

ON THE COMPOSITION AND ORIGIN OF LARGE AND GIANT PARTICLES OBSERVED AT SYOWA STATION, ANTARCTICA

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Abstract: Large and giant aerosol particles were collected by means of a single-stage impactor at Syowa Station and their composition was examined with scanning electron and optical microscopes, X-ray diffraction and phase transition methods. Large and giant particles in the winter season were found to consist mainly of NaCl, Na₂SO₄·10H₂O, MgSO₄·6H₂O, CaSO₄·2H₂O, etc. These components must be of sea salt origin. The increase of these sea salt particles was accompanied by cyclonic snowstorms (blizzard). On the other hand, their concentrations were smaller in the summer season than in the winter season, and another component besides those of the sea salt origin was found in the summer antarctic atmosphere. From the results of X-ray diffraction of the summer samples, this component is considered to be ammonium sulfate.

1. Introduction

It has been considered that large and giant particles whose radii are larger than 0.1 μm play an important role in the radiative transfer and in the formation of cloud droplets in the atmosphere.

It is important to know the composition of aerosol particles, because the particles of different compositions have different behaviors in the atmosphere. For example, some hygroscopic particles can act as cloud condensation nuclei (CCN) and some non-hygroscopic particles are not important for CCN. The visibility through the atmosphere is influenced by the properties and size distributions of aerosol particles, and by the relative humidity.

KIKUCHI (1971) observed the concentration of CCN by using a chemical diffusion chamber at Syowa Station. Although he could not determine distinctly their

properties, he inferred from the spectra of the number concentration in the range from 0 to 1% supersaturations that CCN at Syowa Station have come from man-made sources and marine sources. The particles from man-made sources at Syowa Station must be the pollutant resulting from human activities at the Station, because the concentration of CCN of his results is rather high compared with that of the Aitken particles found by IWAI (1979) and ITO (1980) in the unpolluted air at Syowa Station.

CADLE *et al.* (1968) examined the aerosols between $0.2 \mu\text{m}$ and $2 \mu\text{m}$ in diameter sampled at the Taylor Valley near McMurdo Station, Antarctica. They showed that the aerosol particles contained much higher concentrations of sulfur than similar samples collected in most parts of the world, and that the sulfur was largely in the form of SO_4^{--} . They also showed that the cations were largely NH_4^+ and H^+ and most samples contained little sodium chloride. Consequently, they concluded that the composition of the aerosol particles was sulfuric acid and ammonium sulfate.

Recently, BIGG (1980) showed that the particles collected at the South Pole consist of ammonium sulfate and aerosols with radii larger than $0.25 \mu\text{m}$ were generally rare.

In this article, the composition and origin of large particles in a rather big size range and giant ones sampled at Syowa Station are discussed on the basis of the results of phase transition method, morphological features and X-ray diffraction method.

2. Experiments

Aerosol particles were collected on clean cover glasses by using a 1 mm diameter circular jet impactor which sucked at a flow rate of 8 l min^{-1} . The collection efficiency of this impactor was determined according to RANZ and WONG (1952) (*cf.* FLETCHER, 1962). In the course of the calculation, spherical particles with the density 2.0 g cm^{-3} were assumed. The collection efficiencies of this impactor are as follows; 0%, 20%, 80%, 98% and 100% for the diameter of $0.1 \mu\text{m}$, $0.2 \mu\text{m}$, $0.3 \mu\text{m}$, $0.4 \mu\text{m}$ and $>0.5 \mu\text{m}$, respectively. That is, almost all the particles larger than $0.4 \mu\text{m}$ in diameter were collected.

The phase transition method is similar to that reported by MÉSZÁROS (1971). The saturated solution of each of the following salts NH_4NO_3 , NaCl , NH_4Cl , KNO_3 and KH_2PO_4 gives the known relative humidity (R. H.), 67, 76, 80, 94 and 97%, respectively at about 20°C . The first humidity step was produced by dry silica gel. However, as their relative humidity was not measured, actual humidity was not known in dry state.

Morphological features of the particles were examined by means of the scanning electron microscope. These observations were carried out immediately after the sampling of aerosol particles.

Bulk samples were taken with the similar jet impactor for 2 or 3 days in order

to identify the particle composition by the X-ray diffraction method. These samples were packed tight with the cellophane tape and brought back to Japan.

3. Results and Discussion

Figure 1 shows scanning electron micrographs of the particles collected on

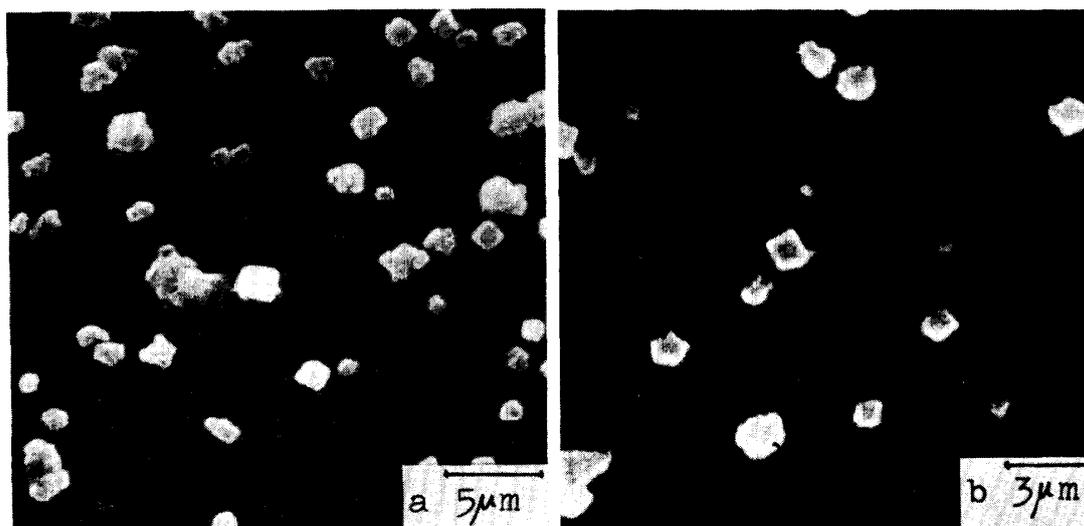


Fig. 1. Scanning electron micrographs of particles collected on August 18 (a) and October 7 (b), 1977.

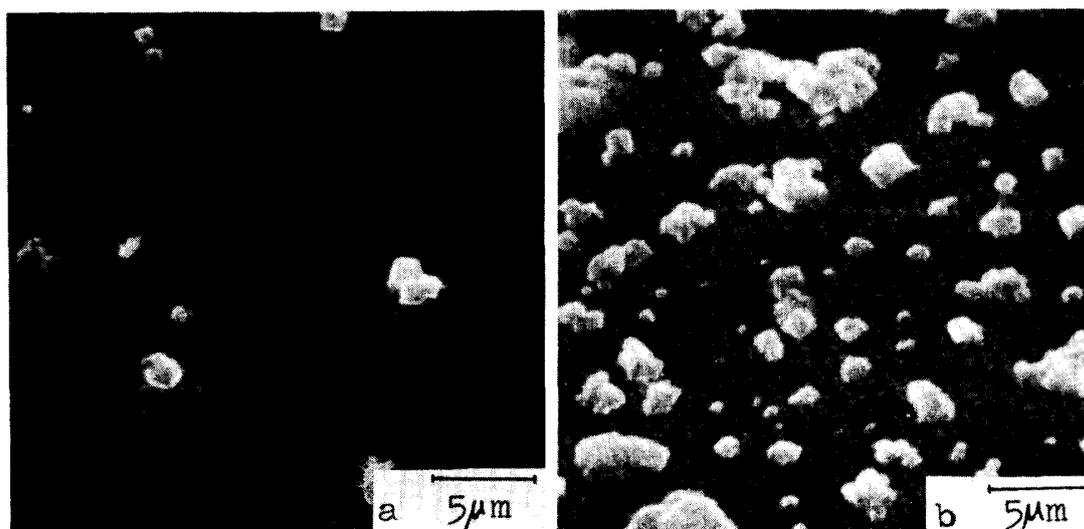


Fig. 2. Scanning electron micrographs of particles collected before (a, May 31) and in the midst of snowstorm (b, June 2), 1977. Sampling duration is 4 minutes for (a) and 1 minute for (b).

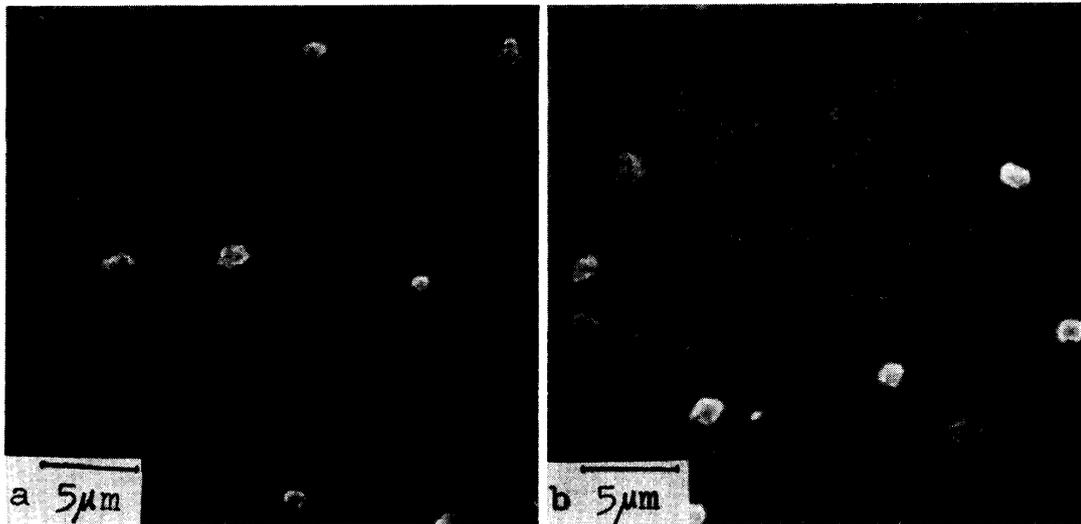


Fig. 3. Scanning electron micrographs of aerosol particles collected on December 15 (a) and 28 (b), 1977.

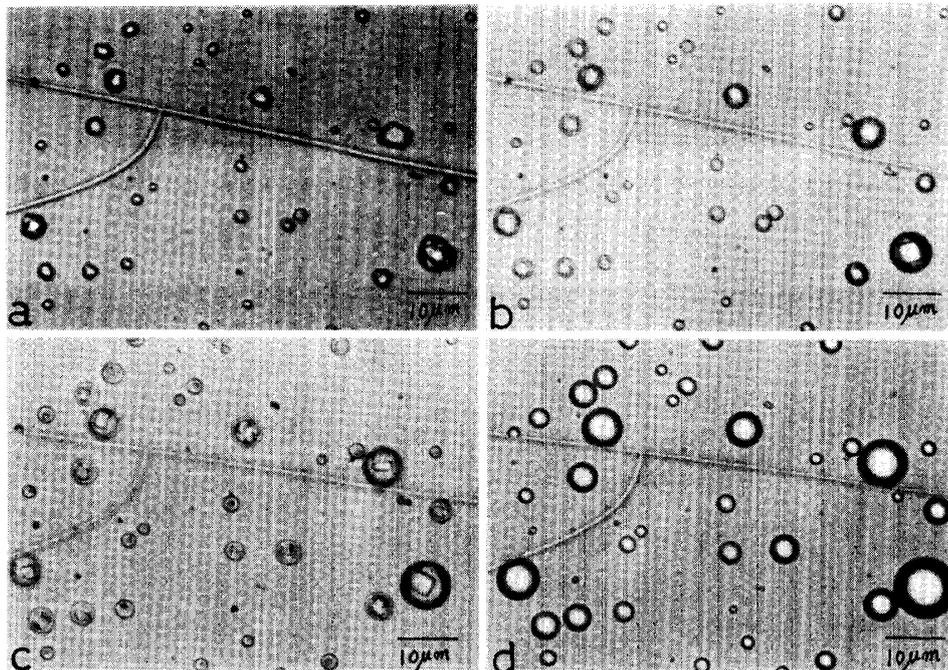


Fig. 4. Phase transition with increasing relative humidity. (a) dry state, (b) 67% R. H., (c) transition period before reaching 76% R. H., (d) 76% R. H.

August 18 and October 7, 1977. Almost all the particles down to $0.3 \mu\text{m}$ crystallized into distinct cubic shapes. From the morphology having cubic shapes, these particles must be of sea salt origin.

Figure 2 shows scanning electron micrographs of aerosol particles collected before and in the midst of snowstorm (blizzard) in the winter season. It seems that the number concentration of large and giant particles having cubic shapes increases markedly in the midst of blizzard compared with that before snowstorm. Note that the sampling duration is different with each other. Total aerosol concentration and meteorological elements during the period of the collection of aerosol particles shown in Fig. 2 are indicated as Fig. 5 in the paper of one of the authors (IWAI, 1979). These increasing cubic shaped aerosol particles accompanied with strong wind and advection of warm air must be of sea salt origin.

Figure 3 shows scanning electron micrographs of aerosol particles collected in the austral summer season (December 15 and 28, 1977). Cubic and rectangular shaped particles with strong contrast must be of sea salt origin in the same sense as shown in Fig. 1, and in addition to these particles, we can see uncontrasted particles. However, we cannot determine the properties of these uncontrasted particles from the morphological features. The authors think that these particles are not of sea salt origin and not soil ones but may be secondary particles originated from a gaseous phase by photochemical reaction in the summer antarctic atmosphere, because few of these particles were found in the polar night season. ONO *et al.* (1981) have discussed on the nature of these particles.

An example of the phase transition of the particles collected on July 14, 1977 is shown in Fig. 4. Almost all the particles in dry stage are in the solid state. Most of the particles become droplets at 67% R. H. However, it is seen that distinct cubic shaped particles remain in droplets (Fig. 4b). Fig. 4c shows the photomicrograph of transition period before reaching equilibrium at 76% R.H. We can see clearly that cubic shaped particles remain in solution droplets and are dissolving. Most of the aerosol particles dissolved completely under the condition of 76% R.H. From these results, major component of these soluble cubic shaped particles is considered to be NaCl and minority sea salt components such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ which are more soluble at lower humidity may also exist.

Figure 5 shows frequency distribution of visibility classified by 10% intervals of R.H. at Syowa Station during the one-year period in 1977. Visibility during snow fall is omitted in statistical treatment for preparing this figure. We can see that the visibility reduces with increasing relative humidity. At the R.H. lower than 60%, the mode of the visibility lies between 40 km and 50 km. At 61–70% R.H., bimodal frequency distribution is seen, one mode lying between 40 km and 50 km and the other between 20 km and 30 km. At 71–80% and 81–90% R.H., the visibility below 20 km exceeds 50% and 75%, respectively.

As extinction of a visible spectral range by water vapor is negligible, reduction of visibility with increasing relative humidity is supposed to be caused by the light scattering due to the growing hygroscopic aerosol particles alike as shown in Fig. 4.

Figure 6 shows two size distributions of aerosol particles collected on June 13

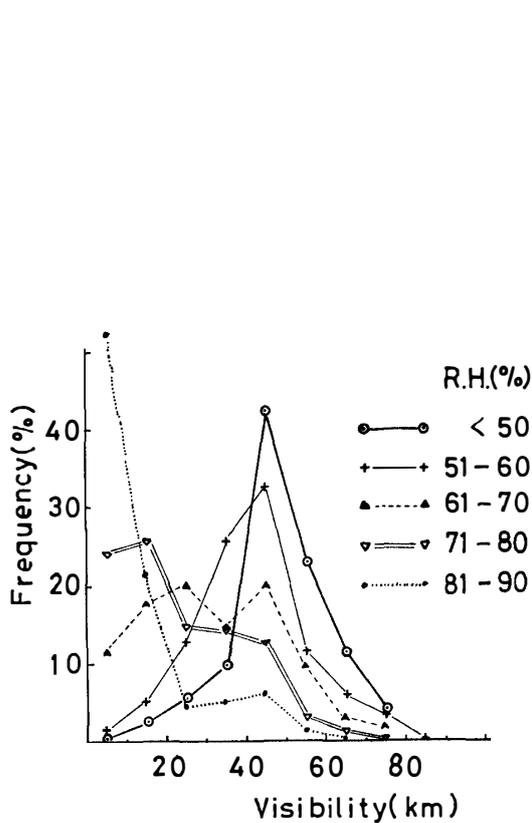


Fig. 5. Frequency distributions of visibility at Syowa Station classified by 10% R. H. each range. Data are based on the routine observations of meteorology during a period from February 1977 to January 1978.

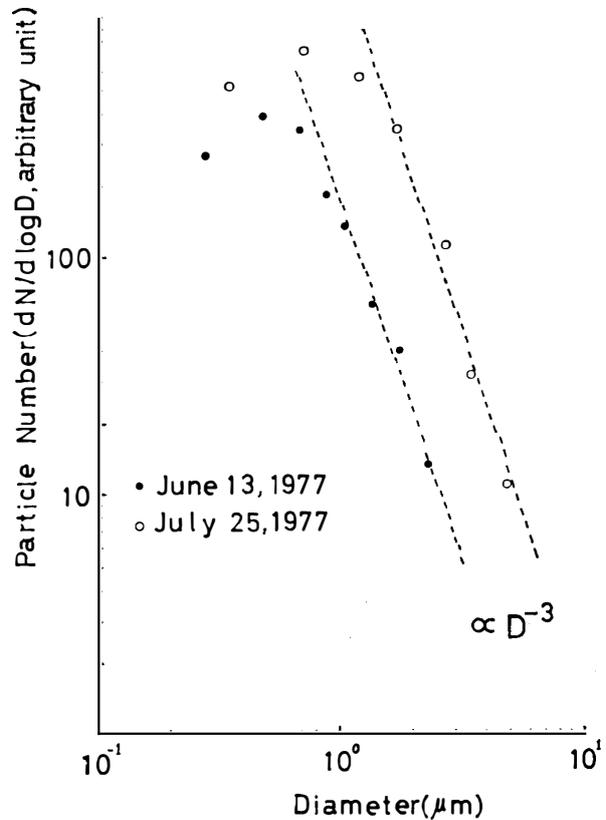


Fig. 6. Examples of size distribution of aerosol particles collected on June 13 and July 25, 1977. Solid and open circles are obtained from scanning electron photomicrographs and from optical photomicrographs, respectively. Ordinate axis is taken in arbitrary unit of $dN/d\log D$.

and July 25, 1977. One (June 13) is obtained from the scanning electron micrographs and the other (July 25) from the optical micrographs. As the sampled air volume associated with the photomicrographs cannot be specified distinctly, the axes of the ordinate are taken in arbitrary unit of $dN/d\log D$, where N is the arbitrary number concentration and D is the diameter of the particles. In the size range larger than about $1 \mu\text{m}$, $dN/d\log D$ is proportional to D^{-3} in both cases.

Table 1 shows the results of interplanar distance and intensity of diffraction lines of X-ray from aerosol particles collected during the period from June 28 to July 2, 1977. During this sampling period, strong snowstorm hit the Station.

NaCl , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and KCl are found. These components are undoubtedly originated from sea salts. From the intensity of the

Table 1. Identified components of bulk aerosols collected during the period from June 28 to July 2, 1977 at Syowa Station. Diffraction lines considered to be $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ appear but are disregarded, because this material is unlikely to exist in the natural atmosphere.

2θ	d	I	NaCl		$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		KCl		$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$		$\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 < 12\text{H}_2\text{O}$	
			d	I	d	I	d	I	d	I	d	I	d	I
9.6	9.21	M											9.2	0.67
11.6	7.63	S			7.56	1.00								
14.6	6.07	W												
16.5	5.37	W												
17.3	5.13	VW									5.10	0.24		
18.7	4.75	W					4.80	0.42					4.72	0.13
20.0	4.44	VW									4.40	1.00		
20.7	4.29	W			4.29	1.00								
23.3	3.82	M			3.81	0.15	3.82	0.27						
24.2	3.68	W												
25.5	3.49	VW												
27.2	3.28	W												
27.3	3.27	W											3.29	0.40
27.6	3.23	W	3.25	0.05			3.22	0.50			3.20	0.12		
28.3	3.15	S											3.20	0.13
28.5	3.13	S					3.10	0.50	3.13	1.00				
30.6	2.92	W					2.93	0.07			2.92	0.60	2.95	0.10
31.7	2.82	VS	2.81	1.00			2.80	0.27						
45.4	2.00	W	1.99	0.83	1.99	0.04					2.00	0.20	2.02	0.10
47.8	1.90	W			1.90	0.16	1.92	0.17					1.90	0.07
50.1	1.81	VW			1.81	0.10			1.81	0.14				
58.7	1.57	W							1.57	0.06			1.57	0.10
66.2	1.41	S	1.41	0.13					1.40	0.17				
75.2	1.26	W	1.26	0.33										

Cu K_α -line

diffraction lines, NaCl is considered to be a dominant component. However, it is very difficult to analyze quantitatively the existence ratio of the component, because the amount of bulk aerosol sample is too small to analyze and the crystals in bulk sample are not randomly oriented. Scanning electron and optical photomicrographs of aerosol particles collected on July 2, 1977 are shown in the paper of one of the authors (Iwai, 1981) in this issue. These results are in marked contrast to that of the composition of aerosol particles collected in the summer antarctic atmosphere reported by CADLE *et al.* (1968) who showed that most samples contained little sodium chloride. The diffraction lines corresponding to $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ are seen in the data. As this material is not likely to exist as natural aerosol particles, we will exclude it here.

Further, specific electric conductivity of melted fresh snow collected on July 2, 1977 was about $2000 \mu\text{S cm}^{-1}$. From this fact, it seems that a large quantity of sea salts were transported by the cyclonic snowstorm accompanied with strong wind.

Table 2 shows the results of interplanar distance and intensity of diffraction lines of X-ray from aerosol samples collected during the period from December 28 to 31, 1977. $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and NaCl are found. However, the intensity of diffraction line from NaCl is weak. This means that NaCl is scarce in the summer season. It is worth to note that $(\text{NH}_4)_2\text{SO}_4$ is present in these samples.

Table 3 shows the identified components of aerosol particles collected during the whole year of 1977 at Syowa Station. Most of these components are of sea salt

Table 2. Identified components of bulk aerosols sampled during the period from December 28 to 31, 1977 at Syowa Station.

2θ	d	I	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		$(\text{NH}_4)_2\text{SO}_4$		NaCl	
			d	I	d	I	d	I	d	I
6.7	13.1	S								
16.7	5.32	M	5.35	0.20			5.2	0.20		
16.9	5.24	M								
18.1	4.90	M								
19.2	4.62	W								
20.6	4.31	W			4.29	1.00	4.36	1.00		
23.5	3.79	W	3.76	0.10	3.81	0.15				
26.9	3.31	W			4.29	1.00				
28.6	3.12	VW					3.12	0.40		
29.1	3.07	VW			3.06	0.63				
29.4	3.04	W					3.03	0.40		
31.6	2.83	W							2.82	1.00
33.7	2.66	M	2.66	0.40	2.68	0.50	2.67	0.07		
34.4	2.61	W								
35.2	2.55	VW								
40.8	2.21	VW	2.21	0.07						

CuK α -line

Table 3. Identified components of aerosol particles by the X-ray diffraction method, sampled during period shown in the left column.

Date	NaCl	Na ₂ SO ₄	Na ₂ SO ₄ ·10H ₂ O	MgSO ₄ ·6H ₂ O	MgSO ₄ ·7H ₂ O	CaSO ₄ ·2H ₂ O	KCl	(NH ₄) ₂ SO ₄
4-6 Mar. 1977	○	○		○		○		
26 Apr.	○					○		
5-6 May	○	○						
25-28 May	○	○						
14-16 July	○			○				
28 June-2 July	○		○	○		○	○	
29-30 July	○	○				○		
4-9 Aug.	○	○						
8-10 Sept.	○		○			○		
25-29 Sep.	○							
31 Oct.-2 Nov.	○					○		
23-25 Nov.	○							
29 Nov.	○							
28-31 Dec.	○			○	○			○
7-9 Jan. 1978								

origin. Ammonium sulfate was found in the summer sample, but as it was detected only once, further observation is necessary to discuss in detail on the nature and origin of ammonium sulfate.

We can see the evaporites which are deposited not only in the area along the Prince Olav Coast but also in the so-called Dry Valley area (TORII and YAMAGATA, 1973). The composition of the evaporites along the Prince Olav Coast has been identified with the X-ray diffraction method by HIRABAYASHI and OSSAKA (1976). According to their results, identified mineral and chemical compositions obtained from East Ongul Island are as follows. Hallite (NaCl), thenardite (Na₂SO₄), gypsum (CaSO₄·2H₂O), epsomite (MgSO₄·7H₂O) and hexahydrate (MgSO₄·6H₂O). The composition of the evaporites is mostly the same as that of the aerosol particles described above. Therefore, these evaporites must have originated from the deposited aerosol particles which were transported by snowstorms accompanied with marine air.

4. Conclusion

Large particles and giant particles collected in 1977 at Syowa Station were examined with the phase transition method and the X-ray diffraction method. Their morphological features are examined with the scanning electron microscope.

We can conclude from our results that the large and giant particles at Syowa Station have originated mostly from sea salts. Especially, they increase during the snowstorms (blizzard) which hit the observation station once in three or four days on the average in the winter season. Concentration of sea salt particles in the summer

season is lower than in the winter season, because snowstorms accompanied with strong marine wind are scarce in the summer season.

Annual variation of the concentration of these particles at Syowa Station is in marked contrast to that of Aitken particles reported by IWAI (1979) and ITO (1980). This means apparently that the origin of large and giant particles is different from that of Aitken particles.

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