

FEATURES OF AEROSOL PARTICLES IN THE REMOTE OCEANIC ATMOSPHERE

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Abstract: Collections of individual submicrometer particles were carried out with a low-pressure impactor on board of ship over the ocean of the Southern Hemisphere in December 1982, February 1984 and March 1984. The collected samples were examined by using a transmission electron microscope in order to investigate the morphological features of individual particles of 0.04–0.1 μm radius, together with the particle number concentrations. Two types of sulfate-containing particles other than sea-salt particles were found in a wide region and were dominant particles of 0.04–0.1 μm radius. The morphological features were quite different from each other. Particles with distinct outline on the collecting surface had the morphological features similar to ammonium sulfate particles and their estimated concentrations varied largely from 5.5 to 72.6 cm^{-3} . Whereas, particles showing vague outline on the collecting surface were also present in the concentrations ranging from 2.1 to 9.4 cm^{-3} over the Indian Ocean.

1. Introduction

It is important to obtain information on the physicochemical properties of submicrometer particles including Aitken particles in the remote oceanic atmosphere in the fields of meteorology and air chemistry. A few measurements on the composition and concentration of aerosol particles in the remote oceanic atmosphere have been made (*e.g.*, MÉSZÁROS and VISSY, 1974; ONO *et al.*, 1981). Their results showed that particles other than sea-salt particles were present especially in the Aitken size range, and these particles were sulfate-containing particles, but little is known about the composition of aerosol particles in the Aitken size range in the remote oceanic atmosphere.

The aim of this paper is to indicate the morphological features of individual particles of 0.04–0.1 μm radius as well as the particle number concentrations over the ocean of the Southern Hemisphere.

2. Methods

Collections of aerosol particles were carried out on board of ships FUJI and SHIRASE over the ocean of the Southern Hemisphere in December 1982, February 1984 and March 1984. Aerosol particles were collected directly on a carbon-covered nitrocellulose film supported on an electron microscopic grid by using a low-pressure impactor. This impactor was designed to collect particles of 0.03 to 0.35 μm radius (OKADA, 1983). The flow rate of air was 1.3 l min^{-1} at standard pressure. The

sampling time was set from 30 to 60 min for obtaining the samples adequate to the electron microscopic examinations.

The morphological features of individual particles on the film were investigated with a transmission electron microscope (Hitachi HS-9). The samples were irradiated by electron beam at weak intensity to avoid the destruction of particles. The detection of sulfate ions in individual particles was applied to some samples by a single particle method proposed by BIGG *et al.* (1974). Together with the morphological analysis of particles, number concentrations of particles were evaluated from the counting of particles on the collecting surface.

3. Number Concentration of Aerosol Particles

Figure 1 shows the number concentrations of aerosol particles with radii between 0.04 and 0.1 μm over the ocean of the Southern Hemisphere. Sampling points and wind data are also indicated in the figure. The sampling sites are divided into five regions: region I, the Java Sea; region II, the Indian Ocean near Western Australia

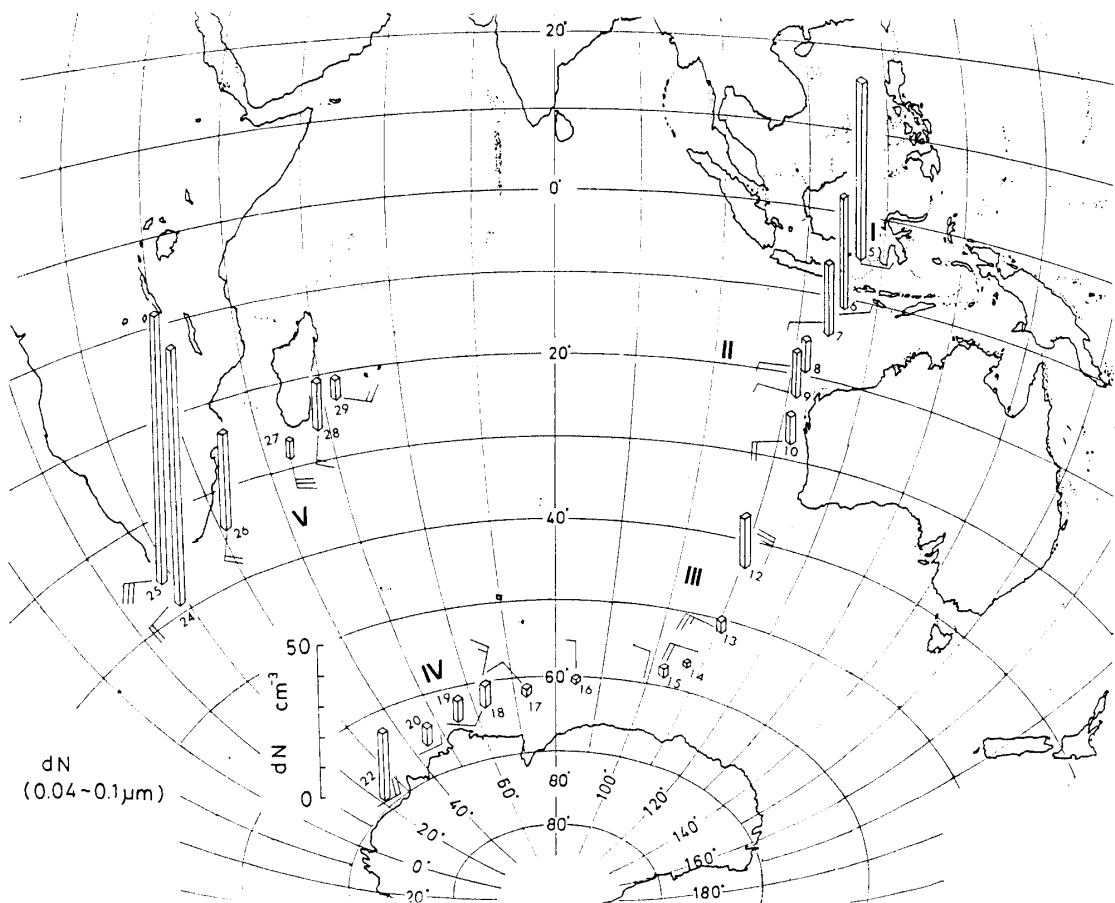


Fig. 1. Number concentration of aerosol particles of 0.04–0.1 μm radius over the ocean of the Southern Hemisphere. Sampling point with number and wind data are also indicated in the figure. The number concentration was estimated on the basis of the counting of particles on the collecting surface of an electron microscopic grid.

Table 1. Situation of the sampling with the low-pressure impactor. The measurements were carried out on board of research ships FUJI (sampling points from 5 to 20) and SHIRASE (sampling points from 22 to 29). A pump was stopped for 9 and 2 min at the sampling points 16 and 19, respectively.

Region	Sampling points	Location	Period (LST)	Temperature (°C)	Wind direc	Wind speed (m/s)	Relative humidity (%)	Weather
I	5	5°15'S 117°19'E	1240-1310	27.1	NW	1	73	fine
	6	10°08'S 115°19'E	1202-1232	30.0	ENE	2	68	fine
II	7	14°43' 114°38'	1200-1232	29.8	WSW	4	68	fine
	8	19°17' 113°39'	1232-1307	28.3	W	3	72	fine
III	9	23°53' 112°47'	1218-1248	25.8	WNW	3	84	fine
	10	28°25' 113°09'	1201-1231	22.0	WSW	10	65	fine
	12	43°44'S 110°06'E	1200-1230	13.7	N	13	85	fine
	13	53°48' 110°17'	1650-1520	3.0	(WNW)	(13)	86	sleet
	14	57°32' 108°39'	1701-1731	1.8	W	11	93	cloudy
	15	58°18' 104°33'	0727-0757	0.9	N	5	83	cloudy
IV	16	60°30'S 82°54'E	[1700-1723] [1732-1802]	0.7	NNW	1	82	cloudy
	17	62°04' 73°31'	1643-1751	0.6	NW	5	94	cloudy
V	18	63°46' 62°53'	1657-1757	0.9	NE	7	95	cloudy
	19	64°56' 55°23'	[0802-0840] [0842-0854]	0.2	E	6	92	cloudy
	20	66°58' 45°40'	1202-1302	1.3	E	2	85	cloudy
	22	69°06' 22°58'	1228-1328	-7.9	SE	10	82	cloudy
	24	39°55'S 19°07'E	1704-1804	18.7	W	10	67	fine
	25	36°18' 18°04'	1311-1336	20.2	NW	14	69	cloudy
	26	34°13' 30°05'	1248-1348	21.9	SSW	11	54	fine
	27	29°09' 43°23'	1216-1258	20.5	S	14	57	fine
	28	26°35' 48°47'	1225-1325	23.1	SSW	8	52	fine
	29	23°54' 52°38'	1445-1545	25.3	ESE	8	55	fine

(10°–30°S); region III, the Indian Ocean (40°–60°S); region IV, the Southern Ocean (>60°S) and region V, the Indian Ocean near Africa (20°–40°S). Detailed information on the sampling situations is given in Table 1. The collections at points 5 to 20 were carried out in December 1982, and the collections at points 22 to 29 were carried out in February and March 1984. Spatial distribution of particles is characterized as follows:

The number concentrations of particles of 0.04–0.1 μm radius ranged widely from 0.88 to 88.6 cm^{-3} over the ocean. The minimum concentration was present at the sampling point of 14, whereas the maximum concentration was found at point 25, off the coast of Africa. The concentrations tend to decrease from 57.8 to 9.6 cm^{-3} at points 5 to 10. The decrease in the concentrations seems to correspond to the change of wind direction from east to west. In region III, the concentrations are in low values ranging from 0.88 to 3.2 cm^{-3} at the points other than 12. The concentration at the point 12 shows a relatively large value of 16.2 cm^{-3} in the presence of a strong north wind. The concentrations in region IV range from 0.93 to 21.8 cm^{-3} and they tend to increase in the presence of wind from east to south. The concentrations in region V range from 5.7 to 88.6 cm^{-3} . Although the maximum concentration is found in the ocean near South Africa, the concentrations decrease largely from point 25 to 29 in association with a wind from the south. These results imply that the increase in number concentration would be attributed to the invasion of air from the coastal area and/or over the land. Similar trends of the number concentration of particles of 0.02–0.1 μm radius were obtained in regions I to IV by Iwai *et al.* (1979).

4. Features of Individual Aerosol Particles

In order to evaluate the chemical composition of individual particles, morphological features of them were investigated for the samples collected in regions II, IV

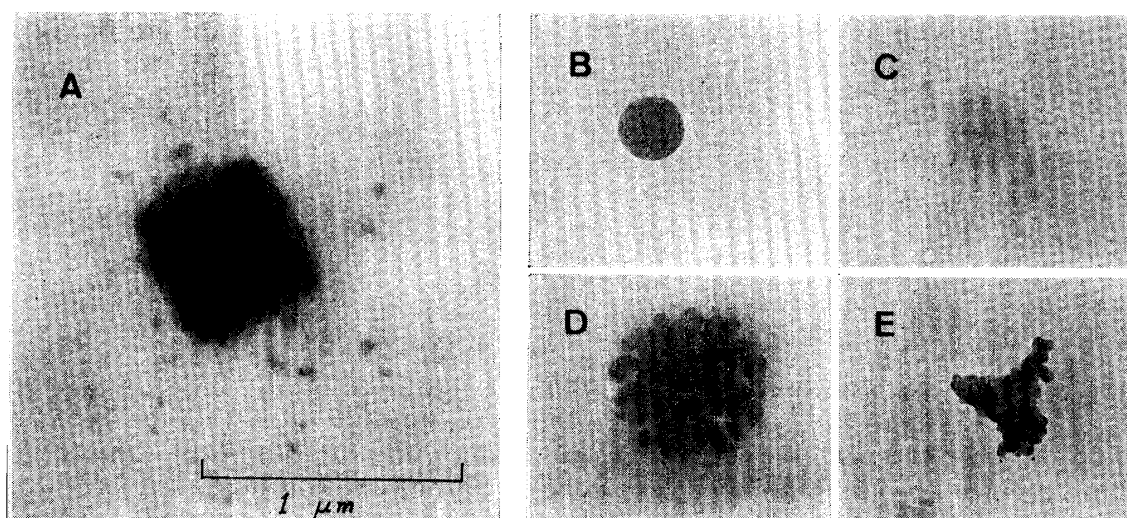


Fig. 2. Morphological features of individual particles on the collecting surface. The scale of these electron micrographs is shown in the micrograph of type A particle.

and V by electron microscopy. Figure 2 shows the typical morphological features of individual particles collected over the ocean. The scale of these electron micrographs is equal to that shown in the micrograph of type A particle. Type A particle contains electron-dense and cubic-shaped material surrounded by some material. Atmospheric particles showing cubic shape are usually found in the maritime air and are mainly made up of sodium chloride as stated by FRANK and LODGE (1967). On the basis of their results, type A particle was identified to be sea-salt particle containing

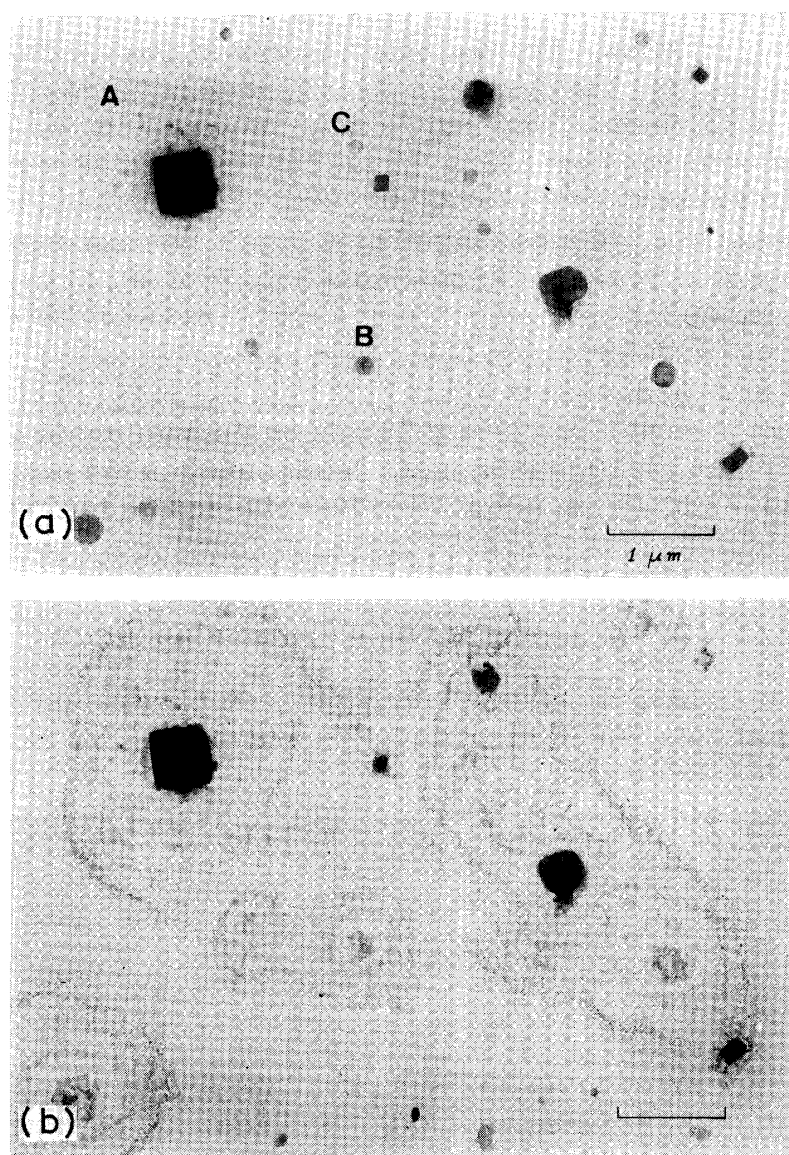


Fig. 3. *a.* Electron micrograph of particles collected over the ocean at point 26, off the coast of Africa. This photograph was taken before the evaporation of barium chloride. Particles termed A, B and C are seen in the figure. *b.* Electron micrograph of reaction product of barium chloride with particles shown in Fig. 3a after exposure to octanol vapor for 24 h at room temperature. The thickness of a vapor-deposited thin film of barium chloride is 20 Å. From a close comparison of electron micrographs, particles termed A, B and C gave a positive sulfate reaction and they contain sulfate ions.

sodium chloride. Similar to the findings of MÉSZÁROS and VISSY (1974) and ONO *et al.* (1981), particles other than sea-salt particles were found to be mainly in the Aitken size range over the remote oceanic areas. Type B particle has the morphological features similar to ammonium sulfate particle (HEARD and WIFFEN, 1969). This particle shows distinct circular outline on the collecting surface. Whereas, type C particle is flat and shows vague circular outline on the collecting surface. Figure 3a shows the electron micrograph of aerosol particles collected at point 26. A, B and C types of particles are found in the electron micrograph. Figure 3b shows the electron micrograph of reaction product of barium chloride with particles shown in Fig. 3a. The detailed explanation of the procedure was given elsewhere (OKADA *et al.*, 1983; OKADA, 1985). From a close comparison of two electron micrographs, the Liesegang's rings of reaction product (barium sulfate) are seen around A, B and C types of particles. Hence, it can be said that these three types of particles contain sulfate ions. Although sulfate ions are present in type A particles (sea-salt), the sulfate ions might have originated from seawater. On the basis of sulfate test and morphological analysis, type B particle would be ammonium sulfate particle. Type D particle mainly contains crystalline material showing "flower-like" appearance on the collecting surface. Similar particles were often collected in the polluted atmosphere and they contained sulfate ions (OKADA *et al.*, 1982; WU, 1985). Though not clarified in this paper, type D particle would also contain sulfate ions. And part of the crystalline material is similar in morphological features to type B particle. Then, the material in type B and type D particles would not be much different. However, it is to be noted that type D particles were often present as an admixture of crystalline material and noncrystalline material. The noncrystalline material was similar in morphological features to type

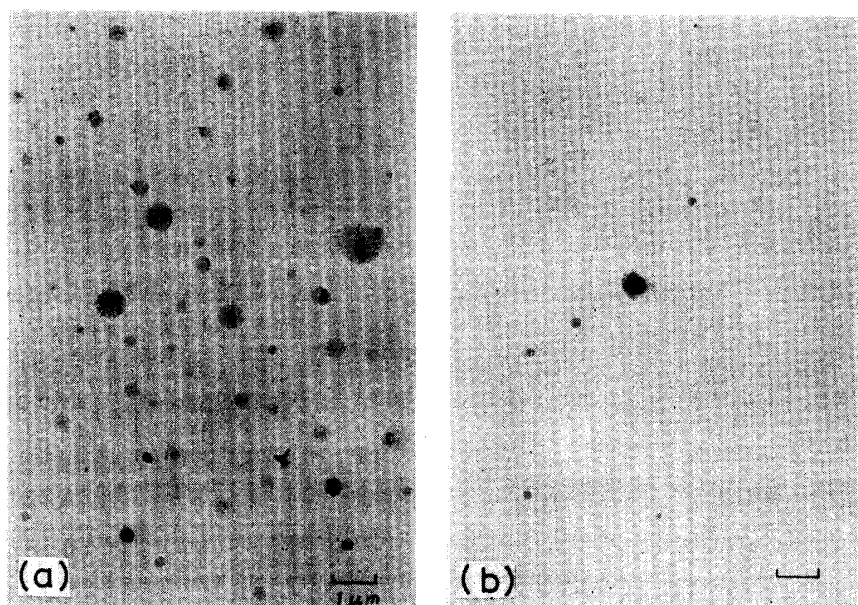


Fig. 4. a. Aerosol particles collected over the Java Sea (sampling point 5) during the period from 1240 to 1310 LST on 4 December 1982. b. Aerosol particles over the ocean off the coast of Western Australia (sampling point 10) during the period from 1201 to 1231 LST on 9 December 1982.

C particles which contain sulfate ions and show vague outline on the collecting surface. The chemical composition of type C particle was not known at present. Type E particle is irregular in shape and is composed of aggregations of electron-dense spherules. Type E particle would be made up of water-insoluble material and probably

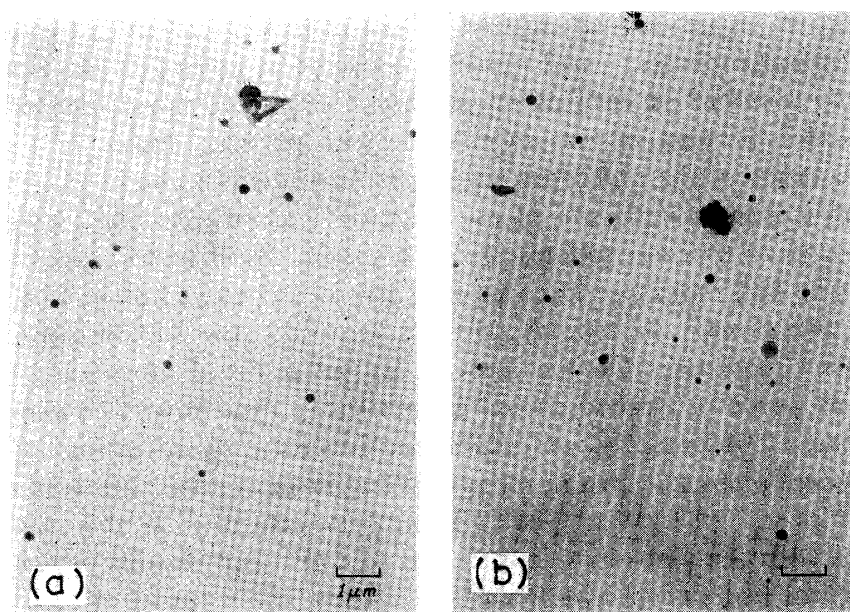


Fig. 5. a. Aerosol particles over the Southern Ocean near Antarctica (sampling point 18). The sample was collected during the period from 1657 to 1757 LST on 27 December 1982. b. Aerosol particles over the Southern Ocean (sampling point 22). The sample was collected during the period from 1228 to 1328 LST on 18 February 1984.

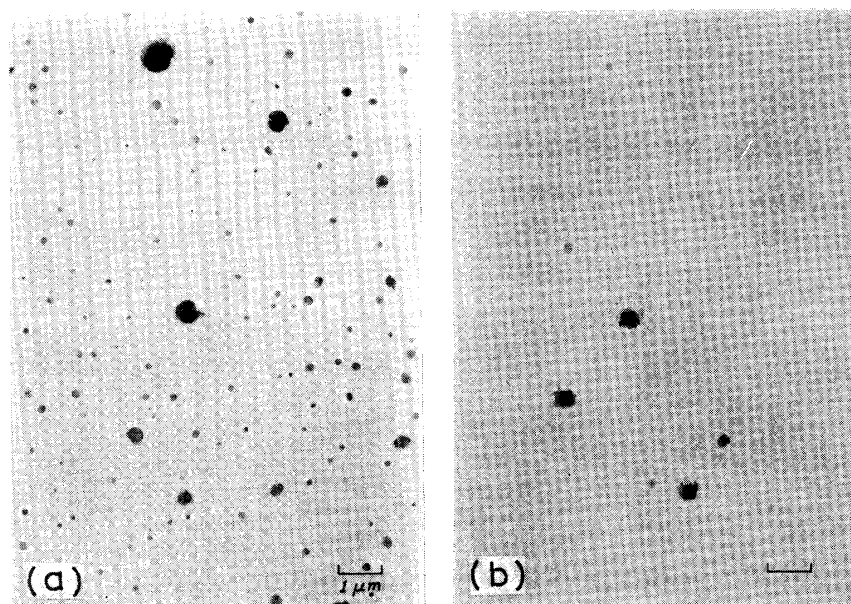


Fig. 6. a. Aerosol particles collected over the ocean off the coast of South Africa (sampling point 25) during the period from 1311 to 1336 LST on 2 March 1984. b. Aerosol particles over the ocean (sampling point 27) collected during the period from 1216 to 1258 LST on 9 March 1984.

a combustion product. MÉSZÁROS and VISSY (1974) pointed out the presence of sulfuric acid particles and long-shaped particles over the ocean of the Southern Hemisphere. However, such particles were hardly detected in our samples.

Some electron micrographs of aerosol particles collected with the low-pressure impactor over the ocean are indicated in Figs. 4, 5 and 6. Figure 4a shows the electron micrograph of particles collected over the Java Sea (sampling point 5). Figure 4a indicates that type D particles coexist with type B and type C particles. Instead of type D particles, type B particles (probably ammonium sulfate) are dominant other than sea-salt particles over the ocean off the coast of Western Australia (sampling point 10) as shown in Fig. 4b. Figure 5 shows the electron micrographs of particles collected at points 18 and 22 in the Southern Ocean near Antarctica. Most particles are those termed type B particles over the Southern Ocean. Figure 6 shows the electron micrographs of particles over region V near Africa. Particles termed B are found to be dominant particles of $0.04\text{--}0.1\ \mu\text{m}$ radius at the point 25, off the coast of South Africa. Type B particles should produce a high number concentration in this area (see Fig. 1). Figure 6b shows the micrograph of particles at point 27. It is found in Fig. 6b that particles other than sea-salt particles are those termed type C particles showing vague circular outline on the collecting surface.

Figure 7 summarizes the number fraction of particles ($0.04\text{--}0.1\ \mu\text{m}$ radius) termed A, B, C, D, E and others at the sampling points in regions II, IV and V. The data at point 27 might not be so accurate owing to the small number of collected particles.

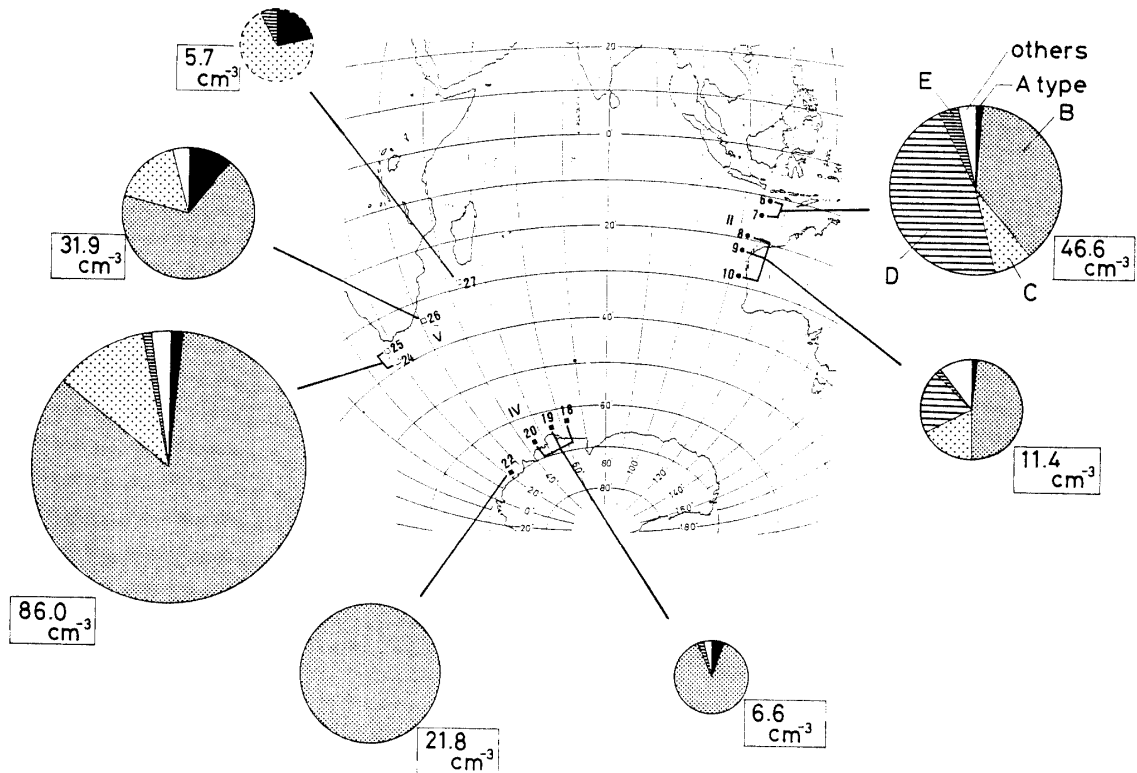


Fig. 7. Number fraction of particles of $0.04\text{--}0.1\ \mu\text{m}$ radius termed A, B, C, D, E and others at the sampling points in regions II, IV and V. The number concentration of the particles is indicated in the square. The area of circle is proportional to the concentration.

The number concentration of particles is indicated in the square. The area of circle is proportional to the number concentration. As shown in Fig. 7, more than 80% of the particles are those other than sea-salt particles. Type B particles (probably ammonium sulfate) are detected in the number fractions more than 0.4. A high number fraction of type B particles, more than 0.7, was present in region IV and at points 24, 25 and 26 in region V. The number concentration of type B particles ranged largely from 5.5 to 72.6 cm^{-3} , whereas type C particles were hardly detected over the Southern Ocean and their concentrations showed relatively small change from 2.1 to 9.4 cm^{-3} .

Although type D particles were detected in region II, type B and type C particles were present in a wide region over the ocean of the Southern Hemisphere. The present study implies that particles of 0.04–0.1 μm over the ocean would be characterized by particles termed B and C. Though type B particles (probably ammonium sulfate) were the dominant particles of 0.04–0.1 μm radius, it will be also important to obtain the chemical form of type C particles in order to assess the behavior of sulfur in the oceanic atmosphere.

5. Summary

Collections of individual submicrometer particles were carried out with a low-pressure impactor on board of research ships FUJI and SHIRASE over the oceanic areas of the Southern Hemisphere in December 1982, February 1984 and March 1984. The morphological features and the number concentration of particles of 0.04–0.1 μm radius were investigated by electron microscopic examinations.

The following results were obtained;

(1) Number concentrations of aerosol particles of 0.04–0.1 μm radius ranged from 0.88 to 88.6 cm^{-3} over the Indian Ocean and the Southern Ocean. The number concentration seemed to increase owing to the invasion of air from the coastal area and/or over the land.

(2) Similar to the findings of MÉSZÁROS and VISSY (1974) and ONO *et al.* (1981), particles containing sulfate ions coexisted with sea-salt particles in the Aitken size range (0.04–0.1 μm radius). Two types of sulfate-containing particles were detected in a wide region over the ocean. A large number fractions of particles of 0.04–0.1 μm radius showed morphological features similar to ammonium sulfate particles and the concentrations ranged largely from 5.5 to 72.6 cm^{-3} . Although the chemical composition was not assessed, sulfate-containing particles showing noncrystalline features and vague circular outline on the collecting surface were also present over the Indian Ocean in the concentrations ranging from 2.1 to 9.4 cm^{-3} .

(3) Particles containing sulfuric acid and long-shaped particles which were detected by MÉSZÁROS and VISSY (1974) were hardly detected in our samples.

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