

Individual particle analysis of Antarctic aerosols

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ABSTRACT

Aerosol samples were collected on Nucleopore filters at the South Pole Station. The particles were analyzed with an electron microscope for their morphology, size distribution, and concentration. The chemical composition of individual particles was determined with an X-ray energy spectrometer. The results provide basic information on the physical and chemical properties of Antarctic aerosols as well as their source and journey.

1. Introduction

The Antarctic continent provides an advantageous site for investigating natural aerosols. On any other continent it is often difficult to investigate natural aerosols because human activities contribute a large amount of pollution to the atmosphere and hence disturb the natural aerosol balance. The Antarctic is isolated from civilization, and anthropogenic aerosols—both local and imported from other continents—add little to the aerosol budget. Yet, the Antarctic atmosphere does not provide a typical or general case of natural aerosols; instead, it should be regarded as a unique case of clean air. Unlike other continents, the Antarctic produces few native aerosols: its land is completely covered with snow, so no dust can be swept from the ground except perhaps from mountain peaks above the glaciation; its surrounding ocean is always frozen, so little sea-spray aerosol can form; and there is no vegetation to introduce biological aerosols. Therefore, most Antarctic aerosols are imported from a distance. It would be interesting to find out what these aerosols are, where they come from, and how they arrive on this continent.

Many reports have dealt with Antarctic aerosols (Fischer et al., 1969; Zoller et al., 1974; Kuhn, 1972; Gladney et al., 1972; Mizuta et al., 1974; Hogan, 1975). Some of these investigators measured the aerosols' concentration, others studied their chemical composition with bulk analyses. Because of the very low concentration of

Antarctic aerosols, a high volume of air must be collected to sample them, and a very sensitive and precise technique must be applied. But the results provide only general information on all aerosols and cannot help us trace the origins of individual aerosols.

For this report, we have analyzed particles individually and related their morphology and size to their chemical composition. The information could help determine the sources and journeys of individual particles.

2. Methods of sampling and analysis

On November 23, 24, and 25, 1977, aerosol samples were taken at Amundsen-Scott Station (2800 m above MSL) at the South Pole. A clean air facility building is located 290 m upwind of the main camp. Air samples were drawn from the roof of the building, 17 m from the ground, through an aluminum pipe onto Nucleopore filters (47 mm diameter with pore size $0.1 \mu\text{m}$) with a mechanical pump. The aluminum pipe (15 cm in diameter) has an anodized surface which has been tested that it does not contribute any significant aerosol. The flow rate was regulated to 10 l min^{-1} , the sampling periods varied from 30 min to 12 h, the sample volumes were from 300 l to 7200 l. The filters were then sectioned into three parts for analysis. One part was coated with carbon and analyzed with a scanning electron microscope (SEM) interfaced with an X-ray energy spectrometer (XES). This

procedure has been reported in detail previously (Parungo et al., 1978). The second part was replicated on SiO film and examined with a transmission electron microscope (TEM) according to the procedure reported by Frank et al. (1970). The remaining part was placed in an isothermal diffusion chamber (Bigg et al., 1963) to measure ice nucleus concentrations.

The resolution guaranteed by the manufacturers is 100 Å (0.01 μm) for SEM (American Optical Corp.) and 10 Å (0.001 μm) for TEM (RCA). However, only occasionally have these resolutions been achieved. The confident operational resolutions are 500 Å for the SEM and 50 Å for the TEM.

For elemental analysis by XES the voltage was regulated to 20 kV and the acquisition time was kept 30 s. Light elements with atomic number $Z < 9$ do not emit detectable X-rays. So common elements such as H, C, N, and O cannot be identified by XES. Furthermore, the penetration depth is only a few micrometers, elements which are

covered by thick layers of other elements may fail to be detected. However, most particles analyzed have a size smaller than this range. Therefore the matrix effect can be ignored.

3. Results and discussion

3.1. Particle concentration and size distribution

Because TEM has better resolution than the SEM, counting and sizing of particles were based on TEM photographs. Approximately 1000 particles were analyzed for particle size distribution. Since low-volume samples did not provide enough particles to give a significant result, only high-volume samples were selected to measure particle concentration and size distribution. Fig. 1 shows the results. The concentration of total particles was approximately 10^2 cm^{-3} , and particle number size distribution showed single mode at 0.08 μm. The results appeared very consistent except for one sample collected on November 24 from 1220 to 1438, in which the concentration reached 10^3 cm^{-3} . This is probably due to local pollution, which could have been carried to the sampling site from the camp by the shifting winds. This sample was disregarded for natural aerosol analysis.

3.2. Analysis of individual particles

The instrumental system SEM-XES is able to depict a particle and also to determine its elemental composition. Fig. 2 through 6 show a selection of particles that have been observed during the analysis. It appears that they are typical of various origins as discussed in the text. Fig. 2 shows Antarctic particles collected on a Nuclepore filter (the 0.1 μm pores are visible in the background) and X-ray energy spectra of five marked particles. All the particles are different in shape, size and chemical composition. The major components of these particles are Al and Si, and the minor components are Fe, Cr, and S. The multiple elemental composition resembles soil, rock, or sand, suggesting earth crust origin. They originate either in the Antarctic mountain ranges or have been transported from other continents.

Fig. 3 shows a large particle imbedded in a liquid drop. The X-ray spectrum indicates that it contains mainly Na and Cl with small amounts of F, S, and Ca. It probably came from marine air.

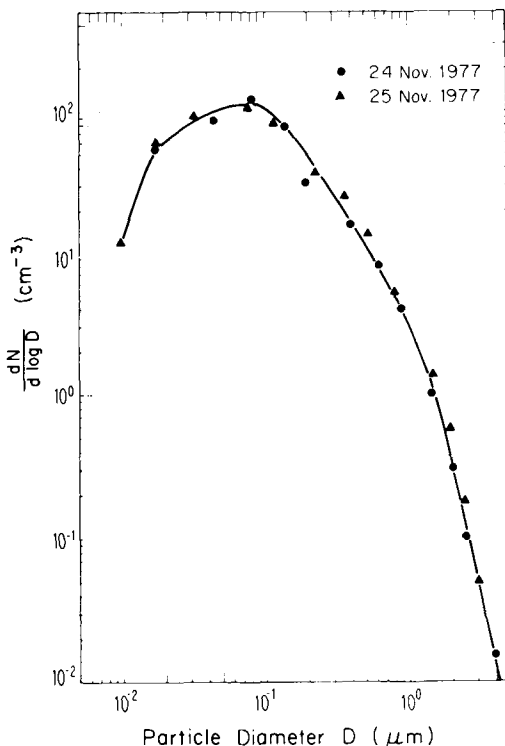


Fig. 1. Size distribution and concentration in Antarctic aerosol samples.

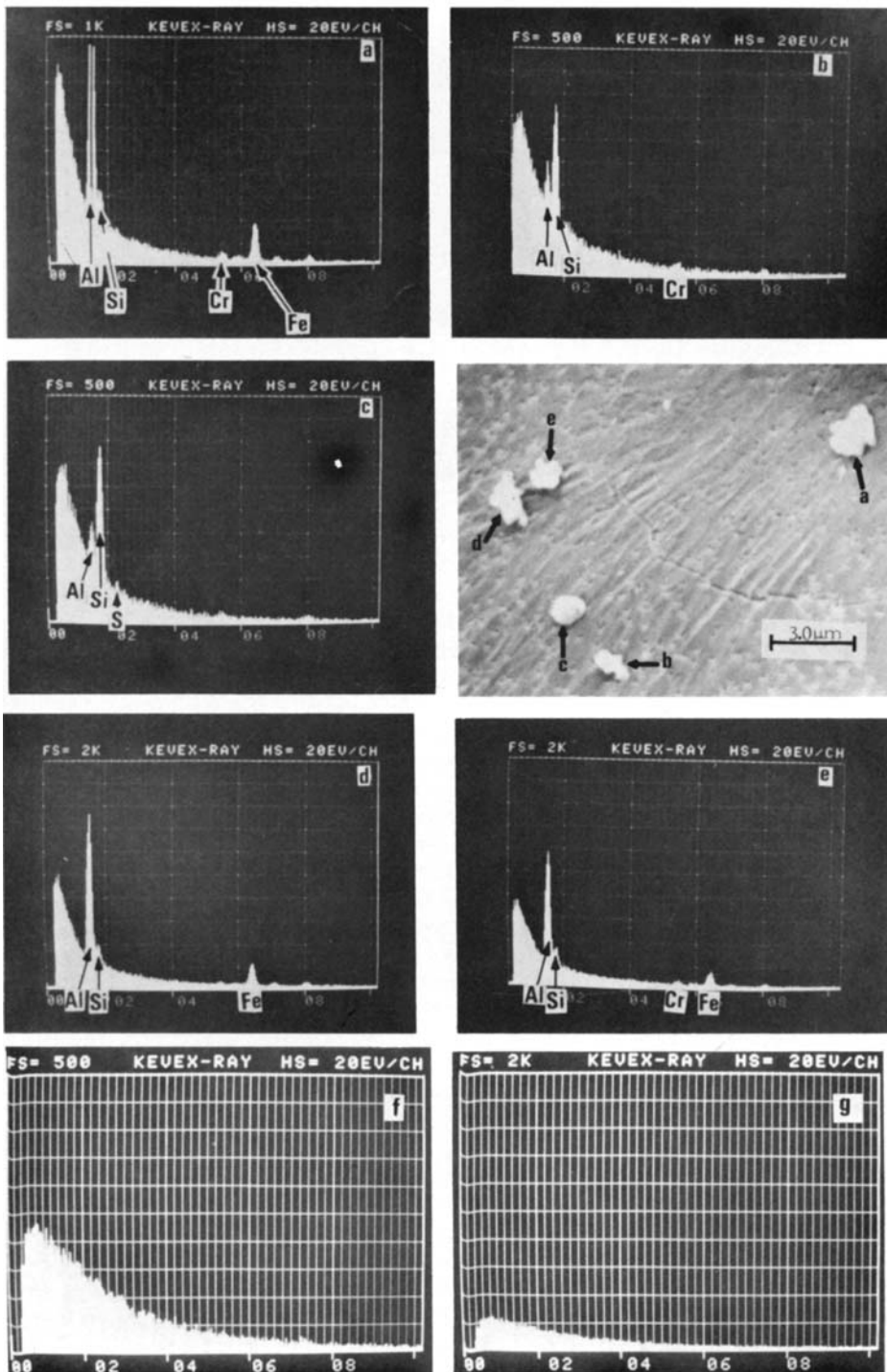


Fig. 2. An electron micrograph of particles collected on a Nuclepore filter, and X-ray energy spectra of five indicated particles (a to e) and of blank filters (f and g).

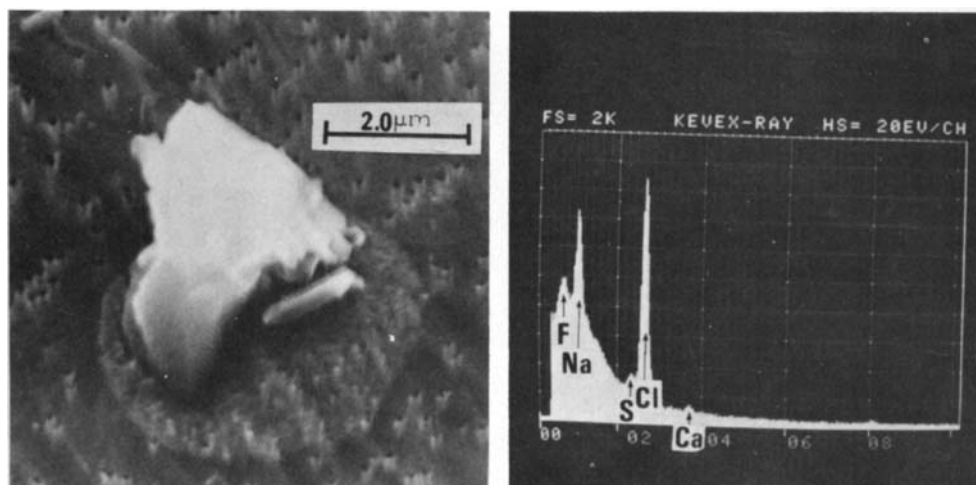


Fig. 3. A particle in a liquid drop, its elemental composition suggesting marine origin.

Fig. 4 shows several giant ($d \geq 2 \mu\text{m}$) and large ($0.2 \mu\text{m} < d < 2 \mu\text{m}$) particles. Their elemental compositions are Fe, Cr, Ni, and Al, which are major constituents of meteors. It is very possible that the particles are of extraterrestrial origin and come from meteor showers. Because the Antarctic aerosol concentration is so low, any meteorite dust present would make a strong contribution to the total budget.

In Fig. 5, particle (a) depicts only Fe X-ray, which can be the element Fe or its oxides; particle (b) shows S and K should be K_2SO_4 ; particle (c) shows Cu only, which could be the Cu element or its oxides; and particle (d) shows S only, which is probably $(\text{NH}_4)_2\text{SO}_4$ (light elements do not yield detectable X-rays). That volatile metallic elements, such as Fe and Cu or their oxides, exist unaccompanied by other elements in a particle usually suggests that the high-temperature dispersion process and vapor phase condensation are responsible. Thus, particles (a) and (c) could have come from a volcanic eruption. The active volcano, Mt Erebus, on Ross Island is 900 miles (1400 km) from the South Pole Station and has been fuming continuously with occasional eruptions.

More than half of the Aitken particles ($d < 0.2 \mu\text{m}$) contain S. Particles (b) and (d) in Fig. 5 are two examples. In addition, we found that 3% to 10% of the total particles on filter samples are sulfuric acid droplets or partially neutralized sulfuric acid particles, as shown in Fig. 6 (a) and (b). Examination by electron microscope (Frank

and Lodge, 1967) shows that H_2SO_4 droplets have a unique appearance, with many tiny satellite particles surrounding a large nucleus particle. When such a particle was subjected to the high intensive electron beam in the vacuum chamber of SEM, H_2SO_4 evaporated and left only the neutralized portion to emit X-rays. Particle (a) in Fig. 6 shows a weak S peak representing H_2SO_4 with contamination by $(\text{NH}_4)_2\text{SO}_4$. Particle (b) shows Cr and S, indicating that part of the H_2SO_4 had been neutralized by a chromium base. The arrowed particles do not yield any detectable X-rays; their morphology indicates that they are pure H_2SO_4 . The high percentages of sulfuric acid and sulfate particles in Antarctic aerosols are generally thought to be from the stratosphere (e.g., Fischer et al., 1969; Hogan, 1975); the subsidence inversion caused by the Antarctic atmospheric circulation lowers the tropopause and carries the sulfates in the Junge layer downward.

Particle (c) in Fig. 6 did not produce detectable X-rays. It appears as a large carbon soot particle, which is probably an incomplete combustion product from the nearby camp.

One hundred particles were analyzed individually with the SEM-XES system. The elemental composition of total analyzed particles is summarized in Fig. 7 (top). It indicates the percentage (in number) of particles containing a certain element (e.g., 53% of the particles contain Al, 51% of the particles, Si, etc.), but not mass percentage. Particles were classified into three groups: giant

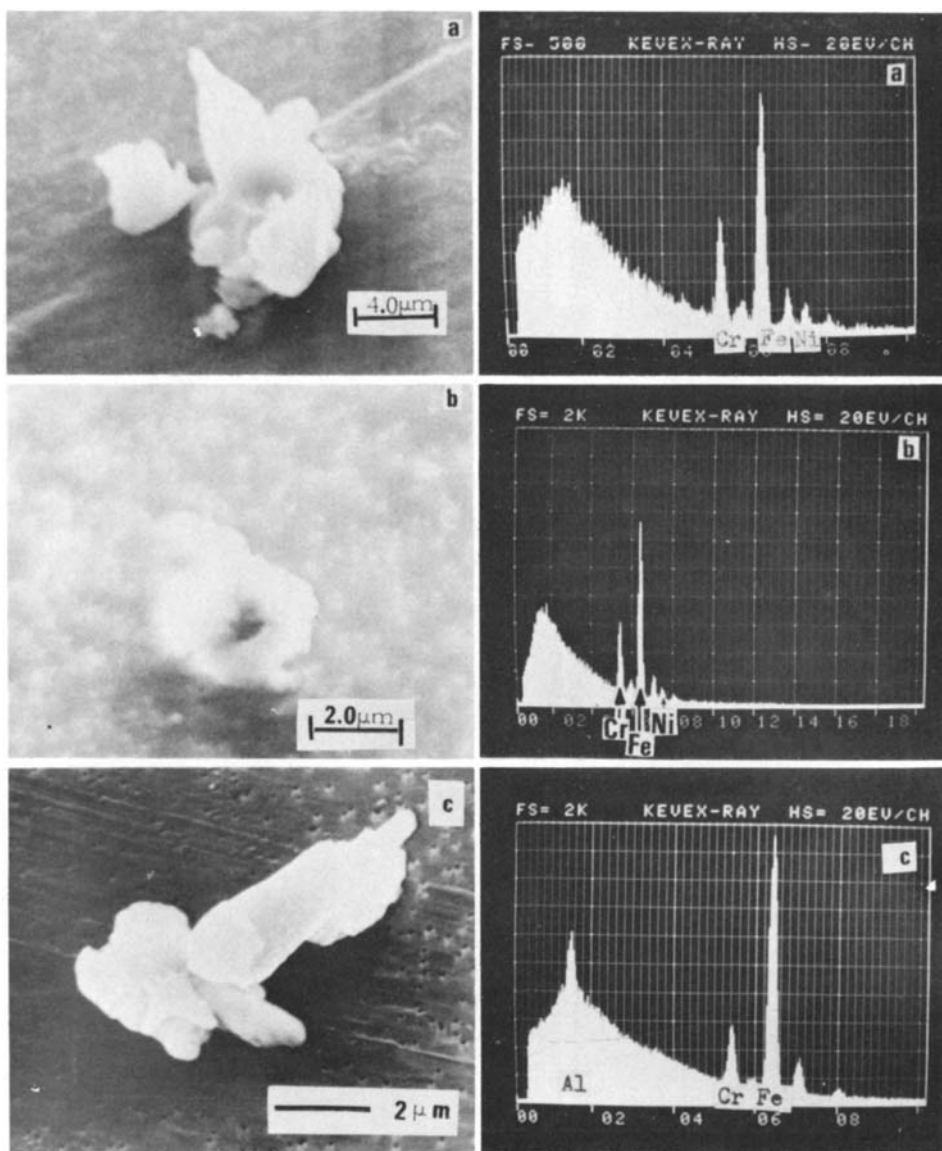


Fig. 4. Three particles containing Fe, Ni, Cr, or Al, indicating possible extraterrestrial origin.

particles ($d \geq 2 \mu\text{m}$), large particles ($0.2 \mu\text{m} < d < 2 \mu\text{m}$), and Aitken particles ($d \leq 0.2 \mu\text{m}$). The elemental compositions of each group are also shown in Fig. 7. It indicates that more than 50% of the giant particles contain Al and Si, more than 20% contain S, Cl, K, and Fe. For Aitken particles, more than 50% contain Al and S; 35% contain Si; other elements are in minute percentages. The Aitken particles containing S are probably the

products of SO_2 gas to sulfate particle conversion and Aitken particles containing Si and Al may come from sublimation of snow on the ground.

3.3. Ice nucleation activity

Since the Antarctic is covered with snow and ice, it is generally believed that a major fraction of the aerosols originate from the surface, i.e., when snow or ice sublimates ice nuclei are emitted into and

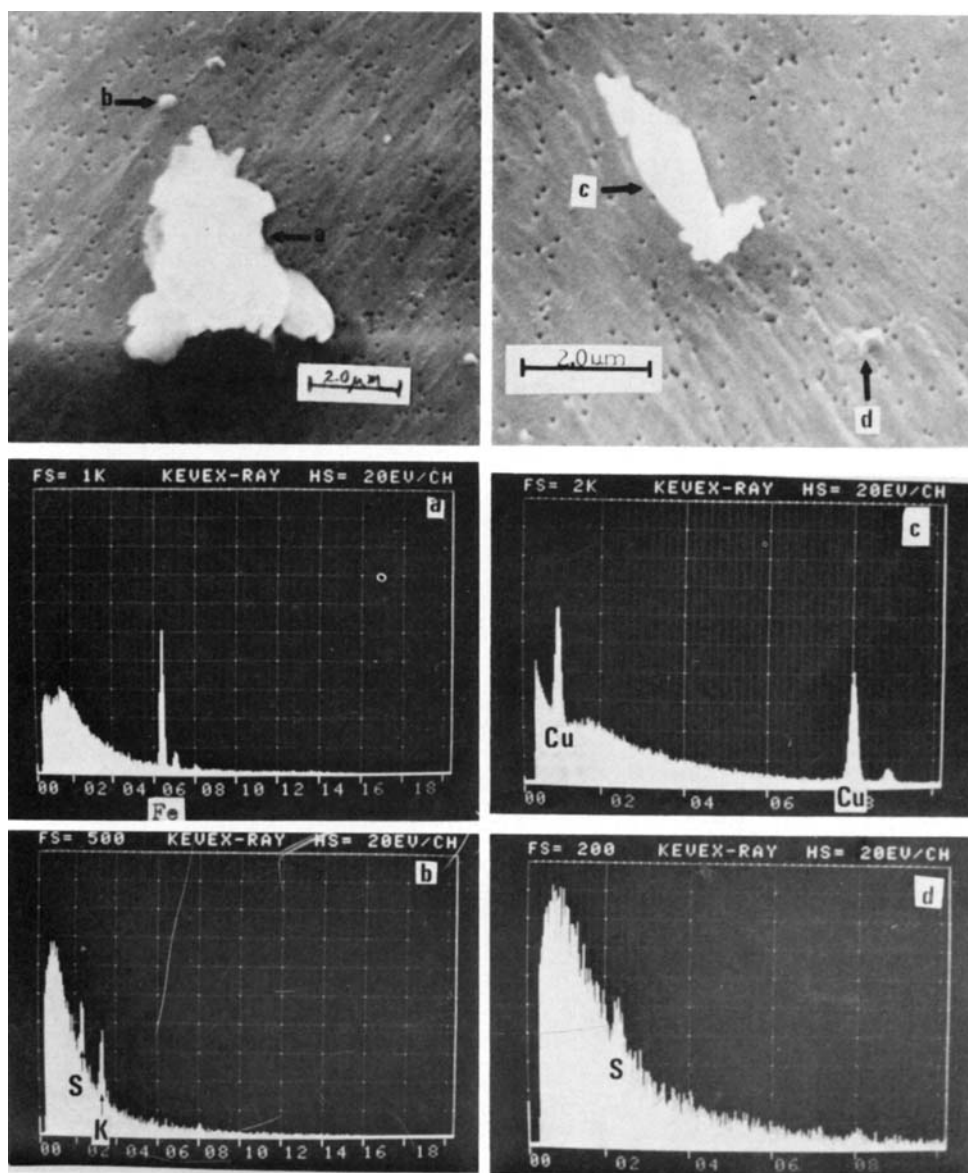


Fig. 5. The two large particles are Fe (a) and Cu (c); the two small particles (b and d) are both sulfates.

remain in the atmosphere. If this occurs, the Antarctic aerosols are probably active ice nuclei. We tested the ice nucleation activity of the aerosols in a sub-freezing thermal-diffusion chamber and found that at -10°C , practically no ice crystals were initiated by the aerosols. At -15°C the ice nucleus concentration was measured as 0.1 l^{-1} , and at -20°C it was 0.3 l^{-1} . Considering the particle

concentration as 10^2 cm^{-3} or 10^5 l^{-1} , it is estimated that fewer than three out of a million particles act as ice nuclei at temperatures warmer than -20°C which is compatible with the findings concerning natural aerosols of other continents. However, one must bear in mind that the average year-round temperature at the pole is -56°C , and that more particles will be activated as ice nuclei at

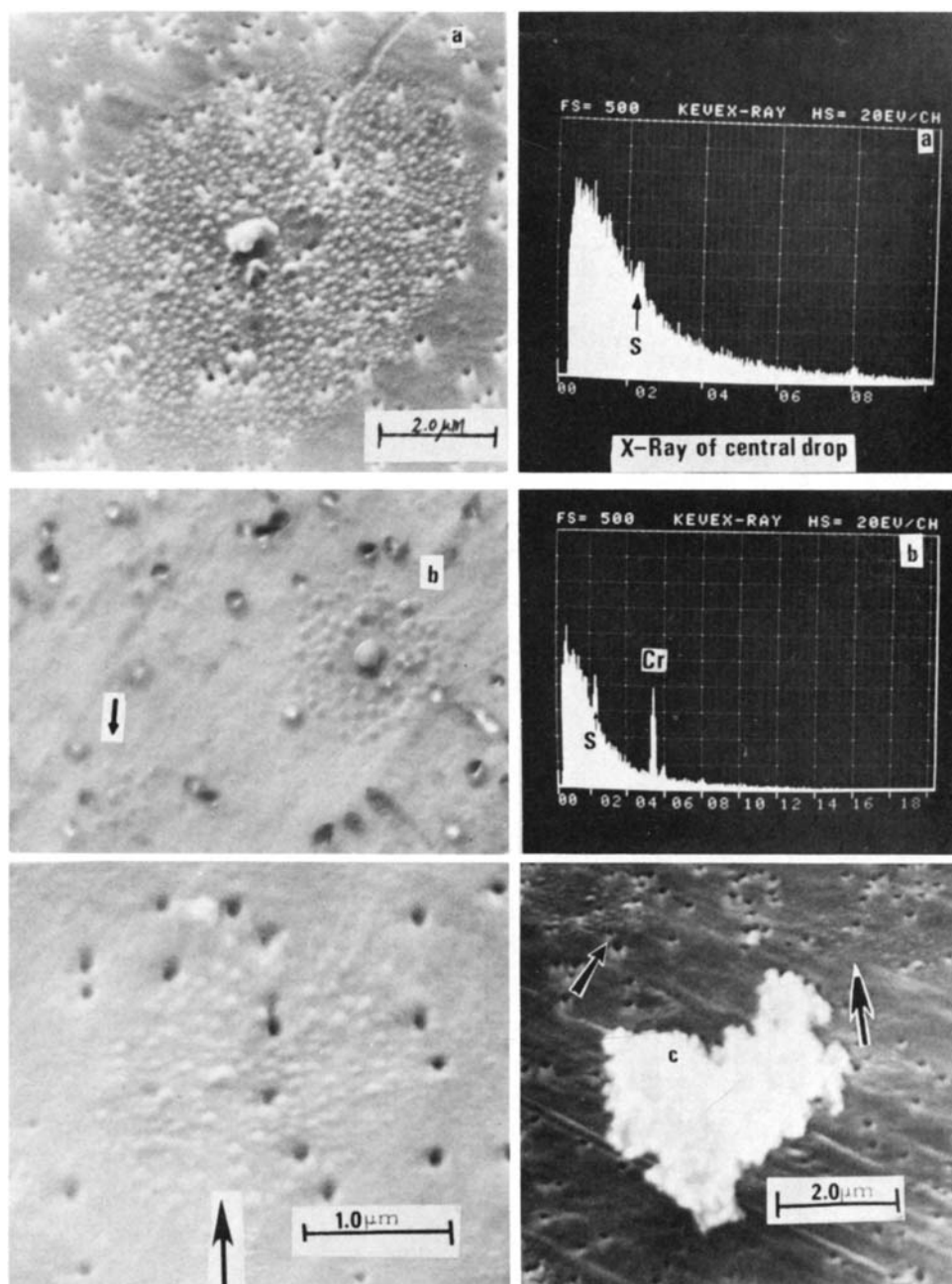


Fig. 6. Particles of sulfuric acid (a), sulfate (b), and soot (c).

the colder temperature. Furthermore, particles (other than ice nuclei) washed-out by snow can also be released into the atmosphere by sublimation of snow. Therefore, the results of ice nucleus

measurements do not exclude snow or ice as one of the sources of Antarctic aerosols; instead, they merely demonstrate that the Antarctic aerosols show no specific ice nucleation activity.

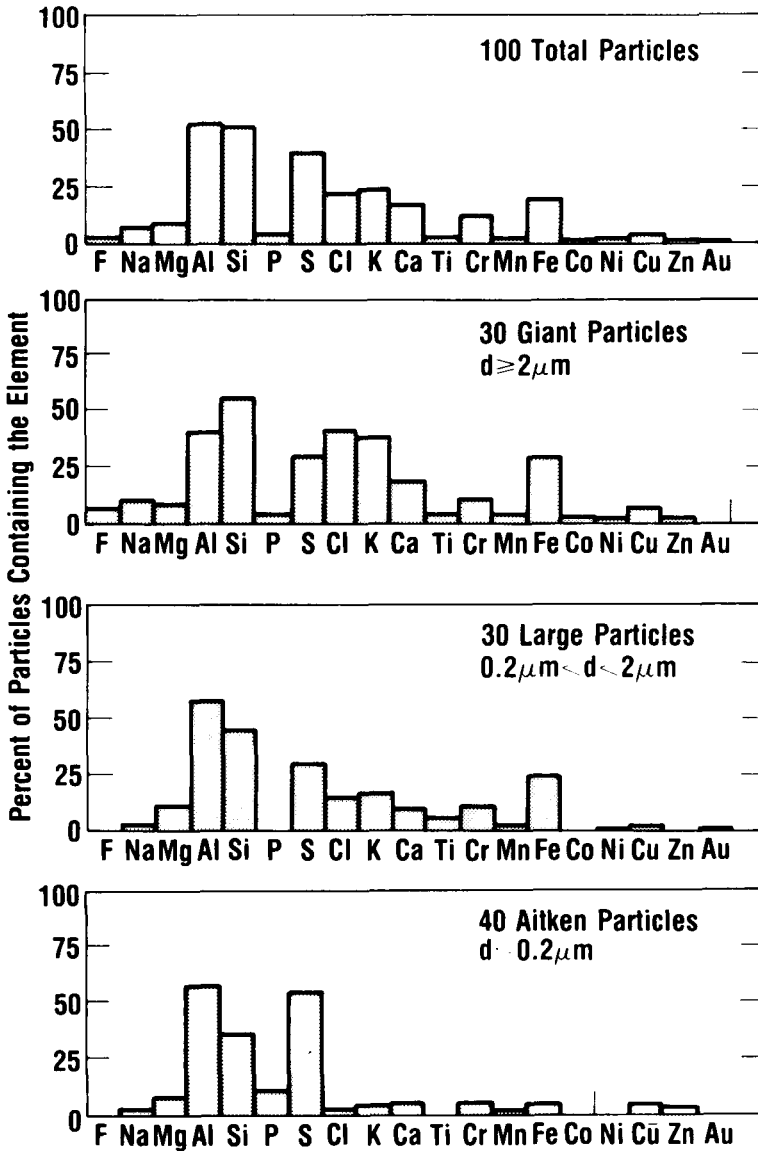


Fig. 7. Frequency of elements present in the particles.

4. Conclusion

With SEM-XES techniques we can trace the origin of a particle by analyzing its individual chemical composition.

Our data present evidence for various origins of Antarctic aerosol particles, such as the sur-

rounding oceans, the Antarctic mountain ranges, other continents, meteors, volcanoes (specifically Mt Erebus), and the stratosphere (particularly the Aitken nuclei). The technique can be used to monitor Antarctic aerosols' concentration, size distribution and chemical composition.

REFERENCES

- Bigg, E. K., Mossop, S. S., Meade, R. T. and Thorndike, S. C. 1963. The measurement of ice nucleus concentration by means of Millipore filters. *J. Appl. Meteor.* 2, 266–269.
- Fischer, W. H., Lodge, P., Jr., Pate, J. B. and Cadle, R. D. 1969. Antarctic atmospheric chemistry: Preliminary exploration. *Sci.* 164, 66–67.
- Frank, E. R. and Lodge, J. P., Jr. 1967. Morphologic identification of airborne particles with the electron microscope. *J. Microsc.* 6, 449–456.
- Frank, E. R., Spurny, K. R., Shesley, D. C. and Lodge, J. P., Jr. 1970. The use of Nucleopore filter in light and electron microscopy of aerosols. *J. Microsc.* 9, 735–740.
- Gladney, E. S., Zoller, W. H., Duce, R. A. and Jones, A. G. 1972. Aluminum and manganese in atmospheric particulates from McMurdo and South Pole Stations. *Antarctic J.* 7, 171–173.
- Hogan, A. W. 1975. Antarctic aerosols. *J. Appl. Meteor.* 14, 550–559.
- Kuhn, M. 1972. Global pollution in Antarctic air documented by solar radiation depletion. *Antarctic J.* 7, 35–37.
- Mizuta, H., Teresawa, K., Ishihara, K., Hirano, K., Karasawa, M., Suzuki, M., Yoshinaga, Y., Kitazume, M., Endo, Y. and Yoneyama, E. 1974. Design of high-volume air samples for the Antarctic. *J. Japan Soc. Air Pollution* 9, 254–261.
- Parungo, F. P., Ackerman, E., Proulx, H. and Pueschel, R. 1978. Nucleation properties of fly ash in a coal-fired power-plant plume. *Atmos. Environ.* 12, 929–935.
- Zoller, W. H., Gladney, E. S. and Duce, R. A. 1974. Atmospheric concentrations and sources of trace metals at South Pole. *Sci.* 183, 198–200.

АНАЛИЗ ИНДИВИДУАЛЬНЫХ ЧАСТИЦ АНТАРКТИЧЕСКОГО АЭРОЗОЛЯ

На станции Южный полюс производился отбор проб аэрозоля на фильтры типа "Нуклеопор". С помощью электронного микроскопа анализировалась морфология частиц, а также их концентрация и распределение по размерам. Химический состав отдельных частиц оп-

еделялся рентгеновским спектрометром. Результаты дают основную информацию как о физических и химических свойствах антарктического аэрозоля, так и об их источниках и их переносе.