Breid Bay (Antarctica), whereas ammoniated sulfate aerosol was predominant in Borneo and over ocean near land. The degree of ammoniation of sulfate aerosol was negatively correlated with the distance from land. Small non-acid aerosols in the Aitken particle size range occasionally coexisted with sulfuric acid containing aerosol over the ocean. The long range transport process of air masses from land to ocean might control the content of ammonium in aerosol.

1. Introduction

Sulfate is a dominant component of secondary atmospheric aerosols in the troposphere and the stratosphere. Usually, sulfate aerosol has the chemical form of sulfuric acid and its neutralization products with ammonia. JUNGE (1953, 1954) found that submicron sulfate aerosol is ubiquitously present in the troposphere and showed that the average molar ratio of NH_4^+ to SO_4^{2-} of fine aerosol composition collected in urban and rural areas corresponds to a mixture of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 .

Since NH_3 is the only alkaline gas in the atmosphere, it can be rapidly neutralized by acidic gases and/or droplets. This neutralization is recognized as an important transfer process of particulate matter. The neutralized aerosol is generally stable in the atmosphere, and thereby its distribution can be affected by dynamic air motion.

Recently, great effort has been directed toward the "background" aerosol, be-

cause of its roles in various global processes; sulfur cycle in the marine-atmosphere system, acid rain problem, and so on. The neutralization process of sulfuric acid aerosols and its effect on geochemical cycles of sulfate and nitrate are of major interest in the marine atmosphere.

MÉSZÁROS and VISSY (1974) found sulfuric acid particles, ammonium sulfate particles, and mixed particles of ammonium sulfate and sea salt over the oceans far away from land. OKADA *et al.* (1985) collected aerosol particles on board the "SHIRASE" over the region from Japan to Antarctica and classified them into several types by morphological observation. These types varied according to sampling location. CLARKE *et al.* (1987) showed from the vaporization character of marine aerosol that sulfuric acid and neutralized sulfate are contained in aerosol particles in the fine particle size range.

The Antarctic marine atmosphere is especially interesting, since the region is remote from anthropogenic sources. Therefore this area should yield knowledge on "background" aerosols. The degree of ammoniation of sulfate aerosol strongly depends on influence from land areas. The relation between size distributions and content of particles containing NH_4^+ should be helpful for better understanding of the formation process and transport process of existing aerosol.

Aerosols were sampled on board the R/V "SHIRASE" over the ocean from Japan to Antarctica in 1986 (the 28th Japanese Antarctic Research Expedition; JARE-28). Aerosol samplings on land were carried out at Pontianak (0°S, 109°18'E) on Borneo in July 1987. Molecular state, degree of ammoniation and size distributions of sulfate particles were examined under an electron microscope.

2. Chemical Test and Samplings

2.1. Chemical test of individual particles

Sulfuric acid contained in individual particles was identified by the vapor-deposited calcium thin film method (ONO *et al.*, 1983). This method avoids possible contamination of sulfuric acid by ammonia as pointed out by HAYES *et al.* (1980). First, electron microscope screens (EM screens) were covered with collodion film. Second, carbon was evaporated onto the EM screens. Particles collected on carbon film were shadowed by vapor deposition of Au-Pd alloy for the morphological observation.

A tangstein boat, in which metal calcium ingot of 0.5 mg was loaded, was set 14 cm appart from the EM screens with depression of 45°. Calcium (0.5 mg) was evaporated onto carbon-coated EM screens in a vacuum chamber, and a thin film of about 1 nm was formed. Morphology of calcium reaction rings was observed by transmission electron microscope (TEM).

In the dry atmosphere (*e.g.*, 10% r.h.), particles containing sulfuric acid react with calcium and form reaction rings, whereas ammonium sulfate particles cannot reacted with a calcium thin film at all. Ammonium sulfate contained in sulfuric acid particles is determined as nonreacting material in the reaction ring (YAMATO and ONO, 1985).

The sizes of particles and their reaction rings were measured with a degitizer (Logitec, model K-510 mkz) from photographs of TEM. Radii of sulfuric acid par-

ticles were evaluated assuming that the shape of particles collected on the carbon film is half spherical cap. Radii of the particles were divided into ten equal logarithmic intervals for one order size range, and size distributions were determined.

2.2. Sampling of aerosols

Aerosol particles were collected with a two-stage impactor on EM screens coated with carbon or calcium. The flow rate of the impactor was 2.2 l/min. Nozzle diameters of the first and second stages of the impactor were 1.0 and 0.5 mm, respectively. Sulfate particles (fine or Aitken particle size range) were collected mainly by the second stage of the impactor, while the first stage was used to cut sea salt particles off. Each sampling time was 10 min; thus the sampling volume was 22 l.

Prior to impaction of particles on calcium thin film, water vapor in ambient air must be removed with a diffusion drier in order to distinguish sulfuric acid from ammonium sulfate. A buffer drier (2 l in volume) was connected next to the diffusion

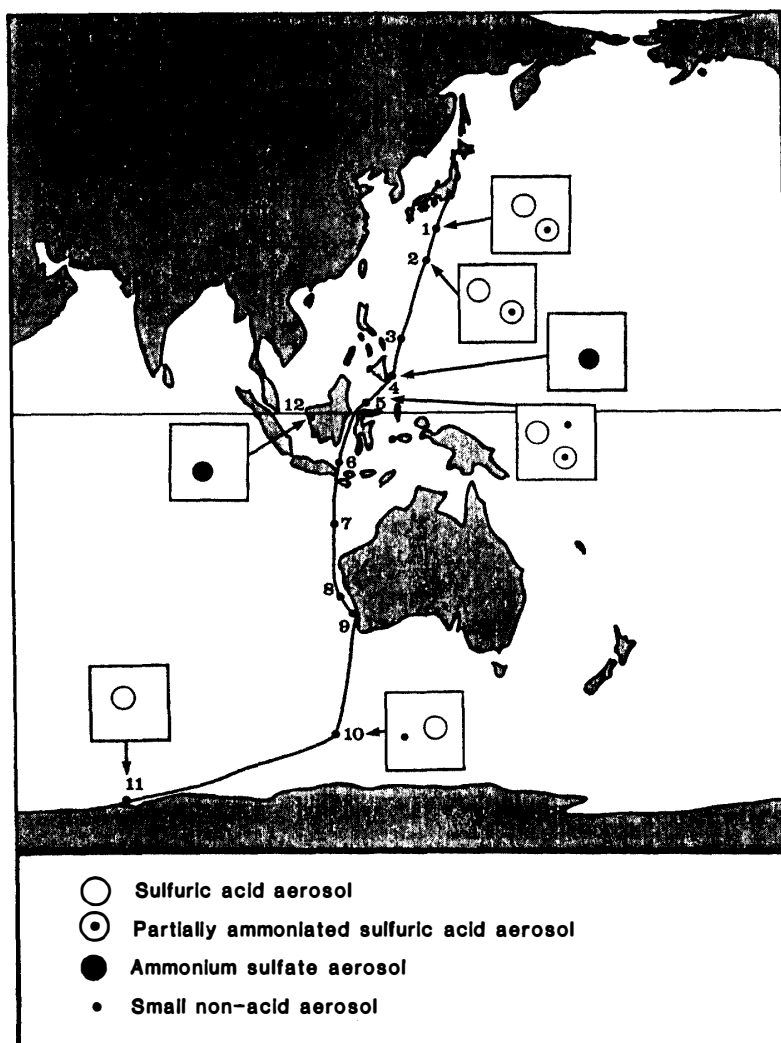


Fig. 1. A map showing the sampling locations (numbered from 1 to 12) and dominant aerosol populations (indicated by symbols) during a cruise from Japan to Antarctica (JARE-28, 1986), and in Borneo island (1987).

Table 1. A List giving aerosol sampling conditions on board the "SHIRASE" in 1986 and at Pontianak on Borneo in 1987.

Ocean (Japan-Antarctica), by "SHIRASE", 1986						
No.	Date	Time	Location	T(°C)	RH(%)	Contamination
1	11/15	12:30	29°58'N, 136°59'E	24.0	79	
2	11/16	12:20	24°01'N, 133°58'E	26.7	76	
3	11/18	12:10	12°12'N, 129°03'E	25.7	93	Yes
4	11/19	12:20	6°20'N, 127°20'E	29.0	79	
5	11/20	12:20	2°44'N, 122°15'E	29.0	77	
6	11/22	12:40	7°27'S, 116°22'E	29.0	70	Yes
7	11/24	8:00	17°15'S, 113°49'E	25.9	80	Yes
8	11/26	9:30	28°25'S, 113°12'E	20.7		Yes
9	11/28	7:20	31°57'S, 115°37'E	20.3		Yes
10	12/8	8:20	53°42'S, 104°52'E	1.2	75	
11	12/21	15:00	70°12'S, 23°47'E	-1.9		
Land (Pontianak, Borneo Island), 1987						
12	7/23	10:20	0°S, 109°18'E	24.8	96	

drier for sufficient removal of water vapor. Ambient air of low relative humidity about 5–10% could be obtained with this equipment. After sampling, EM screens were kept in a dry sealed container.

Sampling locations shown in Fig. 1 were numbered from No. 1 to No. 11 (on board the "SHIRASE") and No. 12 (on Borneo). Samplings were performed 12 times at Pontianak on Borneo from July 16 to July 27, 1987. Temperature and relative humidity in this period were 25–32°C and 73–96%, respectively. Weather conditions during sampling on board the ship are listed in Table 1. Five samples were contaminated by the ship. The samples reported here are non-contaminated.

3. Electron Microscopic Observation of Aerosol Particles

3.1. Aerosols sampled over the North Pacific Ocean

Figure 2 shows the aerosol collected over the North Pacific Ocean (No. 1, No. 2). Particles of No. 2 have a ring of small satellite particles. All particles reacted with calcium. These particles are identified to be sulfuric acid-containing particles.

Electron-dense materials are found in some of these reaction rings, suggesting that the particles are not pure sulfuric acid particles but sulfuric acid particles partially neutralized by ammonia. The degree of ammoniation of No. 1 is a little larger than that of No. 2.

3.2. Aerosol sampled near or on land

Aerosols on land or near land are shown in Fig. 3. Aerosol particles on Borneo (No. 12) and near Mindanao (No. 4) are fully neutralized with ammonia, since they resemble ammonium sulfate in morphology (No. 4, No. 12) and do not react with calcium (No. 12).

Two aerosol populations coexisted at a short distance offshore (No. 5). One is sulfuric acid-containing particles (indicated by "S" in the figure) which reacted with

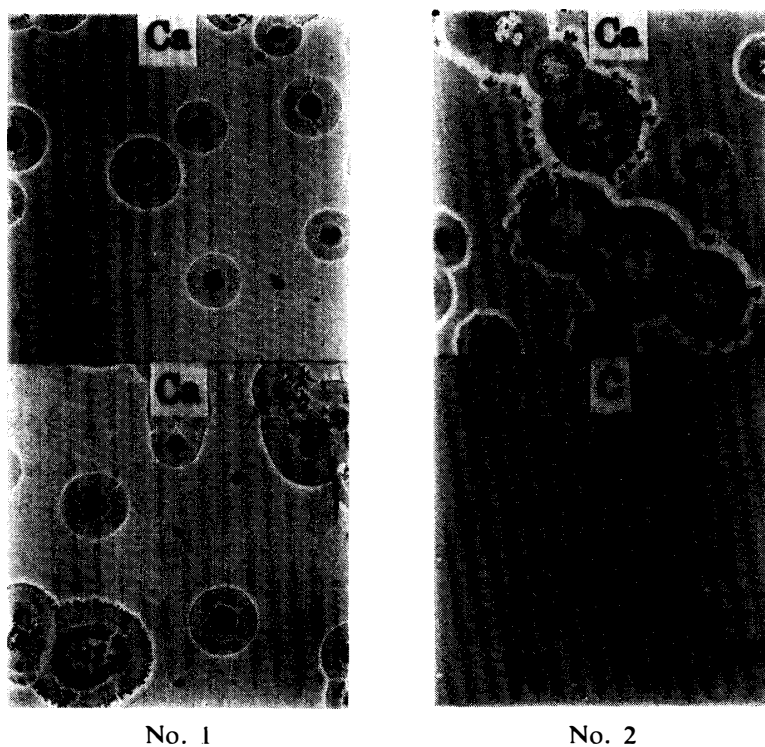


Fig. 2. Aerosol particles collected over the North Pacific Ocean (No. 1, No. 2). "Ca" and "C" in the figure show that the particles were collected on surfaces coated with calcium and carbon, respectively.

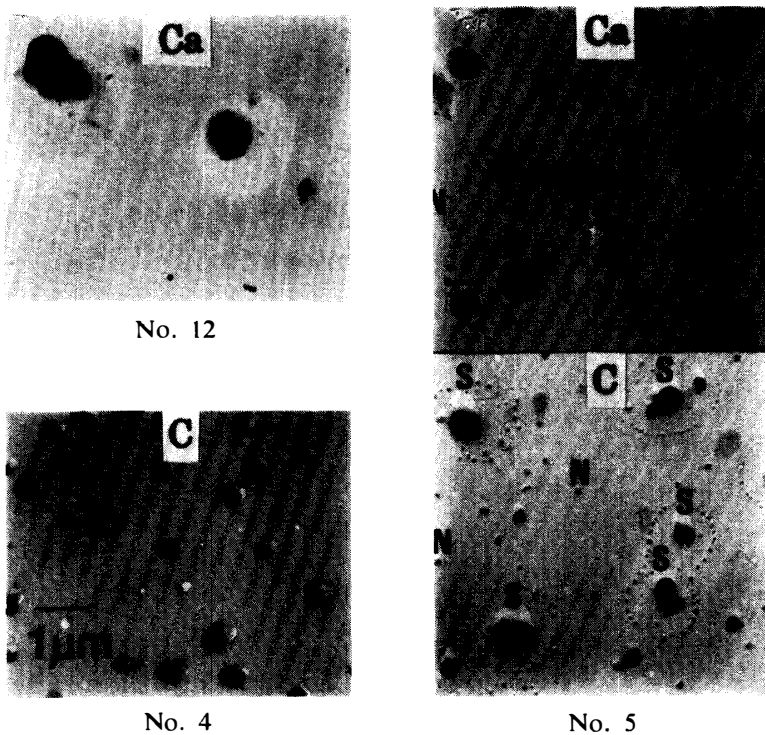


Fig. 3. As for Fig. 2 except for aerosol particles in Borneo island (No. 12) and near land (No. 4, No. 5).

calcium. Only one halo ring surrounds the central particles, whereas pure sulfuric acid particles usually have multiple halo rings. Hence, they are possibly partially ammoniated sulfuric acid particles. Another population is small non-acid particles (indicated by "N") which did not react with calcium. However, it is not certain that these particles are composed of ammonium sulfate.

3.3. Aerosols sampled near Antarctica

Aerosol particles collected over the ocean near Antarctica (No. 10) and in Breid Bay (No. 11) are shown in Fig. 4. Particles (No. 10) indicated by "S" are accompanied by multiple halo rings, which is the indication of sulfuric acid particles. The particles indicated by "N" are small non-acid particles. These two populations coexisted in this region, as in sample No. 5.

All particles collected in Breid Bay (No. 11) reacted completely with calcium and non-reactive materials (indication for ammonium sulfate) were not found in the reaction rings. They are identified to be sulfuric acid particles. Small non-acid aerosol were not found. Sulfuric acid particles from the unique aerosol population present in this region. This finding is similar to that obtained in Antarctica (YAMATO *et al.*, 1987a, b).

It should be noted that the acidity of sulfuric acid particles in these two regions (No. 10, No. 11) is larger than that of sulfuric acid particles in other regions (*e.g.*, No. 1, No. 2, No. 5). In other words, ammoniation of sulfuric acid particles near Antarctica was less dominant than in other regions.

3.4. Ammonium compound contained in sulfuric acid particles

A detailed picture showing the calcium reaction rings of No. 5 is given in Fig. 5. Electron-dense non-reactive materials (indicated by arrows) are found in the calcium reaction rings. Such a double structure was found for internally mixed particle composed of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ (YAMATO and ONO, 1985). Thus these materials can be identified to be ammonium sulfate contained in sulfuric acid particles. Similar materials are found in the calcium reaction rings of No. 1 and No. 2. The sulfuric acid particles in these regions were partially neutralized with ammonia.

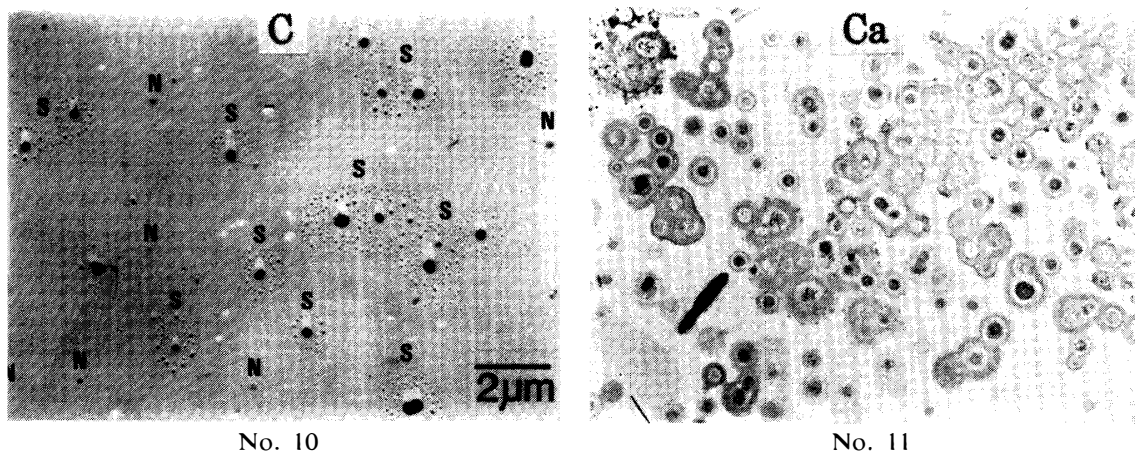


Fig. 4. As for Fig. 2 except for aerosol particles over the ocean between Australia and Antarctica (No. 10) and in Breid Bay, Antarctica (No. 11).



Fig. 5. Calcium reaction rings of aerosol particles near land (No. 5). Arrows indicate non-reacting materials (possibly ammonium sulfate) contained in sulfuric acid particles.

Comparing the size and frequency of the non-reactive materials qualitatively, the degree of ammoniation of the particle (No. 5) is larger than that of No. 1. The parameter of No. 1 is larger than that of No. 2. In the vicinity of land, sulfate particles were fully neutralized by ammonia (No. 4).

3.5. Spatial distribution of aerosols

Spatial distribution of predominant aerosol populations is illustrated in Fig. 1. Populations of aerosols are indicated with symbols. Distribution of sea salt particles is not shown in the figure, because they are present ubiquitously near the sea surface. Symbols are not shown for five contaminated samples (No. 3, No. 6, No. 7, No. 8, No. 9).

The dominant aerosol near Antarctica (No. 10, No. 11) is sulfuric acid particles. Sulfuric acid particles were partially neutralized by ammonia near Japan (No. 1, No. 2) and near land (No. 5). Fully ammoniated sulfate aerosol was present on land (No. 12) or near land (No. 4). The degree of ammoniation of particle is negatively correlated with distance from land, except for No. 11 in the vicinity of Antarctica, where there are no strong ammonia sources. This tendency implies that the extension of ammonia-rich air masses originating from land is the cause of the ammoniation of sulfate aerosol over the ocean.

4. Size Distributions According to Aerosol Population

Figure 6 shows the bi-modal size distribution of aerosols collected over the ocean between Australia and Antarctica (No. 10). Sulfuric acid particles were distributed from Aitken to large particle size range, whereas most small non-acid particles are in the Aitken particle size range. It should be noted that the number concentration of sulfuric acid aerosol (6 cm^{-3}) is the same magnitude as that (6.6 cm^{-3}) of type B particles over the ocean near Antarctica measured by OKADA *et al.* (1985). Possibly, the two aerosols are in the same population.

Total volumes of sulfuric acid particles and small non-acid particles were com-

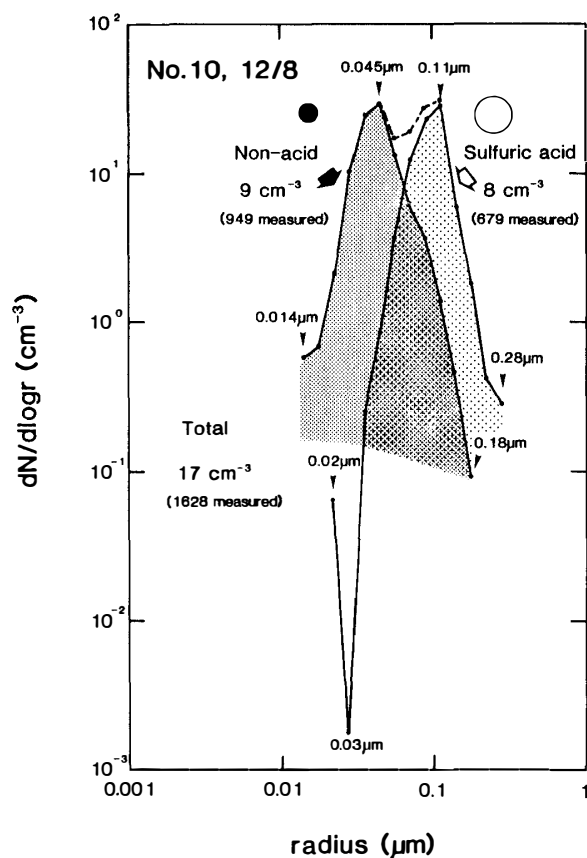


Fig. 6. Size distribution (uncorrected by impaction efficiency) of sulfuric acid particles and small non-acid particles over the ocean between Australia and Antarctica (No. 10).

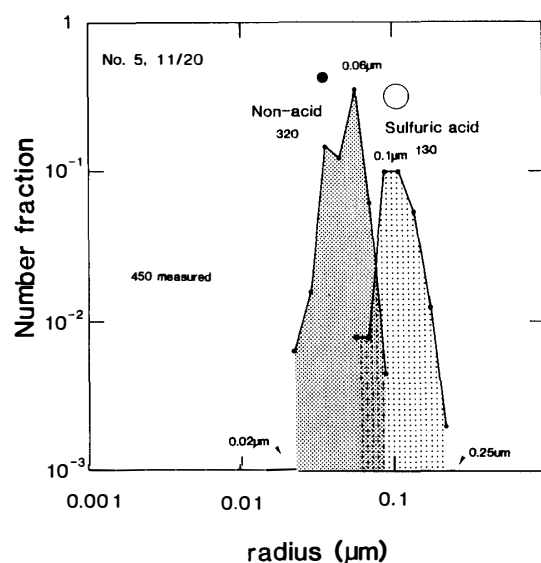


Fig. 7. Normalized size distribution (uncorrected by impaction efficiency) of sulfuric acid containing particles and small non-acid particles over the ocean near Sulawesi island (No. 5).

pared assuming that their modal radii were representative radii of each size distribution. Sulfuric acid aerosol is about 13 times non-acid aerosol in total volume. Hence, except for sea salt particles, most aerosol masses over the ocean near Antarctica are due to sulfuric acid particles.

The size distribution of No. 5 (Fig. 7) like that of No. 10 (Fig. 6) is bi-modal. The number fraction of small non-acid aerosol is about 2.5 times that of sulfuric acid particles, and this value is larger than that of No. 10 (about 1.1 times) near Antarctica.

Sulfate aerosol which has a modal radius at about $0.1 \mu\text{m}$ is ubiquously present over the ocean, whereas small non-acid aerosol is sometimes present and sometimes absent. Obviously, the origin of small non-acid aerosol is different from that of sulfuric acid aerosol. Small non-acid aerosol was probably transported from land area, since the sampling position (No. 5) was close to Sulawesi island and Borneo. Considering that small non-acid aerosol were not present in Breid Bay (No. 11), there is a possibility that these small non-acid aerosols were transported from Australia. Long-range transport of air from land is likely an important process controlling the content and number concentration of aerosol in remote oceanic regions.

Although the chemical properties of small non-acid aerosols have not been clearly

Table 2. Minimum, modal and maximum radii of size distributions of particles and their calcium reaction rings. "r" and "R" denote the radii of particle and calcium reaction rings, respectively.

No.	Aerosol	Particle (μm)			Ca ring (μm)		
		r_{\min}	r_{mod}	r_{\max}	R_{\min}	R_{mod}	R_{\max}
1	Sulfuric acid	—	—	—	0.32	0.56	1.30
2	Sulfuric acid	0.05	0.11	0.40	0.32	0.56	1.60
4	Ammonium sulfate	0.03	0.09	0.32	—	—	—
5	Sulfuric acid	0.05	0.10	0.25	0.16	0.32	1.00
10	Sulfuric acid	0.02	0.11	0.28	—	—	—
11	Sulfuric acid	—	—	—	0.14	0.35	0.70
12	Ammonium sulfate	—	—	—	—	—	—

identified, they might play the role of nucleation centers in the formation process of sulfuric acid particles. Also, coagulation of small non-acid particles with sulfuric acid particles might lead to the formation of internally mixed particles.

Size ranges of sulfate aerosols collected during the cruise are listed in Table 2. Sulfate aerosol is in accumulation mode with the modal radius being commonly about $0.1 \mu\text{m}$ (although this value depends on the collection efficiency of the used impactor). The corresponding radius of a calcium reaction ring is several times of particle radius. For example, the modal radius of particles ($0.11 \mu\text{m}$) corresponds to that of calcium reaction ring ($0.56 \mu\text{m}$) for the No. 2 sample.

It is interesting to note that the size of particles and calcium reaction rings of No. 1 and No. 2 collected over the North Pacific Ocean were somewhat larger than those of aerosols collected in lower latitude (No. 5) and the southern hemisphere near Antarctica (No. 10, No. 11). Sulfuric acid particles over the Pacific Ocean were larger than that near Antarctica. This difference was presumably concerned with the condition for formation of sulfuric acid particles in these areas (e.g., concentration of SO_2).

5. Discussion

5.1. Origin of ammoniated sulfate particles

The results mentioned in the previous chapter suggest that sulfuric acid aerosol was predominantly present over the ocean far from land. However, this does not mean that they were composed of pure sulfuric acid. Ammonium sulfate is contained in sulfuric acid particles over the North Pacific Ocean (No. 1) and over Sulawesi island (No. 5). Hence, sulfuric acid particles over the ocean are partially neutralized with ambient ammonia.

One origin of ammonia is usually thought to be land. GEORGH and MÜLLER (1974) found that ammonia concentration is lower over the ocean than on land. The extension of ammonia rich air masses promotes the neutralization of sulfuric acid particles.

A second probable source of NH_3 is the ocean itself. QUINN *et al.* (1987) stated that once an air mass is several days from a continent, the primary source of ammonia should be the ocean itself. CLARKE *et al.* (1987) observed that the degree of ammoni-

ation of sulfate aerosol appeared to vary in a regular fashion with upwelling or biological activity, and upwelling might reflect elevated atmospheric ammonia concentration. The effect of upwelling on neutralization of aerosol was discussed also by other investigators (*e.g.*, PARUNGO *et al.*, 1986). It is reasonable to assume that the ammonia concentration over the ocean is the result of superposition of the two ammonia sources. Ammonia of land origin might prevail in the vicinity of land, whereas ammonia from the ocean might dominate over the remote ocean.

The acidity of sulfuric acid aerosols collected near Antarctica (No. 10, No. 11) was larger than that in other regions, probably due to the lack of ammonia source in these regions. From the standpoint that ammonia is produced by man, large acidity of sulfate aerosol implies that air pollution due to man's activity was less pronounced in this region.

5.2. Source of sulfuric acid particles

Knowledge obtained here shows that excess sulfate, which is not originated from sea salt (*e.g.*, GRAVENHORST, 1978), should be attributed to sulfuric acid aerosol. Sulfuric acid particles are generally thought to be produced through gas-to-particle conversion of H_2SO_4 vapor which is produced by photochemical oxidation of SO_2 , OCS, DMS, and so for. Photochemical oxidation of DMS leads to dimethyl sulfoxide, methane sulfonic acid (MSA), sulfur dioxide and sulfuric acid (BENTLEY *et al.*, 1971). HATAKEYAMA *et al.* (1985) showed experimentally that the major sulfur-containing oxidized product of DMS are MSA and SO_2 . In the same "SHIRASE" cruise on which the present observations, KOGA *et al.* (1988) found a positive correlation between MSA and excess sulfate in the Antarctic coastal region. DMS, which emanates from biogenic sources in sea water, is one of the possible precursors of sulfuric acid particles in the remote marine atmosphere.

5.3. Aerosol sampling in the marine atmosphere

Let us consider the sampling conditions on board a ship over the ocean. Relative humidity near the sea surface is usually large (*e.g.*, see Table 1). Figure 8 gives the sulfuric acid weight percentage (%) in equilibrium with ambient relative humidity (after "Kagaku Binran, Kisohen II (NIHON KAGAKUKAI, 1966)").

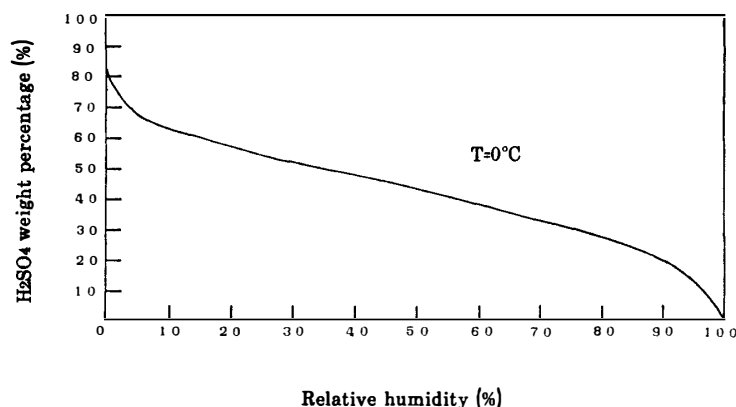


Fig. 8. Sulfuric acid mass fraction in sulfuric acid water solution with respect to relative humidity. This figure was made after "Kagaku Binran, Kisohen II (NIHON KAGAKUKAI, 1966)".

It can be seen that the mass fraction of sulfuric acid decreases with increasing relative humidity. Thus, the acidity of sulfuric acid droplets is small in the humid marine boundary atmosphere near sea surface. These sulfuric acid particles may not have satellite particles. The number concentration of sulfuric acid particles might have been underestimated in previous morphological identifications (*e.g.*, MÉSZÁROS and VISSY, 1974; OKADA *et al.*, 1985).

In addition to ammonia contamination, we suggest that the dilution of sulfuric acid droplets by absorption of water vapor in a humid atmosphere is a second difficulty in morphological identification. Now we recommend that prior to collection by an impactor, particles should be dried sufficiently by a diffusion drier in order to identify correctly the molecular state of sulfate particles.

6. Concluding Remarks

The following conclusions can be deduced from this study in the present observation.

(1) Excess sulfate in the marine atmosphere should be attributed to sulfate or sulfuric acid particles in the large and Aitken particle size ranges, which are probably produced through gas-to-particle conversion of sulfur-bearing gas.

(2) The degree of ammoniation of sulfuric acid particles is negatively correlated with distance from land. This might reflect the extension of the ammonia rich air mass over the ocean. Considering the high acidity of sulfuric acid particles, ammonia concentration might be extremely small over the oceanic region surrounding Antarctica.

(3) A small non-acid aerosol occasionally coexists with sulfuric acid aerosol over the ocean, in a bi-modal size distribution. The origin of the small non-acid aerosol is probably land. Long range transport of land aerosol over the ocean is an important process controlling the number concentration of the particles.

We need quantitative measurement of the degree of ammoniation of sulfate particles by using the calcium thin film method. Trajectory analysis of air masses should be done to identify the possible origin of aerosols. Changes of continental aerosol in number concentration, chemical composition, size distribution, and number mixing ratio during the flow of the air mass over oceans should be examined from the viewpoint of global air pollution in the earth's atmosphere.

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References

- BENTLEY, M. D., DOUGLAS, I. B., LACADIE, J. A. and WHITTIER, D. R. (1971): The photolysis of dimethyl sulphide in air, presented at APCA Meeting, Atlantic City, New Jersey, June 27.
- CLARKE, A. D., AHLQUIST, N. C. and COVERT, D. S. (1987): The Pacific marine aerosol; Evidence

- for natural acid sulfates. *J. Geophys. Res.*, **92**, 4179–4190.
- GEORGI, H. W. and MÜLLER, J. G. (1974): On the distribution of ammonia in the middle and lower troposphere. *Tellus*, **26**, 1–2, 180–184.
- GRAVENHORST, G. (1978): Maritime sulfate over the North Atlantic. *Atmos. Environ.*, **12**, 707–713.
- HATAKEYAMA, S., IZUMI, K. and AKIMOTO, H. (1985): Yield of SO₂ and formation of aerosol in the photo-oxidation of DMS under atmospheric conditions. *Atmos. Environ.*, **19**, 135–141.
- HAYES, D., SNETSINGER, K., FERRY, G., OBERBECK, V. and FARLOW, N. (1980): Reactivity of stratospheric aerosols to small amounts of ammonia in the laboratory environment. *Geophys. Res. Lett.*, **7**, 974–976.
- JUNGE, C. E. (1953): Die Rolle der Aerosole und der gasförmigen Beimengungen der Luft im Spurenstoffhaushalt der Troposphäre. *Tellus*, **5**, 1–26.
- JUNGE, C. E. (1954): The chemical composition of atmospheric aerosols. I. Measurements at Round Hill Field Station, June–July 1953. *J. Meteorol.*, **11**, 323–333.
- KOGA, S., YAMANOUCHI, T., NISHIO, F., ONO, A., IWASAKA, Y. and KAWAGUCHI, S. (1988): Spatial distribution of aerosol-state methanesulfonic acid over the Antarctic Ocean. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **2**, 174.
- MÉSZÁROS, A. and VISSY, K. (1974): Concentration, size distribution and chemical nature of atmospheric aerosol particles in remote oceanic areas. *J. Aerosol Sci.*, **5**, 101–109.
- NIHON KAGAKUKAI, ed. (1966): *Kagaku Binran*, Kisoheon II. Tokyo, Maruzen, 600 p.
- OKADA, K., IWASAKA, Y. and ONO, A. (1985): Features of aerosol particles in the remote oceanic atmosphere. *Mem. Natl Inst. Polar Res., Spec. Issue*, **39**, 30–39.
- ONO, A., YAMATO, M. and YOSHIDA, M. (1983): Molecular state of sulfate aerosols in the remote Everest highlands. *Tellus*, **35B**, 197–205.
- PARUNGO, F. P., NAGAMOTO, C. T., ROSINSKI, J. and HAAGENSEN, P. L. (1986): A study of marine aerosols over the Pacific Ocean. *J. Atmos. Chem.*, **4**, 199–226.
- QUINN, P. K., CHARLSON, R. J. and ZOLLER, W. H. (1987): Ammonia, the dominant base in the remote marine troposphere; A review. *Tellus*, **39B**, 413–425.
- YAMATO, M. and ONO, A. (1985): Electron micrographs of stratospheric aerosol particles. WRI MAP Research Note-8, Water Research Institute, Nagoya University, 48 p.
- YAMATO, M., IWASAKA, Y., ONO, A. and YOSHIDA, M. (1987a): On the sulfate particles in the sub-micron size range collected at Mizuho Station and in East Queen Maud Land, Antarctica; Preliminary results. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **1**, 82–90.
- YAMATO, M., IWASAKA, Y., OKADA, K., ONO, A., NISHIO, F. and FUKABORI, M. (1987b): Evidence for the presence of submicron sulfuric acid particles in the summer Antarctic atmosphere; Preliminary results. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **1**, 74–81.

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