

Evaluation of contamination in preparation of an Antarctic ice core for microparticle analysis with SEM-EDX

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Abstract: A sample treatment method was established for the SEM-EDX analysis of solid microparticles in an Antarctic ice core. The numbers of contamination-particles all through the processes from cutting the specimen from the stored ice core to SEM observation were investigated. An ice core specimen (63.0 g, depth 384.00 m–384.11 m) obtained from Mizuho ice core (No. 840628, M¹-521, depth 383.82 m–384.32 m) was melted at room temperature on a clean bench; 10.9 g of the resulting melt water was filtered with a Nuclepore membrane filter (pore size 0.2 μm , diameter 13 mm). 115 particles were detected from an optical domain of 520 $\mu\text{m} \times 320 \mu\text{m}$, 1/450 of the effective filtration area, randomly selected under SEM observation with 20000 magnification. A parallel experiment for the background revealed that it included about 4–5 contaminated particles. The average size of particles from the ice core specimen was 1.6 μm , and silicate minerals (77%), silica (20%) and other (3%) were classified from the results of EDX analysis. The number of particles in the ice core specimen (Mizuho core at 384 m in depth) was estimated as $4700 \pm 520/\text{g}$ from the results of parallel experiments using synthesized monodispersed hematite particles.

1. Introduction

Various kinds of particles are transported onto the Antarctic ice sheet by the atmospheric circulation (Kamiyama *et al.*, 1987; Kamiyama and Watanabe, 1994). Hara *et al.* (1996) suggested a possibility of transportation of soil particles from other continents to Antarctica in winter on the basis of their analysis of silicate composition in the aerosol particles collected at Syowa Station through the year from February to December 1991. Gaudichet *et al.* (1986) reported that particles in a 905 m deep ice core from Dome C, Antarctica were smaller than 2 μm in diameter and that 40 percent of the particles were illite, quartz, feldspar and clay minerals like chlorite using a transmission electron microscope with energy dispersive X-ray analyzer (TEM-EDX). They also reported the existence of volcanic glassy particles and titania particles in the ice core. From the electron diffractometric results by Kumai (1976), 34% of nuclei of snow crystals taken at South Pole, Antarctica in 1976 were illite. According to

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Gaudichet and Baut-Menard (1982), the percentage of illite in suspended particle matter (SPM) in the north Pacific was 18–47% in April–June. Solid particles in Antarctic snow deposited before the Industrial Revolution are considered to be other than cosmic and volcanic dusts, originated from arid regions in South America and Australia (Gaudichet *et al.*, 1986).

In 1983–1984, the 24th and 25th Japanese Antarctic Research Expeditions (JARE-24 and 25) drilled an ice core down to 700.56 m at Mizuho Station. Many studies have been carried out on its physical properties (*e.g.*, Higashi *et al.*, 1988), oxygen isotopes and chemical compositions. For the change in the numbers of solid microparticles in the ice cores, a Coulter Counter has been utilized (Fujii and Watanabe, 1988). But few studies on morphology and composition of dusts in Antarctic ice cores have been done.

Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) provides both morphological and compositional information if a quantitative collection of microparticles can be secured. Higashi *et al.* (1990) reported SEM observation of microparticles in the Mizuho ice core. Few studies, however, with SEM-EDX have been reported for the analysis of microparticles in the Mizuho ice core. For reliable analysis, a simple procedure with accurate background contamination estimation is indispensable. Most previous reports lack descriptions of contamination estimation for each procedure to support their reliability.

The authors established a simple and reliable filtration method for solid microparticles in ice core samples, to be coupled with SEM-EDX observation and applied it to the ice core sample from Mizuho Station taken at the depth of 384 m.

2. Experiment

2.1. Sample

The sample used in this experiment is ice at a depth of 383.82 m–384.32 m (No. 840628, M'521) of a 700 m deep Mizuho ice core, preserved in a cold room of the National Institute of Polar Research. Three ice pieces (sample M1–3) shown in Table 1 were cut from a 50 cm ice core with a band saw in the cold room. According to a previous study on microparticle concentration of the Mizuho ice core (Fujii and Watanabe, 1988), the assumed number concentration of solid microparticles in this specimen was estimated to be 15000/mL for particles larger than $0.63\mu\text{m}$ in diameter. The expected number of particles was estimated as large as 300 in an observation area ($520\mu\text{m} \times 320\mu\text{m}$) for a filtrated sample of a 10 g core.

Table 1. Ice core specimens and their weights.

Procedure	Specimen		
	M 1	M 2	M 3
Upper depth (m)	383.82	383.90	384.00
Lower depth (m)	383.90	384.00	384.11
Length (cm)	7.5	10.1	10.4
Weight (g)	229.2	281.5	286.4

2.2. Reagents and water

The reagents used in this work were all of guaranteed reagent purity, from Kanto Chemical Co., Inc. Nitric acid, sodium hydroxide solution, methanol, acetone and detergent solution (Extran MA02 neutral, MERCK Co.) were used for cleaning and rinsing plastic apparatus. Tap water was deionized and was purified through a Milli-XQ (Millipore Co.). Ultrapure water (Tampure-A, Tama Chemicals Co.) was also used to make an artificial ice piece which was frozen at -20°C without breaking the seal (Sample A).

As reference particles for the experiment on filtration homogeneity (See Section 2.3.6), monodispersed cubic hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles were synthesized in our laboratory according to a previously reported method (Hamada *et al.*, 1986). The particle size of cubic hematite was measured as $1.2\mu\text{m}$ with standard deviation of $0.13\mu\text{m}$ electron microscopically.

2.3. Method

2.3.1. Instruments

Electron microscopic specimens were vapor-deposited with an ion sputter (Hitachi E-1030) and observed with a scanning electron microscope (Hitachi S-5000) with an energy dispersive X-ray analyzer (Kevex-SIGMA). The number of particles in the air of a clean bench in which filtration was carried out was confirmed to be $0.6\text{ particles L}^{-1}\text{ min}^{-1}$, $0.3\text{--}5\mu\text{m}$ in diameter with a portable laser particle counter (model TF-500, KANOMAX Co.).

For filtration, a polycarbonate type Nuclepore membrane filter (13 mm in diameter, effective diameter of 9.8 mm , pore size $0.2\mu\text{m}$) and polypropylene disposable micro-syringe (20 mL) were used. All vessels used were of teflon and polypropylene. Zirconia fine ceramic knives (blade length: 140 mm and 90 mm, Kyocera) were used to remove the contaminated surface layers of the ice samples.

2.3.2. Cleaning and rinsing

Polypropylene sample containers and vessels were immersed in detergent solution (5%) for one day and washed with deionized water. Then they were immersed in sodium hydroxide solution (1 mol dm^{-3}) for one day followed by immersion in nitric acid (4 mol dm^{-3}). After rinsing with deionized water, they were boiled in deionized water for 4 hours in a stainless steel tank on a clean bench, and then rinsed three times with ultrapure water ultrasonically for 15 min. The same rinsing procedures were applied for syringes, filter holders, ceramic knives and tweezers without alkaline or acid washing. After rinsing, utensils were kept in IC packs (dust-free plastic bags for semiconductor IC) on a clean bench.

2.3.3. Removal of contaminated surface layer and sample preparation

Table 2 shows a summary of procedures for removal of the contaminated surface layer on ice core specimens. Steps #1 to #7 were carried out in a cold laboratory at -20°C at the National Institute of Polar Research. The surface layer was removed twice through steps #5 and #9. Steps #8 to #14 were carried out on a clean bench at the Science University of Tokyo. In step #10, stainless steel tongs were used to hold the sample piece in order to avoid contamination from handling. Step #15 was carried out in the SEM-EDX room at the Science University of Tokyo without air conditioning.

Table 2. Preparation procedures of ice core specimen for SEM-EDX observation.

No.	Procedure
1	Measure the size and weigh the core specimen with a top loading electronic balance.
2	Clean the band saw with cutting Sample A.
3	Cut a 10 cm length of core specimen with the cleaned band saw.
4	Weigh the core specimen with a top loading electronic balance.
5	Remove surface contaminated surface layers of the core specimen for 1-2 mm depth with a ceramic knife (1st surface layer removal).
6	Put the specimen into a polypropylene container and measure the size.
7	Refrigerate.
8	Weigh the specimen with a top loading electronic balance.
9	Remove the surface layer with a ceramic knife (2nd surface layer removal).
10	Cut the specimen with a ceramic knife to the required size holding it with Tongs, and preserve the rest in a polypropylene container.
11	Weigh the specimen with a top loading electronic balance.
12	Melt the specimen at room temperature and disperse particles ultrasonically. Take 10 mL with a sampling microsyringe. Filter under pressure.
13	Dry the filter in a polypropylene container.
14	Cut the filter to 3 mm × 5 mm and fix it on a SEM sample plate.
15	Vapor-deposit Pt-Pd and observe particles with SEM.

* Procedures #1~#7 : at National Institute of Polar Research.

Procedures #8~#14: in clean bench at Science University of Tokyo.

Procedures #15: in SEM-EDX room at Science University of Tokyo.

2.3.4. Observation with SEM-EDX

In order to prevent contamination spectra and reduce background noise from material of the SEM sample plate, adhesive copper tape (80 μ m in thickness of copper) and carbon tape were fixed on the SEM sample plate. The vapor-deposition apparatus was dismantled before the experiment; dust was removed from all the parts with cleaning paste, and rinsed with methanol and acetone ultrasonically. The sampling ports and sample holder of the SEM apparatus were wiped off thoroughly with methanol and acetone.

2.3.5. Evaluation procedures of contamination particles in blank test

Steps from the second removal of the surface layer of a core sample (step #9 in Table 2) for the SEM observation were defined as the blank test in this experiment. The case without the second removal of contaminated surface layer was also compared. 100 g of a simulated core sample (frozen ultrapure water, Sample A) was prepared with a band saw and kept in a stock freezer after removal of the contaminated surface layer. In case 1, the contamination of ambient particles during the minimum required procedures from instruments, plastic apparatus and SEM-EDX observation was evaluated. In case 2, the contamination of ambient particles in case 1 was added those from filtration and desiccation procedures using ultrapure water. In case 3, two removals for the contaminated surface layer (steps #5 to #9 in Table 2) of Sample A were added to those of case 2; the second removal (step #9 in Table 2) was omitted in case 4 to show the effectiveness of the removal.

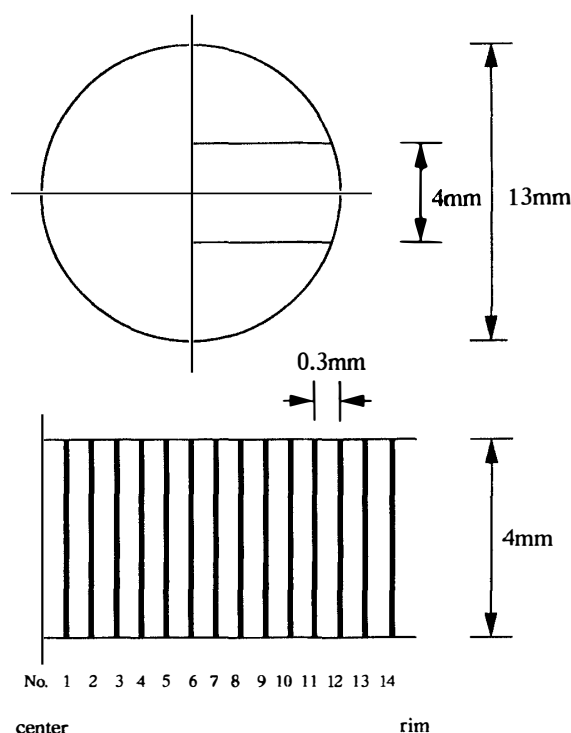


Fig. 1. Observation area ($30\mu\text{m} \times 4\text{mm}$) for distribution of hematite particles on filter.

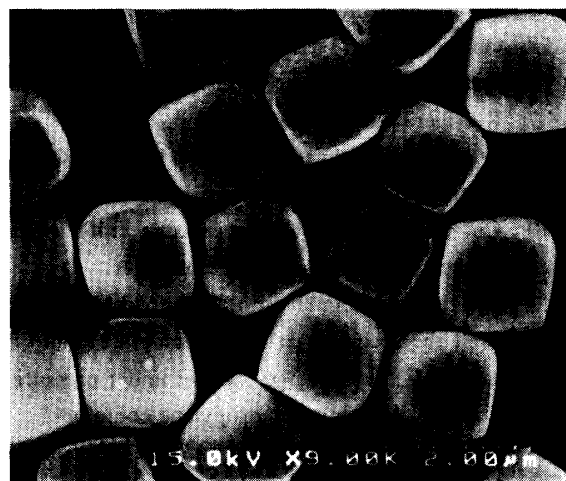


Fig. 2. SEM image of monodispersed hematite particles.

2.3.6. Distribution of particles on a filter

For the pressure filtering step, the effective filtering area was 75mm^2 , based on the 9.8mm filter holder diameter when a filter 13mm in diameter was used. The observation area under electron microscopic view, however, was only 0.17mm^2 , $520\mu\text{m} \times 320\mu\text{m}$, only $1/450$ of the total filtering area. Fourteen observation areas with 0.3mm spacing were selected as shown in Fig. 1 for the examination of homogenized filtration. No particles of $0.2\text{--}0.6\mu\text{m}$ were observed. We suspected that these particles were strongly adsorbed to the vessel wall and accumulated in the filter pores. Therefore, the following discussion is limited to particles larger than $0.6\mu\text{m}$ in diameter. In order to represent the total number of particles seen under a microscopic, the homogeneity of distribution of particles on a filter should be assured. Synthesized monodispersed cubic hematite was used as model particles. Figure 2 shows a microscopic view of the hematite particles.

The synthesized monodispersed particles were dispersed in ultrapure water ultrasonically, and the solution filtered under pressure with a Nuclepore membrane filter with pore size of $0.2\mu\text{m}$. After drying, vapor deposition of Pt-Pd was done on a $4\text{mm} \times 6.5\text{mm}$ rectangular area as shown in Fig. 1. The number of particles was counted under 2000 magnification in each observation area of $30\mu\text{m} \times 4\text{mm}$ with 0.3mm spacing.

3. Results and discussion

3.1. Contamination particles in blank procedures

(1) Number of contamination particles

Table 3 shows the result of the cases explained in Section 2.3.5 in numbers of contamination particles. In case 1, a new filter contains 3.2 of particles on average in an area of $520\mu\text{m} \times 320\mu\text{m}$, the number was not much increased when ultrapure water was filtered with this type of filter (case 2). After removing surface layers of ice sample with a ceramic knife, no fragments of the ceramic knife were found. The numbers of particles were almost the same in the case of a new filter (case 1), of a filter which was used for ultrapure water filtration (case 2), and of a filter which was used for filtration of Sample A with the surface layer removed twice (case 3). However, an increase of contamination particles was observed in case 4, when the second removal of the contaminated surface layer (step #9 in Table 2) was omitted.

Table 3. Numbers of contamination particles observed in $520\mu\text{m} \times 320\mu\text{m}$ through four kinds of blank procedures, cases 1-4.

Case	Filter	Number of measurement	Total number	Mean number /measurement	Mean diameter (μm)
1	New	8	26	3.2	2.0
2	After filtration of 10mL ultrapure water ^{a)}	8	25	3.1	1.9
3	After filtration of 10mL Sample A ^{b)}	4	18	4.5	2.3
4	After filtration of 10mL Sample A ^{c)}	3	38	13	—

^{a)} Without freezing.

^{b)} Procedures #2 to #10 in Table 2 were applied.

^{c)} The second removal of contaminated surface layer (step #9 in Table 2) was omitted.

From the results through cases 1 to 3, no possibility for contamination during the filtration procedure was assured. The increase of contamination in case 4 suggests that the main contamination comes from exposure of the filter to the open air for vapor-deposition and the introduction into the sample chamber of the electron microscope. As a result, the mean blank value of contamination particles in this experiment was estimated to be 4.5 particles in an area of $520\mu\text{m} \times 320\mu\text{m}$ when the second removal step was carried out.

Figure 3 shows the particle size distribution of 69 of total contamination particles detected in cases 1 to 3. Their diameters were distributed widely in the range between 0.5 and $5\mu\text{m}$. The morphology of particles was irregular.

(2) Composition and morphology of contamination particles

Table 4 shows the number distribution of contamination particles against their major components. Among 69 contamination particles detected, 31 particles (45%) were silicate, which were composed of Si and O, 28 were carbonaceous particles (41%) with Si and Cr as minor constituents, and 10 were miscellaneous particles (14%) which were composed of Cu, Cr, Fe and Ni as major components. Figures 4A-4K show their representative SEM images.

The morphology of most silicate particles (4A-4D) indicates the presence of

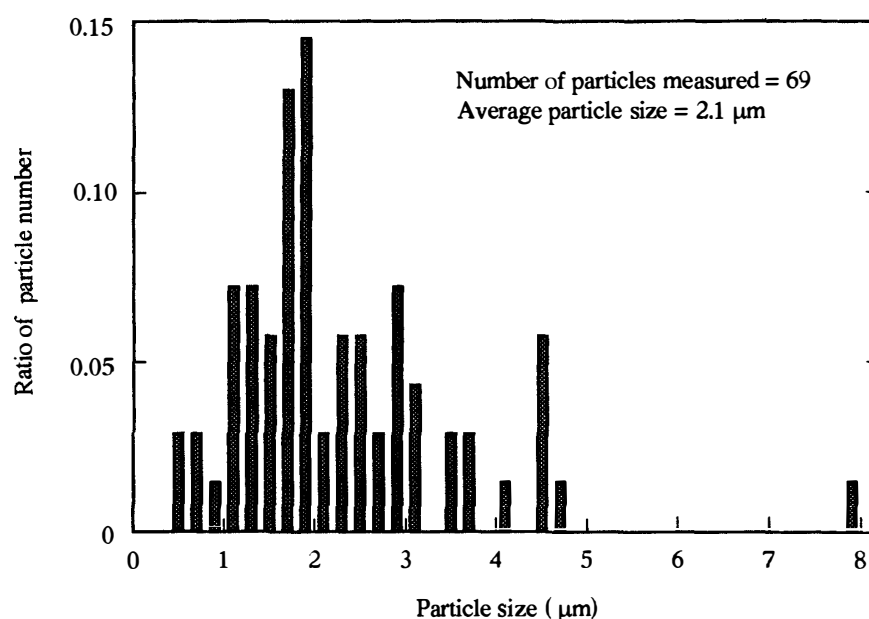


Fig. 3. Size distribution of contamination particles.

Table 4. Distribution of contaminated particles against major components in 20 measurements.

Main component	Si	Carbonaceous	Miscellaneous
Number of particles	31	28	10
Percentage	45	41	14

quartz, cracked silicate minerals and colloidal silica, which might originate from the instruments used. However, neither particulate aerosol matter nor clay mineral particles containing Al, Ca, Mg, K or Fe were found. Figures 4E–4G show carbonaceous particles containing trace Cr, Si and S, which are suspected to be organic particles from the filter or other artificial sources. Particle 4H is an aggregation of alumina particles ($150\text{ nm}\phi$); particle 4K is a metallic copper particle. These particles are suspected to be contamination from the vapor-deposition apparatus or electron microscope. Neither bioparticles nor ceramic particles from the knife material were observed. A carbon coating technique is often used for EDX measurement but gives too many contamination particles. Therefore, Pt-Pd vapor-deposition was adopted.

3.2. Distribution of filtered hematite particles on a Nuclepore membrane filter

For estimation of the total number of collected particles on a filter, it is important to apply the method of filtration homogeneously on the filter surface. Pressure filtration was compared with suction filtration using monodispersed hematite particles observing the numbers of collected particles from the center to the rim.

Figure 5 shows distributions of hematite particles on a filter from the center to the rim after pressure filtration. The experiment was carried out four times. The ordinate indicates the ratios of detected number of particles in an observation area ($30\mu\text{m} \times 4\text{ mm}$) on a filter to the sum for 14 observation areas. Total numbers of particles

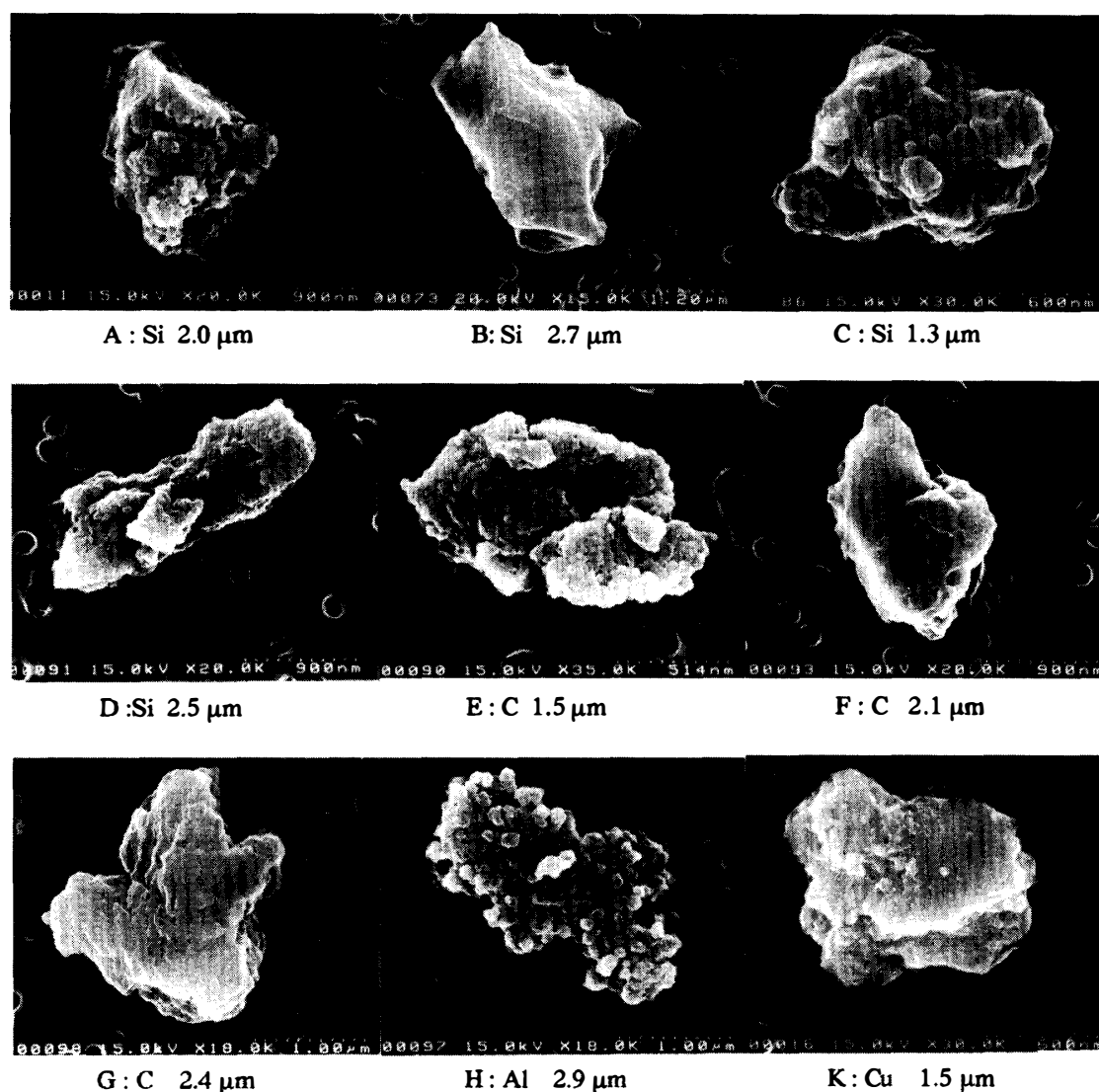


Fig. 4. SEM images of typical contamination particles. A–D: silica particles, E–G: carbonaceous particles, H, K: miscellaneous particles.

observed in 14 observation areas in each experiment were 7556, 7163, 7405 and 7725, respectively. Thus, the mean number of total particles in an observation area was 533 with relative standard deviation of 0.11. This shows that the hematite particles are evenly distributed on the surface of a filter. When suction filtration was applied, number of particles distributed in the center (No. 1–9), 12–60% higher than those in the same area around the rim (No. 10–14) with relative standard deviation of 0.25 as shown in Fig. 6. Based on these results, the pressure filtration method was applied in the main study.

3.3. Number and size distributions of microparticles in the Mizuho ice core

In a cold room of the National Institute of Polar Research, contaminated surface layers of three Mizuho ice samples, M1–M3, were removed (step #5 in Table 2) and

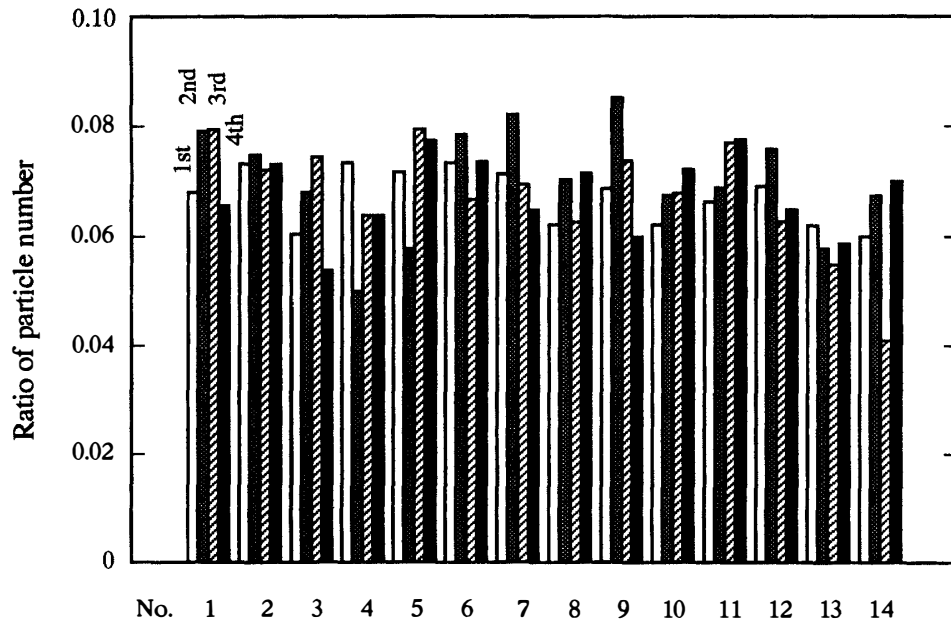


Fig. 5. Distribution of hematite particles in 14 observation areas ($30\mu\text{m} \times 4\text{mm}$) from center to rim of filter by pressure filtration. Total number of hematite particles observed at each experiment: 1st experiment; 7556, 2nd experiment; 7163, 3rd experiment; 7405 and 4th experiment; 7723.

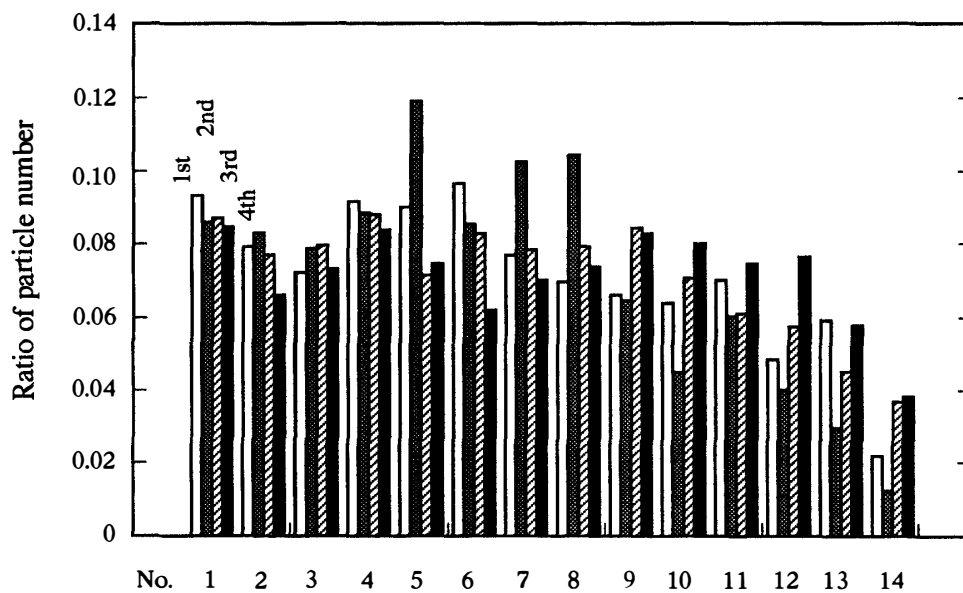


Fig. 6. Distribution of hematite particles in 14 observation areas ($30\mu\text{m} \times 4\text{mm}$) from center to rim of filter by suction filtration. Total number of hematite particles observed at each experiment: 1st experiment; 6375, 2nd experiment; 3336, 3rd experiment; 3827 and 4th experiment; 5410.

their sample weights were measured as shown in Table 5. Pieces of about 50 g were cut from samples M1 and M2 with a ceramic knife and melted at room temperature on a clean bench. 10 mL of melt water was filtered under pressure.

In this experiment, Mizuho samples M1 and M2 were treated by the procedures in Table 2. However, because the experiments were in the initial stage, the second surface layer removal with a ceramic knife was not carried out. The experiments in 3.1 revealed the existence of contamination of 13 particles in $520\mu\text{m} \times 320\mu\text{m}$ on a filter. All of the steps in Table 2 were applied to M3.

Table 5 shows the results for numbers of microparticles in Mizuho ice core samples M1–M3 in an observation area of $520\mu\text{m} \times 320\mu\text{m}$ (0.17mm^2) on the filter. For M1, three repeated experiments for filtration gave 132, 140 and 150, which contained the contamination value of 13 caused from omission of the second surface removal (Case 4 in Table 3). M2 gave a value similar to that for M1. For M3, for which surface

Table 5. Particle number in Mizuho ice core.

Sample	Weight in Proc. #4 (g)	Weight in Proc. #11 (g)	Weight of filtrated solution (g)	Particle number ^{a)}	Corrected particle number/10 g ^{b)}
M 1	161.1	—			
M 1-1			8.6	132 ^{c)}	145
M 1-2			9.9	140 ^{c)}	133
M 1-3			9.9	150 ^{c)}	143
M 2	178.0	—	9.9	150 ^{c)}	143
M 3	198.2	63.0 ^{d)}	10.9	115 ^{e)}	105

^{a)} Observation area of $520\mu\text{m} \times 320\mu\text{m}$.

^{b)} Calculated value subtracted number of contamination particles.

^{c)} Measured without the second surface layer removal. Numbers contained 13 for contamination particles (as shown in Table 3, case 4).

^{d)} A piece of 86.1 g was cut from 198.2 g ice core sample after treatment.

^{e)} Twice removals were carried out, contained 4.5 of contamination particles.

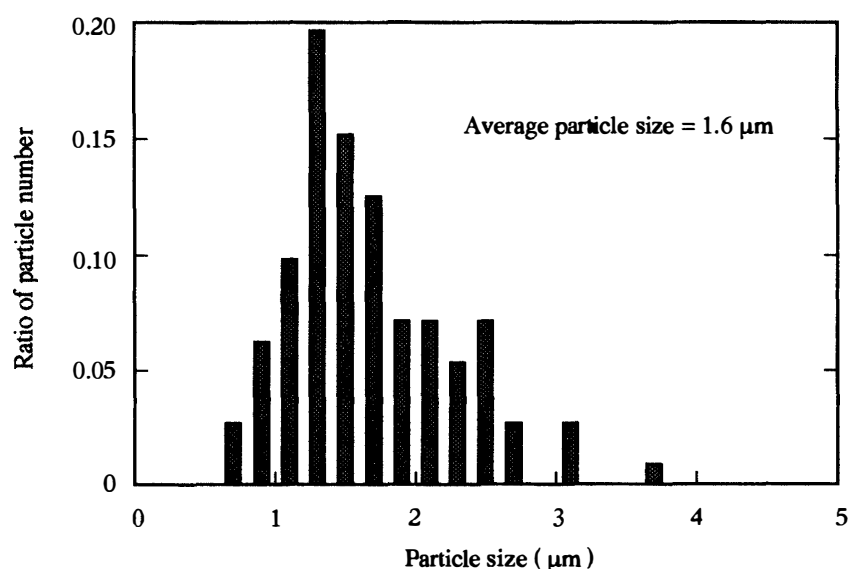


Fig. 7. Size distribution of 115 particles contained in the Mizuho core sample M3 (384.00 m–384.11 m in depth) of 10.9 g.

removal was performed twice, the obtained result was clearly decreased. It still includes 4.5 particles from the filter (Case 3 in Table 3).

Figure 7 shows the distribution of particle size in sample M3 for 115 particles. The mean diameter of these particles was $1.6\mu\text{m}$; they varied from $0.6\mu\text{m}$ to $3.7\mu\text{m}$. The mean diameter of those in samples M1 and M2 was not measured but the size distribution was similar to that of M3. Several particles with diameters of $5\text{--}6\mu\text{m}$ were found in samples M1 and M2. From these results, the total number of particles in the core sample M3 can be estimated to be $4700\pm 520/\text{g}$ of the sample.

3.4. Elements in particles in Mizuho ice core sample M3

115 particles obtained from M3 with EDX spectra were classified as follows: Type

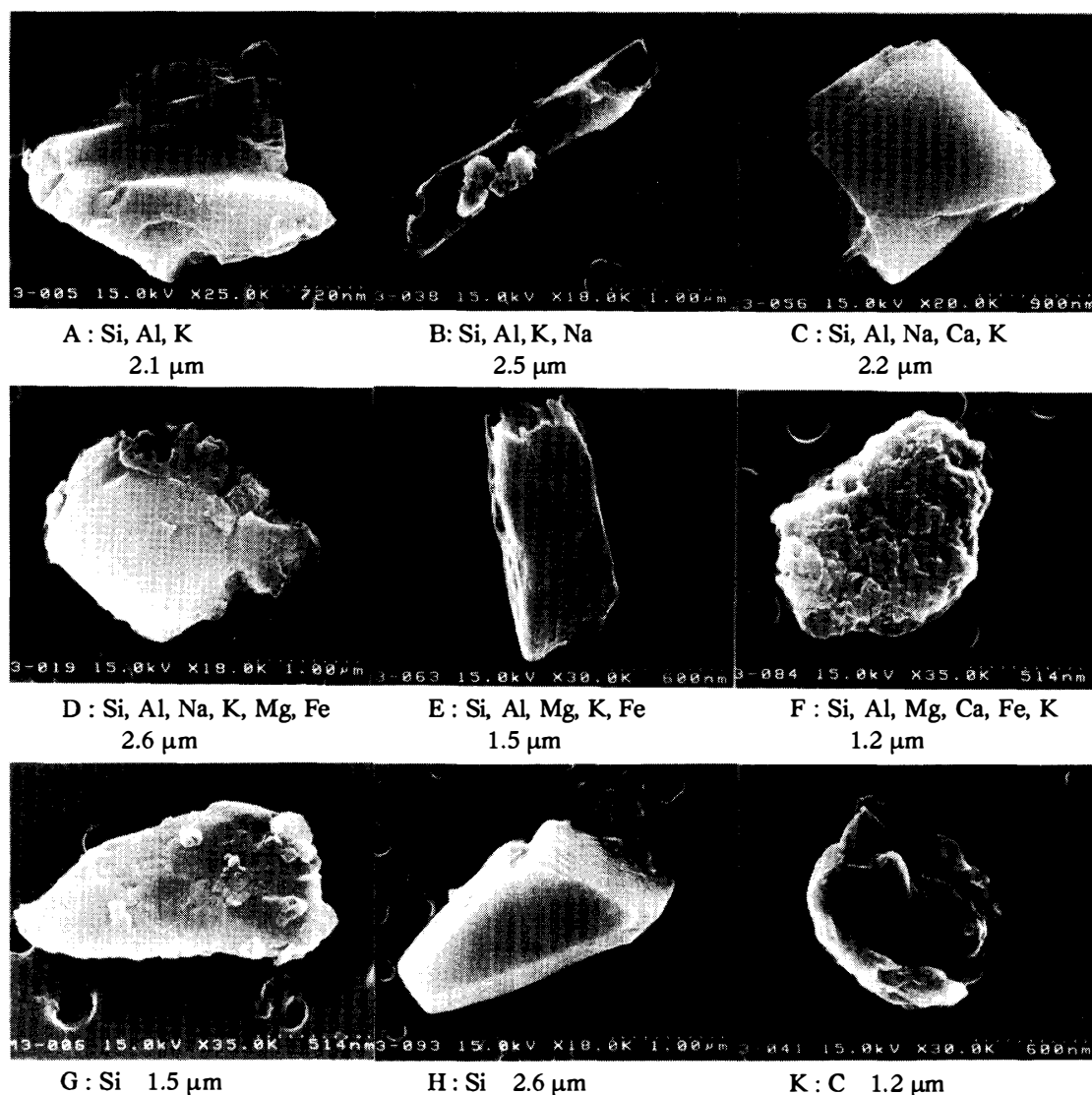


Fig. 8. SEM images of typical microparticles detected in the Mizuho ice core specimen, M3. A–F: silicate particles, G, H: silica particles, K: carbonaceous particles accompanying trace of Si, Al and Fe.

A containing Si, Al and K as major components (77%); Type B mainly Si (20%); and Type C, carbonaceous (3%). Figures 8A–8K show the representative morphologies of these particles. Particle 8A consists of Si, Al and K and is estimated to be potassium feldspar or illite. Particles 8B and 8C consist of Na and Ca together with Si, Al and K which suggest being soda potassium feldspar or plagioclase. Particles 8D–8F with different morphology from particles 8A–8C were suspected to be biotite with Si, Al, K, Fe, Mg, Na and Ca. Particles 8G and 8H with Si might be silica. Particle 8K is carbonaceous with trace Si, Al and Fe. These 3 particles (8G–8K) might be contamination particles.

Among particles in the sample, 97% of particles were of minerals. Assuming that all particles are globular with a density of 2.5 g cm^{-3} as those of feldspar minerals, the concentration of solid particles in this core sample can be estimated to be 30 ppb, which is slightly higher than that of solid minerals (10–20 ppb) in drifting snow collected at Mizuho Station in 1982 (Fujii and Ohata, 1982) and that of silicates (2–12 ppb) in surface snow on Mizuho plateau in 1978 (Murozumi *et al.*, 1978).

4. Conclusions

A reliable evaluation procedure for solid microparticles in ice core samples using pressure filtration and SEM observation has been established. Particles contaminated during two surface layer removals on a clean bench, melting, filtration and loading to SEM-EDX apparatus were silicates and carbonaceous particles with an average diameter of $2 \mu\text{m}$. The average contamination for 4 measurements was 4.5 for a measurement under $520 \mu\text{m} \times 320 \mu\text{m}$ view area, which is equivalent to 4% of the total number of solid particles in Mizuho core samples. The main sources of contamination were (1) from the core surface through incomplete removal and from ambient air during treatments under open air, (2) from exposure to open air, especially Pt-Pd vapor-deposition on a filter, (3) from exposure to open air for setting samples for SEM, and (4) from particles with irregular forms originating from the Nuclepore membrane filter. The contamination can be decreased with the improvement of instruments and working atmosphere. Although the proposed method is not efficient, it gives reliable results because of the decreased contamination.

115 particles were observed in a view area of $520 \mu\text{m} \times 320 \mu\text{m}$ for the ice core piece M3 taken at the depth 384.00 m–384.11 m at Mizuho Station. The average diameter of the particles was $1.6 \mu\text{m}$ and the number of particles per gram of the sample was 4700 ± 520 . The 115 particles consisted of feldspar minerals (77%), silica (20%) and miscellaneous constituents (3%).

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