CHEMICAL COMPOSITION OF LARGE AND GIANT AEROSOLS AT SYOWA STATION, ANTARCTICA

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Abstract: Atmospheric large and giant aerosol particles collected at Syowa Station, Antarctica were analyzed by instrumental neutron activation analysis. A large part of the total mass concentration of aerosol particles could be attributed to sea salt particles, both in winter and summer. The weight ratio Cl/Na for giant particles was larger than the bulk sea water ratio, whereas for large particles in summer it was smaller than that of bulk sea water. It can be explained that giant particles in the present study were blowing snow or drifting snow which was chlorine-enriched, and that large particles in summer were attacked by sulfuric acid droplets to release gaseous Cl to the atmosphere.

1. Introduction

The knowledge of the physico-chemical properties of atmospheric aerosols in polar regions is an essential requirement for studying the problems of atmospheric background pollution on a global scale. Antarctica is the only continent where man's activities are almost negligible throughout the area, and is far from the populated continents. The surface of it is almost entirely covered with snow and ice. Therefore the atmosphere over Antarctica may be regarded as a clean atmosphere which has not been directly contaminated by pollutants from anthropogenic sources.

In Antarctica many measurements of atmospheric aerosols have been made. SHAW (1979) reviewed the results of those measurements. Instrumental neutron activation analysis was used for the chemical analysis of atmospheric aerosols at several stations in Antarctica. MAENHAUT *et al.* (1979) determined 36 chemical elements of atmospheric aerosols collected at the South Pole by neutron activation analysis and atomic absorption method. They found that the mass of atmospheric aerosols at the South Pole was dominated ($\sim$80–90%) by sulfate particles and suggested that those sulfate particles were transported to the interior of Antarctica through the upper troposphere or through the lower stratosphere. They also identified two sources of approximately 10% of the aerosol mass as the ocean and crustal weathering, but could not identify the source of volatile elements which were anomalously enriched.

The present work, one of the atmospheric aerosol measurement programs during the 19th Japanese Antarctic Research Expedition (from February 1978 to January 1979), was undertaken to determine the chemical composition of giant and large aerosol particles collected at Syowa Station (69.0°S, 39.6°E) through instrumental neutron activation analysis.

The purpose of the present paper is to discuss the chemical composition and the origin of giant and large aerosol particles at Syowa Station, Antarctica.

2. Sampling

Atmospheric aerosol sampling was carried out at the Environmental Science Laboratory (ESL) of Syowa Station (Fig. 1). The ESL hut is separated from the residental area, where living huts and an engine room for the electric power generator are gathered. The prevailing wind direction is also shown in Fig. 1.

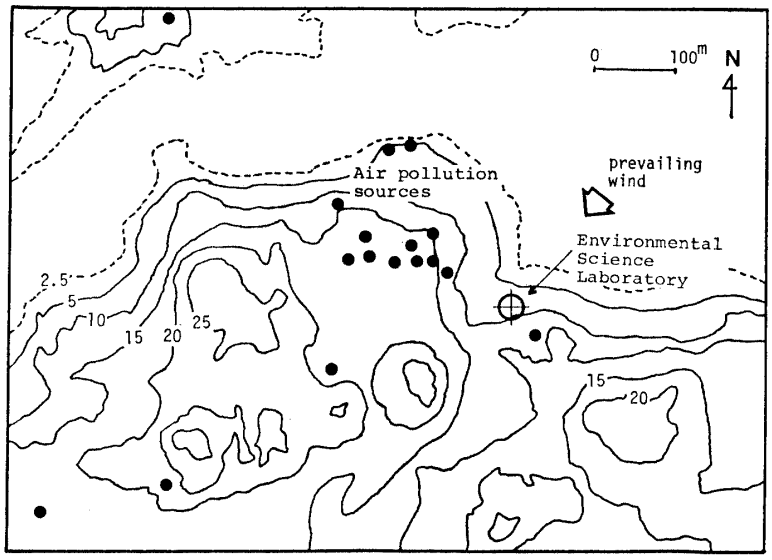

Fig. 1. Location of sampling site at Syowa Station, Antarctica.

Atmospheric aerosol particles were collected with an Andersen sampler which was placed in a room at the northeastern end of the ESL hut. The air sample was introduced into the room at the rate of 100 liters per minute through a polyvinyl chloride pipe with 45 mm inside-diameter and about 4 meters in length. The inside wall of the pipe was coated with glycerine so as to prevent particle loss in the pipe due to electrical forces. The inlet of the pipe was located at a height of about 3 meters above the ground and about 3 meters northeastward of the ESL hut. Aerosol particles larger than 0.47 μm in diameter were classified into 8 size-subranges with

this sampling device. Aerosol particles were impacted on 8 sheets of film which was made of the same material as a Nuclepore filter.

In order to avoid contamination due to man's activity in the station, aerosol particles were collected only for the durations when the outdoor air was thought to be unpolluted, which could be confirmed from the continuous records of wind speed and wind direction and of Aitken particle concentration simultaneously obtained.

Aerosol samples were collected both in the winter, from June 3 to August 6, 1978, and in the summer, from November 7 to December 25, 1978. The cumulative sampling volumes of the air were 985 m^3 in winter and 1255 m^3 in summer, respectively. These samples were sealed into clean vinyl bags and brought back to Japan.

3. Analysis

Aerosol samples were analyzed by instrumental neutron activation analysis.

Each film on which aerosol particles had been collected was divided into six equal segments. Three of them were used for a preliminary analysis, being irradiated

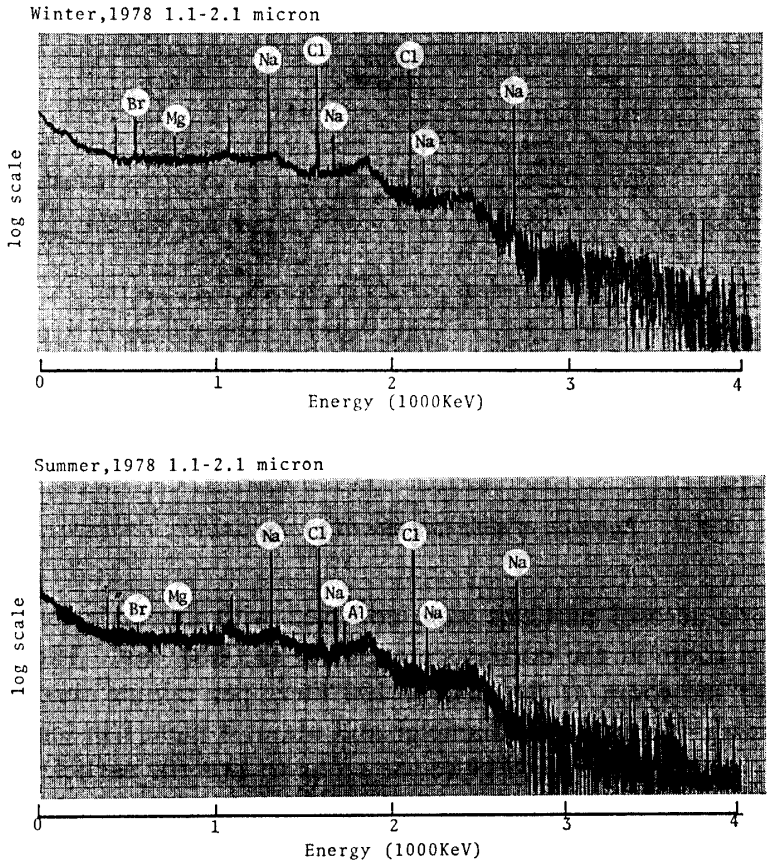

Fig. 2. Gamma ray spectrum from activated aerosol samples.

in a TRIGA-II type nuclear reactor of Rikkyo University, whose thermal neutron flux was 10^{12} n $cm^{-2}s^{-1}$. One segment was for the detection of short-lived elements and the other two segments for the detection of long-lived elements.

Later, two of the rest segments were irradiated in the KRUGA-I type nuclear reactor of Kyoto University, whose thermal neutron flux was 1.9×10^{13} n $cm^{-2}s^{-1}$. A high-resolution Ge(Li) detector was used to count gamma rays from the thus activated samples. Two examples of the gamma ray spectrum were given in Fig. 2. The quantities of chemical elements of the aerosol particles were determined through gamma ray spectroscopy by a computer.

4. Results and Discussion

Fifteen elements were detected, of which 7 could be measured in the present analysis. The mass concentrations of those quantitatively determined elements are shown in Tables 1 and 2, which are the results for the winter and for the summer, respectively. The mass concentration of aerosol particles was so low that the total mass of collected particles on each film was below the detection limit. Therefore the relative contribution of individual chemical elements to the total aerosol mass is not known from the analysis.

Although sulfur content in atmospheric aerosols cannot be ignored even in Antarctica, as reported by MAENHAUT *et al.* (1979), we failed to detect it, probably because the cross section for neutron activation of it was quite small and the sampled air volumes were not enough. The sensitivity for the different elements often depends on the composition of the sample to a certain extent. In this study, marine aerosols

Table 1. Chemical concentrations in atmospheric aerosol at Syowa Station in winter season (ng/m^3).

Stage	Cutoff diameter (μm)	Na	Cl	Br	Mg	Cu	Al	K
1	11.0	—	—	—	—	—	—	—
2	7.0	23	53	0.31	n.d.	n.d.	0.00	n.d.
3	4.7	42	99	0.35	n.d.	n.d.	0.12	n.d.
4	3.3	114	238	0.71	24	n.d.	0.30	n.d.
5	2.1	233	482	***	n.d.	n.d.	n.d.	16.0
6	1.1	350	658	1.30	59	n.d.	n.d.	***
7	0.65	271	567	***	39	n.d.	0.00	***
8	0.43	76	145	***	***	n.d.	1.40	7.7
Total		1109	2242	2.67	122	n.d.	1.82	23.7

n.d.: No detection.
***: Detectable but undetermined.

Table 2. Chemical concentrations in atmospheric aerosol at Syowa Station in summer season (ng/m^3).

Stage	Cutoff diameter (μm)	Na	Cl	Br	Mg	Cu	Al	K
1	11.0	11	27	0.20	n.d.	4.2	2.80	n.d.
2	7.0	4	19	0.14	n.d.	0.0	0.72	n.d.
3	4.7	5	13	0.10	n.d.	0.4	0.04	10.0
4	3.3	22	55	n.d.	n.d.	1.8	0.57	6.9
5	2.1	82	169	0.37	24	2.0	1.70	n.d.
6	1.1	122	236	0.26	26	2.9	0.91	7.9
7	0.65	74	117	n.d.	12	1.2	0.81	n.d.
8	0.43	24	28	0.14	3	3.3	1.10	n.d.
Total		344	664	1.21	65	15.8	8.65	24.8

n.d.: No detection.

dominated at Syowa Station and were in much higher concentration than those at the South Pole, as described below. Therefore the sensitivity for some elements such as sulfur might be limited by the degree of interference from those marine aerosols.

In the tables, it can be easily seen that most of the elements quantitatively determined in the samples for both seasons are common in the sea water. Taking sodium as an index of the oceanic contribution to atmospheric aerosol, and aluminum as an index of the crustal contribution, it can be seen that the oceanic particles were much richer in the particle mass than crustal particles in the air around Syowa Station.

The concentration of the chemical elements thought to be of crustal origin was remarkably high in the giant particles of the sample in the summer. Since giant particles have quite a short residence time in the lower atmosphere, they might originate from the neighborhood of the sampling site. In summer the snow around Syowa Station melted completely and the dry ground surface was exposed; it has soil formed from weathering of rocks. The chemical element of crustal origin which appeared in the giant particles in the summer must have originated from the exposed ground around Syowa Station.

As for the aerosol particles of oceanic origin, the total mass concentration of Na was 1109 ng/m^3 in winter, and 344 ng/m^3 in summer. That of Cl was 2242 ng/m^3 and 664 ng/m^3, respectively. Therefore the mass concentration of marine aerosols in winter was more than three times that in summer. The size-mass distribution of particles containing Na or Cl could be approximately fitted to a log-normal distribution curve with the geometric mean diameter being between 1.7 and 1.9 μm, and the standard deviation on the logarithmic scale being 0.3.

The sea surrounding Syowa Station is almost totally covered with snow and ice throughout the year. In summer it is several tens of kilometers from Syowa Station

to the open sea, whereas in winter it is about 1000 kilometers (KUSUNOKI, 1975). Therefore sea spray particles are thought to have been transported for as long distance as 1000 kilometers to Syowa Station.

The mass concentration ratio for each element to Na is shown in Tables 3 and 4.

Table 3. Mass concentration ratios for marine aerosols in winter season.

Cutoff diameter (μm)	Cl/Na	Br/Na	Mg/Na
11.0			
7.0	2.3	0.013	***
4.7	2.4	0.0083	***
3.3	2.1	0.0062	0.12
2.1	2.1	***	***
1.1	1.9	0.0037	0.21
0.65	2.1	***	0.14
0.43	1.9	***	***
Total	2.0	0.0024	0.11
Values of sea water	1.8	0.0062	0.12

***: Undetermined.

Table 4. Mass concentration ratios for marine aerosols in summer season.

Cutoff diameter (μm)	Cl/Na	Br/Na	Mg/Na
11.0	2.5	0.018	***
7.0	4.4	0.033	***
4.7	2.6	0.019	***
3.3	2.5	***	***
2.1	2.1	0.0045	0.29
1.1	1.9	0.0021	0.21
0.65	1.6	***	0.16
0.43	1.2	0.0058	0.14
Total	2.0	0.0035	0.19
Values of sea water	1.8	0.0062	0.12

***: Undetermined.

The weight ratio Cl/Na for giant particles was larger than that of sea water, *i.e.*, 1.8 in both seasons. If giant particles were transported from the open sea to the station directly, the weight ratio Cl/Na of the present samples should be equal to that of the bulk sea water. It should be reported that the oceanic elements in the snow or firn in East Antarctica were enriched with chlorine. For example, MUROZUMI (1975) did a chemical analysis of the snow in East Antarctica, and reported that the Cl/Na weight ratio was larger than the bulk sea water ratio. Also, BRIAT *et al.* (1974) showed that the Cl/Na weight ratio of firn increased as a function of the distance from the coast of East Antarctica. They have suggested that gaseous chlorine had been trapped in the snow or ice.

Giant particles have a short residence time in the lower atmosphere. Therefore the enrichment of chlorine in the giant particles at Syowa Station could be attributed to such a cause as chlorine enriched blowing snow or drifting snow blown up by a strong wind near the sampling site.

As for the large aerosol particles obtained in the present observation, the weight ratio Cl/Na showed was quite different than that for the giant aerosol particles mentioned above. In the winter the weight ratio Cl/Na for the large aerosol particles

was equal to that of bulk sea water. On the other hand, in the summer season the weight ratio for the large particles was smaller than that of bulk sea water. It has been reported that some of the large aerosol particles in Antarctica are sulfuric acid droplets or sulfate particles (MAENHAUT *et al.*, 1979). So it can be considered that sulfuric acid droplets chemically react with the sea salt particles and release gaseous chlorine, which we call a particle-particle reaction (p-p reaction), and that such a p-p reaction decreases the weight ratio Cl/Na for the large particles in the summer season. Such a reaction can occur in the atmosphere (OKADA *et al.*, 1978) and also on a film sampled. The question as to which is the more realistic feature is an open question now. The key to this problem may be a quantitative chemical analysis of individual particles.

5. Concluding Remarks

The distribution of large and giant aerosol particles at Syowa Station, Antarctica is much more dominated by oceanic particles than crustal particles. The concentration of sea salt particles observed in winter was three times that in summer in mass concentration. The giant particles in the present study were considered to be blowing snow or drifting snow blown up by a strong wind. The large particles in summer showed a chlorine deficiency.

Acknowledgments

We thank Dr. K. TOMURA and the staff of the Rikkyo Nuclear Center for the use of facilities. We wish to thank Dr. TAKEUCHI and the staff of the Kyoto University nuclear reactor institute for the use of their neutron activation facilities. Mr. H. KATSURAGAWA of Toho University gave expert help on neutron activation procedures.

It is a pleasure to thank all members of the wintering party of the 19th Japanese Antarctic Research Expedition for their kind support in making the observations at Syowa Station, Antarctica.

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(Received May 7, 1981; Revised manuscript received June 17, 1981)