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Article

SEM Observations of Microparticles in Antarctic Ice Cores

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Abstract

Microparticles collected from melt water samples of deep ice cores retrieved at Mizuho Station and Advance Camp (AC) in East Queen Maud Land, Antarctica were examined under a scanning electron microscope (SEM), and their elemental composition data were obtained by the energy-dispersive X-ray spectroscopy (EDS). Many observed particles, mainly collected from AC are morphologically classified into 5 categories. These categories were explained with typical photomicrographs and also with EDS data. Comparative studies are carried out with the stratospheric microparticles catalogued in NASA Cosmic Dust Catalogues. In spite of morphological resemblance between the ice core particles and the stratospheric ones, most of the former were of terrestrial origin. One extraterrestrial particle of chondritic elemental composition was found, in addition to several spherical particles which look like Fe-rich siderolite.

Number concentration of microparticles counted on SEM micrographs of low magnification coincides well with that measured by the Coulter counter. Depth variation of the concentration does not show any significant modern anthropogenic effect on the firn of shallow depth. Rough estimate of the influx rate of extraterrestrial microparticles with sizes of 10 μm order derived from our data coincides with that derived astronomically or from the observations of stratospheric microparticles.

1. Introduction

Deep ice cores from Antarctic and Greenland ice sheets contain extensive records of paleoclimate and paleoatmospheric composition in the form of soluble and insoluble impurities, stable isotope variations of ice itself, and variations of gas concentration as CO^2 in air bubbles. The interpretation of these records from a global point of view requires parallel studies of them from various parts of the ice sheets.

Ice cores retrieved for the depth of 700 m at Mizuho Station in 1983 and 1984, and for 200 m at Advance Camp (abbreviated AC hereafter) in 1986 must be important data sources for such records, because any other deep or medium depth boring has never been carried out in the quadrant of 0°−90°E of Antarctica. General descriptions of the drilling of ice cores at Mizuho Station and of data analyses of the 700 m cores were given elsewhere (Narita *et al.*, 1988 ; Higashi *et al.*, 1988). Microparticle concentration, as well as electrical conductivity and stable isotope ratio ($\delta^{18}O$) was studied by Fujii and Watanabe (1988). They found that the overall increase in microparticle concentration at a depth interval of 240−440 m, coincided with the increase of electrical conductivity and the decrease of $\delta^{18}O$. This coincidence was attributed to environmental change in Antarctica which might had occured in the middle of the Holocene (3000−6000 a BP). However, they could not make clear how the concentration change had occured. If we can identify origins of microparticles through their physical and chemical properties, it will be useful for making clear mechanisms of the environmental changes in Antarctica.

In the above respect, several reports on microparticles in Antarctic and Greenland ice cores have been recently published. Gaudichet *et al.* (1986) investigated the mineralogy of microparticles from Dome C ice core samples by using an analytical transmission electron microscope. They examined 225 particles from 6 depths between 246 m and 838 m, which cover well from the Holocene period to the period before the Last Glacial Maximum. They found that mineralogy of particles were all mixed at every depth, and concluded that no specific source of particles could be identified, although supposed to be mainly aeolian terrigenous origin. The particles in Vostok ice core were also analysed mineralogically (Gaudichet *et al.*, 1988). Results of analyses were compared with those of Dome C ice core, for identifying source areas of microparticles. In view of a little uncertainty of their conclusion that the major source of Vostok dust over the last 160 kyrs has probably been South America, they claimed that further analyses must be performed on new ice cores recovered in other Antarctic areas.

In Greenland, Maurette *et al.* (1986) found a large quantities of cosmic dust grains from the blue ice lakes formed on melting surface of the ice sheet. They sieved the sediment from the lake bottom to collect microparticles larger than 100 μm in diameter. Abundant spherical black particles were collected, and examined by scanning electron microscopy. Although the origins of particles on the ice sheet are still uncertain, a large amount of these microparticles (named cryoconite) were identified as extraterrestrial (Maurette *et al.*, 1987). They claimed that these particles are micrometeorites, not ablation products of larger meteorites. Besides this splendid discovery, there are a few studies on microparticles in ice cores from Greenland ice sheet. One of the limited numbers of work which have ever been undertaken, is now to be published in this same volume (Kumai and Langway, 1990).

In this paper, we present some results of scanning electron microscope (SEM) observations of microparticles contained in ice cores, both of 700 m from Mizuho Station and of 200 m from AC in East Queen Maud Land. Although the 700 m cores were first examined, the observations were rather limited with several spotty samples from 337 m, 402 m and 601 m depths. The results in this paper are mainly obtained from the 200 m cores at AC, although some interesting photographs are to be shown with particles from Mizuho cores.

Number of microparticles per unit volume of ice was evaluated by the counting on SEM photographs of low magnification. Depth profile of the number density of microparticles thus obtained could be a chronological record of environment change as that obtained from measurements by a Coulter counter.

SEM photographs of high magnification gave various morphology of the particles, and they were compared with those of various particulate materials, that can be found in some Particle Atlases, NASA Cosmic Dust Catalog etc. Since the shape and surface features of microparticles should reflect their origins and history during they were transported to Antarctica and subjected to weathering on or in the ice sheet, it is valuable to study the morphology from SEM photographs.

Some selected particles were also examined by the energy dispersive X-ray spectroscopy (EDS), for elemental composition analysis. This analysis provides information on the mineralogy of the particles. Because of insufficient quantitative EDS data, the EDS charts were only compared with those in Cosmic Dust Catalogs, which contained data not only for cosmic but for terrestrial dusts.

2. Methods

2.1 Samples

The Mizuho 700 m depth core was drilled in two winters of 1983 and 1984, and a 200 m depth core was retrieved in summer 1985 at Advance Camp (AC, 74°12′S, 34°59′E) by a traverse party aimed to reach a plateau at around 77°S and 35°E (see Fig. 1). Both the whole core were taken back to Tokyo, keeping them in a refrigerated storage of Japanese icebreaker "Shirase", although the upper part of the 700 m core came later than others, after keeping in Mizuho for 2 years. In Tokyo, they are kept in a cold storage of the National Institute of Polar Research (NIPR).

Ice samples were cut from a vertically half-cut 50 cm long ice cores from different depths. One sample had approximately 5 cm thicness which roughly corresponded to one year accumulation of ice at the boring site. However, since the stratigraphy of ice was quite disturbed on the ice sheet around both drilling sites because of the strong catabatic wind, this sample is not necessarily an annual layer of ice deposition. It is rather a mixed deposition for a few years, sometimes including interrupted annual layers (Watanabe, 1978 ; Fujii and Ohata, 1982). Twentyone sam-

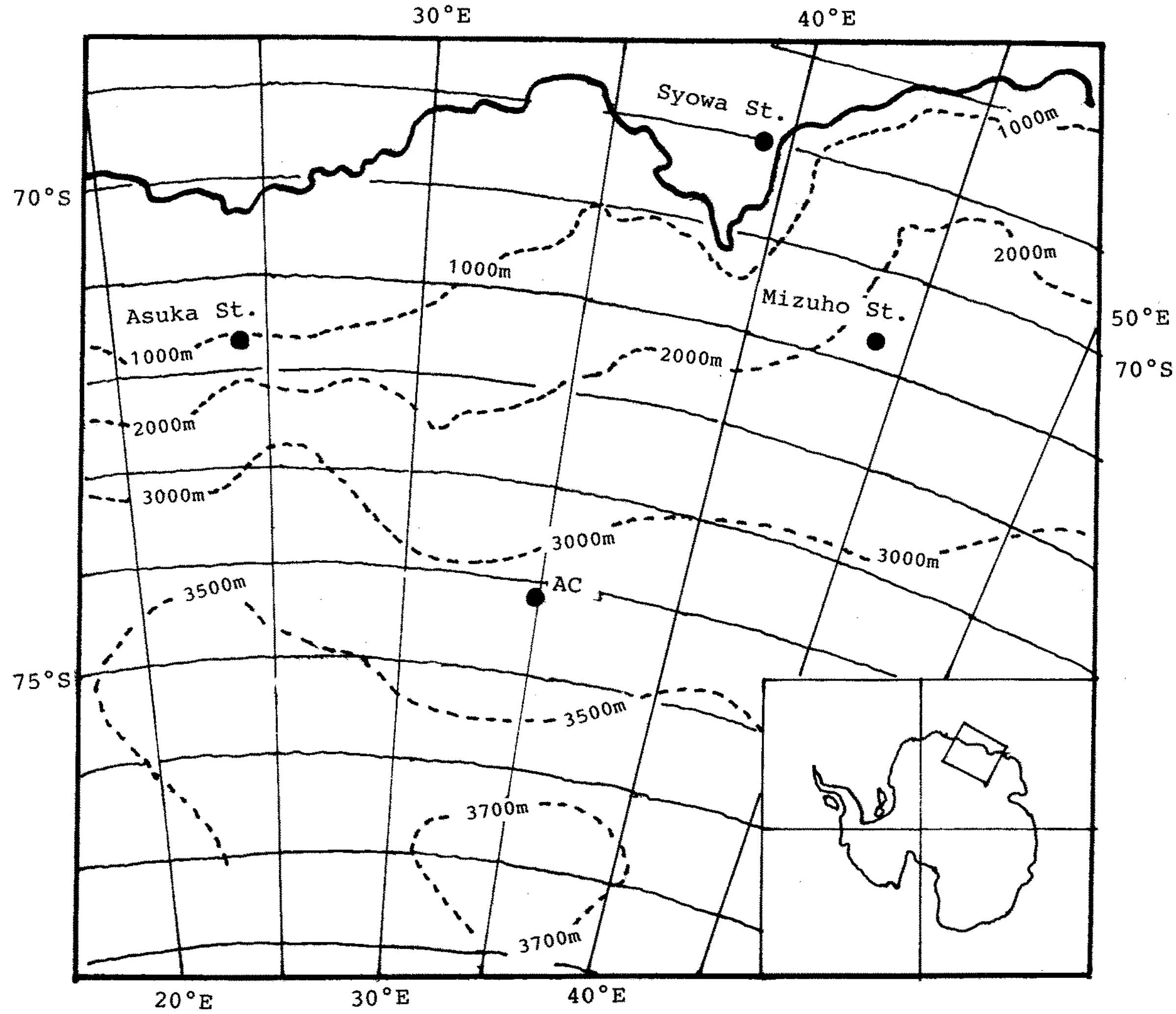


Fig. 1. Boring sites of ice cores in East Queen Maud Land, Antarctica.
Mizuho Station (70°41'S, 44°19'E)
Advance Camp (74°12'S, 34°59'E)

ples were cut from cores of appropriate depths, at 10 m intervals from the top to the bottom of 200 m cores at AC. In view of the depth-age relationship of ice (see Section 4), 10 m interval corresponds approximately 100 years. Three samples, from approximately 337 m, 402 m and 601 m of the Mizuho core were used for a preliminary study.

Only the inner part of every individual ice sample was used to avoid the surface contaminants. Removing the near-surface portion by melting, and rinsing in the melt water, then in clean distilled water, the ice sample was placed in a sterile teflon container and melted in a microwave oven. The melt water of approximately 150 cm^3 was divided into three parts ; 15 cm^3 for counting microparticles with a Coulter counter, 30 cm^3 for electrical conductivity measurement and stable isotope ($\delta^{18}O$) analysis, and remainder of approximately 100 cm^3 for major chemical composition analysis. Methods for measuring the microparticle concentration with a Coulter counter, and for the electrical conductivity were described elsewhere (Fujii and Watanabe, 1988). The last part was filtered through a Nuclepore filter (0.6 μm pore size) using a vacuum suction funnel, and solid microparticles with sizes larger than 0.6 μm were collected on the filter. These procedures were carried out in a class 1000 clean room of the NIPR.

The filters were transported to the electron microscope laboratory of International Christian University (ICU) for examination. Then they were cut into approximately 1 cm diameter circular shape to fit on specimen holders of the SEM (JEOL, JSM -T220). The surface of specimens attached to the holders with adhesive tapes was spatter-coated with Au or C, and periphery of the surface was fringed with conducting graphite paste.

2.2 SEM observations and EDS

Size of microparticles observed by the SEM can be measured easily on phtomicrographs. Generally, the particle size was in a range between several μm and several tens μm. The number concentration of the particles in unit volume of the melt water of ice was converted from the areal concentration measured on photographs of low magnification, according to an equation below. Adopted unit for the concentration here is the number of particles in 0.05 ml of the melt water, the same unit customarily used for the Coulter couter measurement.

$$N=0.05\ mS/sv \qquad (1)$$

where m is the number of particles in a photograph of area s, and S is the area of Nuclepore filter through which v ml of water was infiltrated.

The morphology of microparticles was examined by SEM photographs of high magnification ($\times$3,500–10,000). Details of the method of morphological classification is given in the next section. The energy dispersive X-ray spectroscopic (EDS) analysis was carried out by using apparatus JED-2000 at first and later QX200J both in a laboratory of JEOL. Because of limited machine time, only some selected particles were analysed. Abbreviation EDS is used hereafter, either for the method of the spectroscopy, or for the individual spectrum (spectra) as will be shown in Figs. 3–12.

3. Results of Observations

3.1 Size and concentration of microparticles

Concentrations of the microparticles in ice samples from various depths at AC, evaluated by the method described in the preceding section, are tabulated in Table 1, together with those obtained by the Coulter counter with the same samples. As can be

Table 1. Concentration of microparticles, number in unit volume (0.05 ml) of the melt water of ice samples from different depths, at Advance Camp.

Depth (m)	Counted from SEM photograph			Counted by Coulter counter		
	A, Total	B, >1μm	B/A %	A, Total	B, >1μm	B/A %
0	1326	535	40.3	1893	702	37.1
10	1474	479	32.5	1284	441	34.3
20	1727	491	28.4	1707	495	29.9
30	1443	373	25.8	3201	720	22.5
40	975	254	26.1	642	179	27.9
50	1691	474	28.0	1388	384	27.7
60	1345	344	25.6	1339	435	32.5
70	1498	545	36.4	1709	428	25.0
80	1218	222	18.2	1192	294	24.7
90	216	45	20.8	848	225	26.5
100	498	223	44.8	859	257	29.9
110	761	215	28.2	437	153	35.0
120	707	236	33.3	472	180	30.9
130	693	243	36.1	632	195	30.9
140	504	194	38.6	326	118	36.2
150	467	138	29.6	1354	456	33.7
160	353	127	36.0	347	120	34.6
170	1213	466	38.4	294	111	37.8
180	256	83	32.4	321	112	34.9
190	477	149	31.2	876	251	28.7
200	334	80	24.0	548	179	32.7

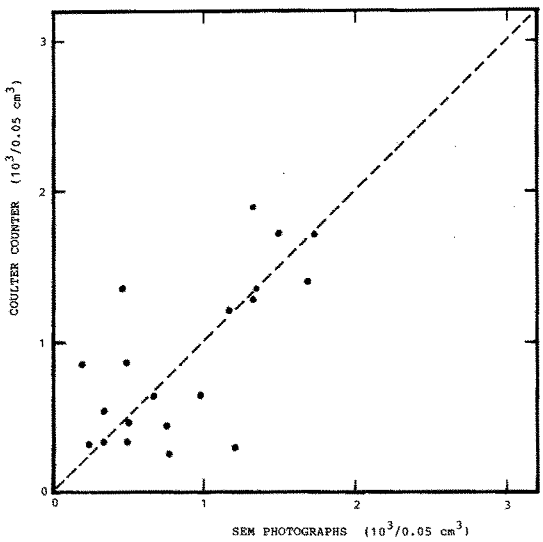


Fig. 2. Relationship between number concentrations of microparticles measured by the SEM and the Coulter counter.

seen in the table, the depth profile of the concentration measured by the SEM is almost parallel to that measured by the Coulter counter. The total concentrations are in the order of 1500/0.05 ml in the upper 80 m depth, whereas they decrease to the order of several hundred in the depth deeper than 90 m. Number ratio of concentrations of particles larger than 1 μm diameter to the total concentrations are also shown in the table by %, and they do not seem to change with depth, though they are little less in case of the Coulter counter measurements than those by the SEM. Relationships between the concentrations at each depth measured by the SEM and the Coulter couter are plotted on Fig. 2. Correlation coefficient between these concentrations is calculated 70%, if the data of 30 m, in which the Coulter counter concentration is exceptionally large, is omitted. This relationship gives a good proof for the reliability of the Coulter counter measurement.

One significant point in the data shown in Table 1 is that microparticle concentrations in the 0 m depth sample measured by either SEM or Coulter counter are almost the same as others above 80 m depth. Despite a different way of removing possible surface contaminants, only cutting down thin surface layer of compacted snow core sample, the sample did not show any singularity among the data. Implication of this point will be discussed later in Section 4.

3.2 Morphology and EDS Analysis of Microparticles

Although there are various shapes of microparticles observed by the SEM, the morphology are tentatively classified as in Table 2, irrespective of their elemental compositions. The morphology can be compared with that of natural terrestrial microparticles like volcanic ashes, clayish minerals and silica sands, which are found in various particle atlases. In this study, we compared our observed particles mainly with stratospheric dusts which have been compiled in many volumes of Cosmic Dust Catalog (abbreviated hereafter CDC ; NASA, 1982–1987).

The catalogs include many SEM photographs of microparticles collected by U-2 aircrafts in the strato-

Table 2. Morphological Classification of Microparticles in Antarctic Ice Cores.

Morphology (abbreviation)	Characters	Figure numbers shown in this paper
Sphere (S)	Complete sphere with smooth or rugged surface.	Fig. 3, Fig. 4
Micro-nodule (N)	Solid of round shape with smooth or wrinkled surface.	Fig. 5, Fig. 6
Aggregate of minute particles (Ap)	Sometimes fluffy.	Fig. 7
Aggregate of flat element (Af)	Sometimes exhibit compacted layer structures.	Fig. 8, Fig. 9
Sharply edged mineral fragment (M)	Polygonal mineral fragment with sharp fringes.	Fig. 10
Diatoms (D)	Fragment of diatoms, die or cylindrical shape.	Fig. 11

sphere. Although they are for distributing particles to investigators concerning origins of interplanetary microparticles, rough estimates of the origins as classified below are given, aided by EDS spectra attached to every SEM photographs. Our partial data of EDS were compared with those in CDC, for identifying qualitatively the mineralogy of particles and distinguishing them whether terrestrial or extraterrestrial origin.

The NASA Cosmic Dust Preliminary Examination Team (CDPET) classified the type of stratospheric microparticles into four categories, C, TCA, TCN and AOS. Although it claims that the classification is a provisional first order identification based on morphology, elemental composition from EDS spectra and optical properties, collective experiences of the CDPET provide reliable judgements on origins of the particles. Here, C represents cosmic dusts (particles of extraterrestrial origin). TCA means terrestrial contamination which is produced artificially, while TCN does terrestrial contamination natural which is originated from natural environments of earth's surface ; various rock minerals, volcanic ash and clay minerals. AOS (aluminum oxide sphere) is a specific particle, essentially classified as one of the TCA, which is produced from solid fuel rocket exhaust, extensive contaminants in the stratosphere since our rocket age.

Size range of particles included in CDC is almost the same as that of our observed microparticles. Morphology of particles also covers almost all found in our observations, with the exeption of artificially produced dusts. In the next several subsections, comparative studies of ice core microparticles with stratospheric microparticles are given in accordance to morphological classification tabulated in Table 2. Origins of the particles are only divided into terrestrial and extraterrestrial according to comparisons in morphology and EDS data, and sometimes are derived from comparisons of morphology found in other particle atlases.

3.3 Spheres, S

Fig. 3 (a) shows a SEM photographs of spherical particle found in 0 m firn sample, together with its EDS in right side. Since the sample was from the ice sheet surface, it was suspected that this might be industrial product like flyash. But, particles with the same surface features and with completely the same EDS (Fe peak only or with weak Ni peak) were found in 50 m (Fig. 3 (b)) and 110 m (Fig. 3 (c)) depths, where the ages of ice were estimated well before the industrial revolution (see Section 4). A spherical particle which exhibited the same surface features as shown in Fig. 3 was ever found at a depth of 1,194 m of the Byrd Station deep ice core (Thompson and Thompson, 1975). Therefore, spherical particles of this kind should not be industrial.

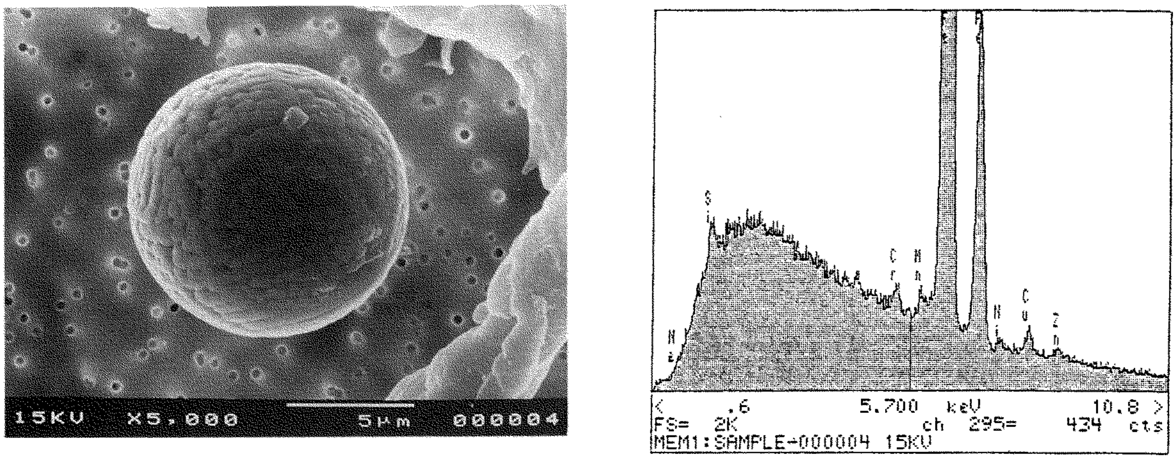
Although there are many spheres registered in the CDC, we can not find any exhibiting the same surface features like those in Fig. 3. EDS which exhibit strong Fe peaks with weak Ni peaks as shown in Fig. 3 were only found with W7029 A9 and W7029 C14 in CDC Vol. 2, No. 1, and with W7027 I6 in CDC Vol. 4, No. 2. Among the above 3 examples in CDC, the first and the third are spheres, but the surface features are not clear in photographs. The second one has an irregular shape which look like mineral fragment. The catalog designates both of W7029 A9 and C14 in type C with a question mark, and W7027 I6 definitely in type C. Therefore, we can conclude that the origin of our Fe-spheres must be extraterrestrial with some reservations, probably be named microsiderolite.

An interesting SEM photograph is Fig. 3 (d), which shows a fractured sphere with similar surface features as others in Fig. 3, and with the same character of the EDS spectrum. It may be inferred from this figure that the spheres of this type has a hollow in it.

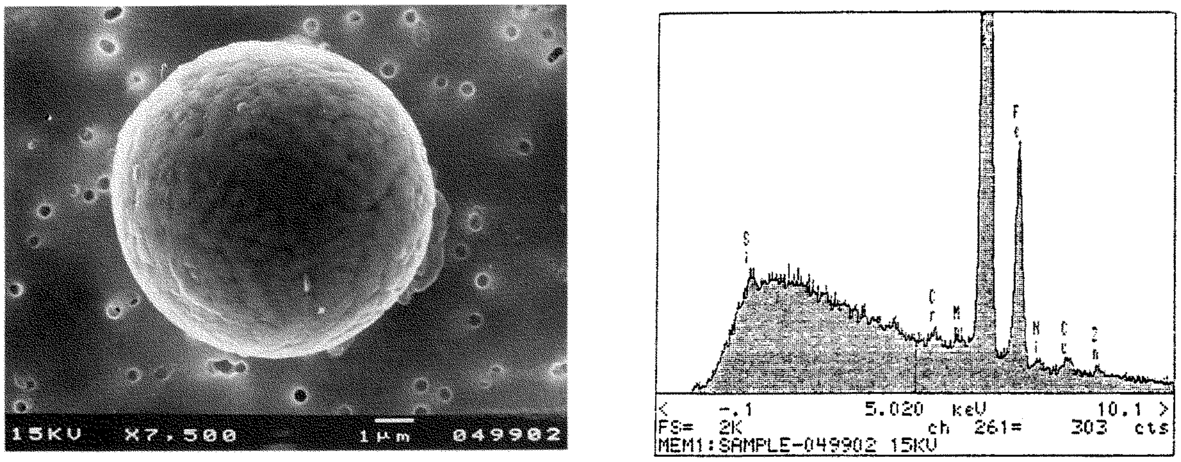
Spheres showing different elemental composition were found as shown in Figs. 4 (a) and (b). Particle (a) which seems to be cracked on smooth surface was found in 20 m depth ice, and particle (b) which shows rugged surface and a hollow in it was found in 120 m depth ice. EDS of these particles do not exhibit any significant peak, having commonly weak Al and Si peaks, with S and Ca in (a) and Fe in (b). They must be of terrestrial origin.

3.4 Micro-nodule, N

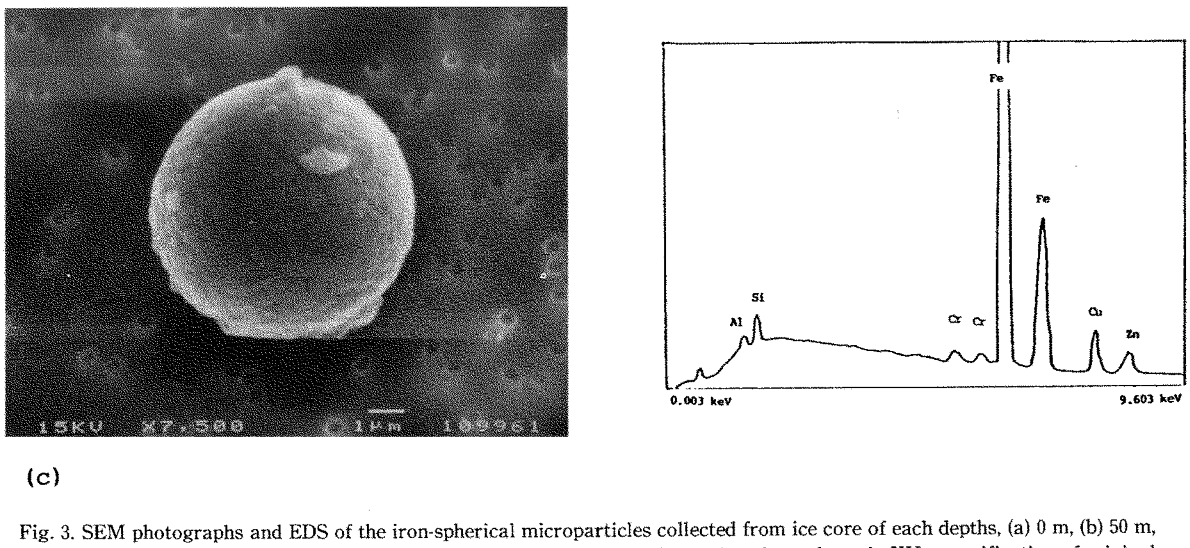
This category is given for microparticles which exhibit the solid round shape with smooth or wrinkled surface. Typical examples are shown in Figs. 5 (a), (b), (c) and (d). Both particles (a) and (b) were found in the firn of 0 m depth. It is often seen that minute particle fragments are attached on their surfaces. Extreme case is particle (c) from 110 m depth ice, of which surface seems to be covered by bead-like minute particles. Since particle (d) from 120 m depth ice looks like to have sharp ridges on the surface, this might be classified as an intermediate type between



(a)

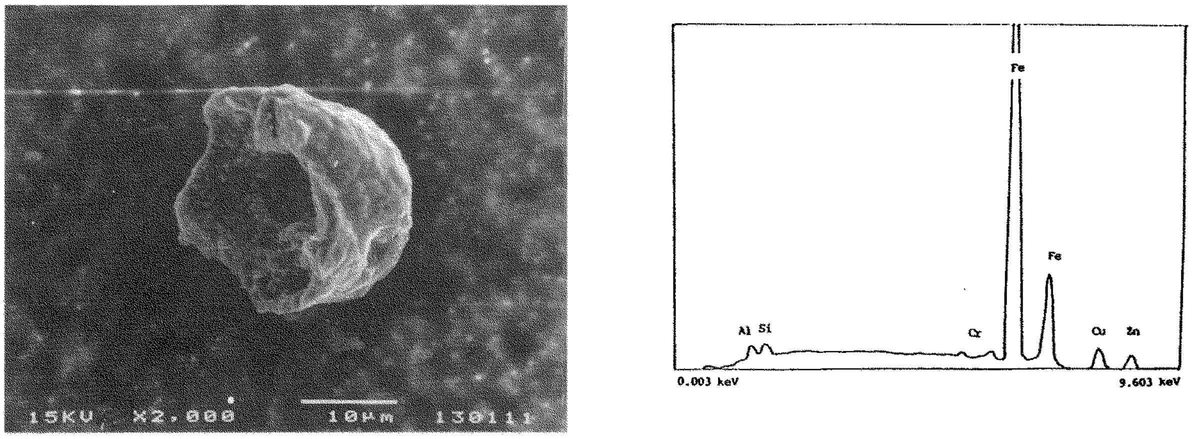


(b)

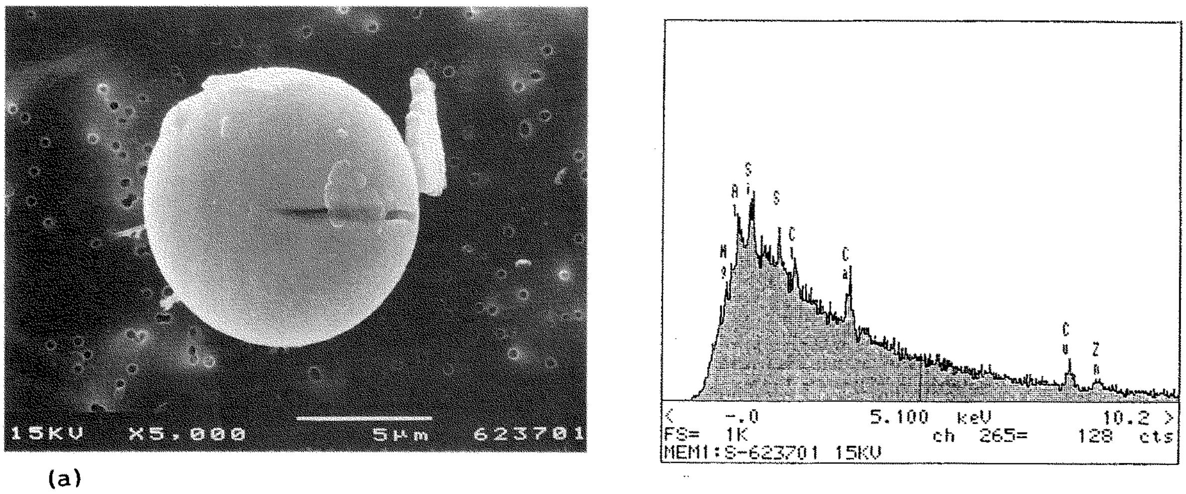


(c)

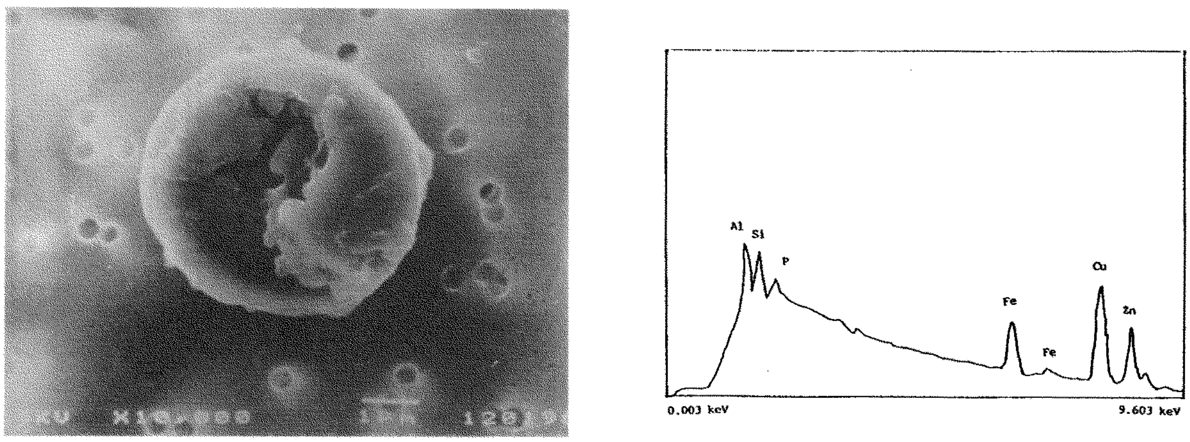
Fig. 3. SEM photographs and EDS of the iron-spherical microparticles collected from ice core of each depths, (a) 0 m, (b) 50 m, (c) 110 m, (d) 30 m. Numerals under each photographs are from left, acceleration voltage in KV, magnification of original image, bar corresponding 1 μm, 5 μm etc. as designated, and sample No. Photo (d) is above Fig. 4 in the next page.



(d)



(a)



(b)

Fig. 4. SEM photographs and EDS of the spherical particles with non-iron elements, (a) 20 m, (b) 120 m.

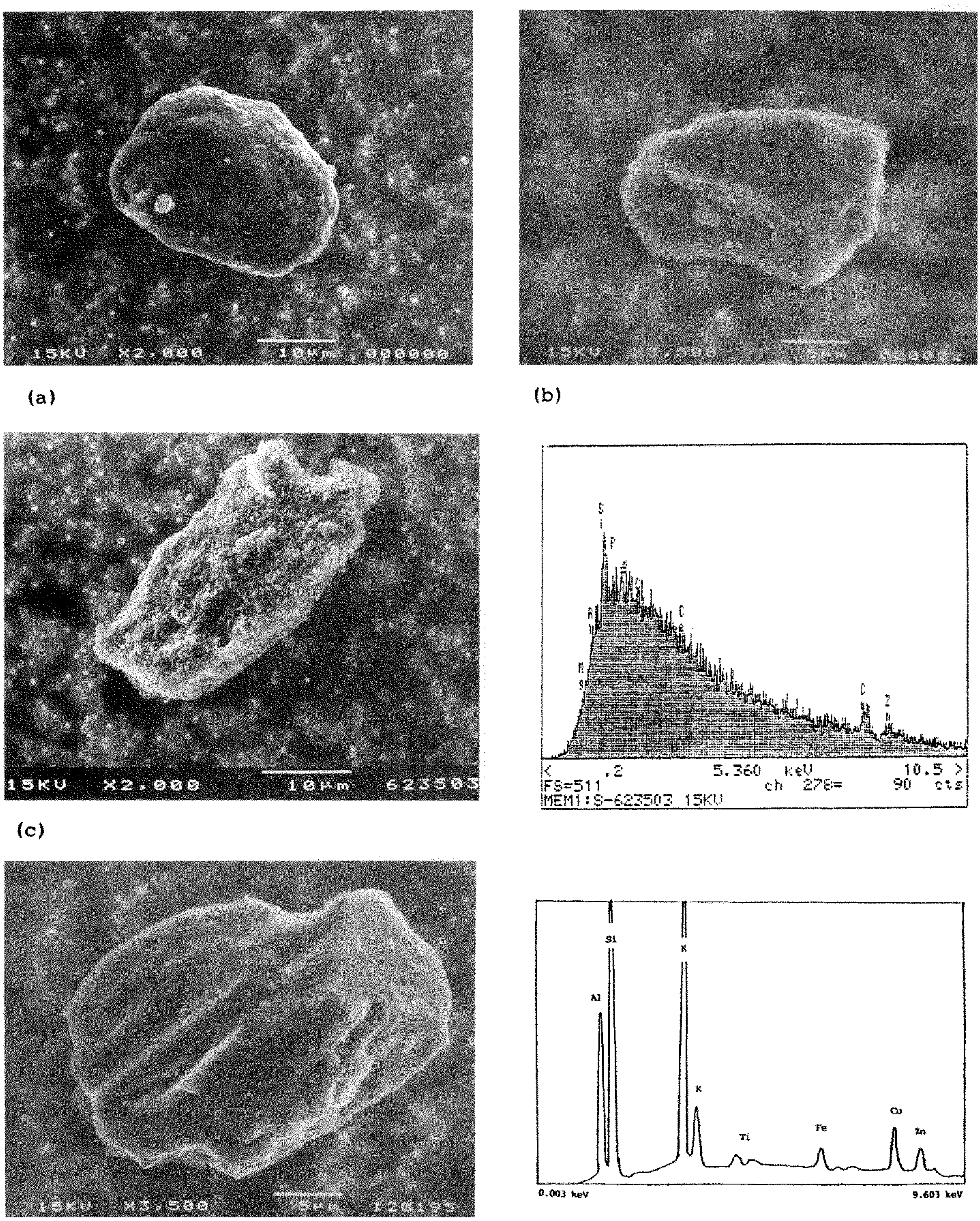
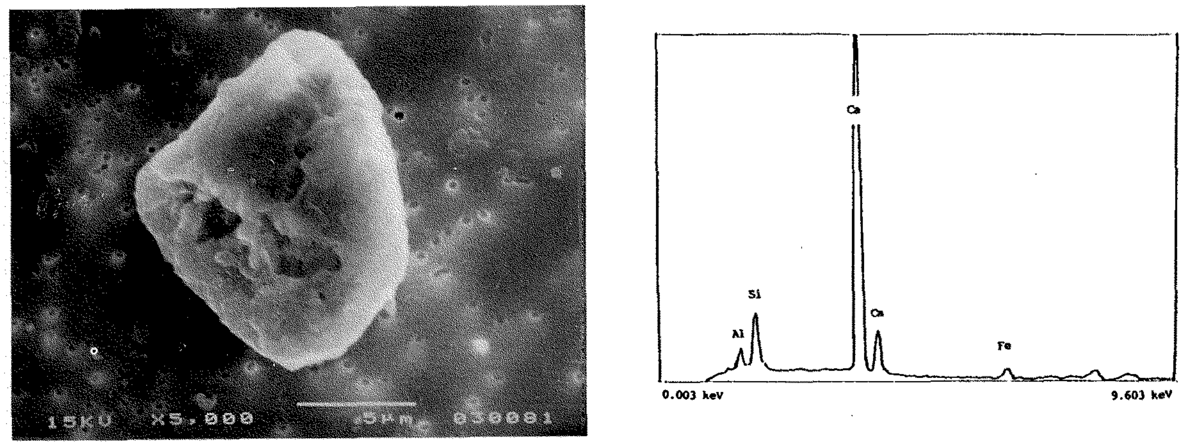
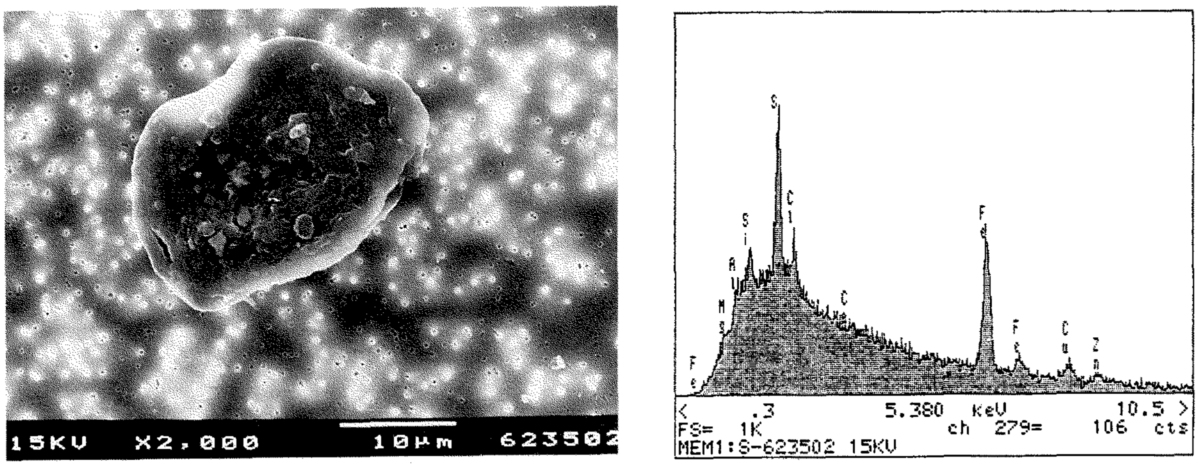


Fig. 5. SEM photographs of the micra-nodule and their EDS, (a) 0 m, (b) 0 m, (c) 110 m and (d) 120 m. No EDS for (a) and (b).



(a)



(b)

Fig. 6. SEM photographs and EDS of the micronodule, (a) Ca-rich from 30 m, (b) of extraterrestrial from 110 m.

the micro-nodule and the sharply edged mineral fragment (M), which will be described later in 3.7. EDS of particle (c) exhibits no significant peak, whereas that of particle (d) has significant peaks of Al, Si and K. These EDS spectra indicate that particles are both of terrestrial origin.

A microparticle in Fig. 6 (a), which was found in 30 m depth ice, exhibit very rugged surface but could be classified in this category, N. Attached EDS shows that the particle has high calcium content. Very similar EDS was found with a TCN particle U2034 A16 in CDC Vol. 9, No. 1. A smooth micronodule in Fig. 6 (b) has a characteristic EDS. Relative abundance of Fe and S against Si indicates that the particle is chondritic, corresponding EDS with the same character in U2023 B8 and 2022 E24 in CDC Vol. 7, No. 1. They are both designated in type C. Therefore, the particle in Fig. 6 (b) found in 110 m depth ice is definitely identified as extraterrestrial origin.

3.5 Aggregate of Minute Particulates, Ap

Microparticles of this type were often found, irrespective of the depth of ice. Particles with sizes of 10~20μm are composed of minute particulates of less than 1 μm size. Three typical examples are shown in Figs 7 (a), (b) and (c). EDS of particle (b) exhibits strong peaks of Al and Si, with weak ones of S, Ca and Fe, but no significant peaks besides weak ones of Al and Si appear in EDS of either particle (a)

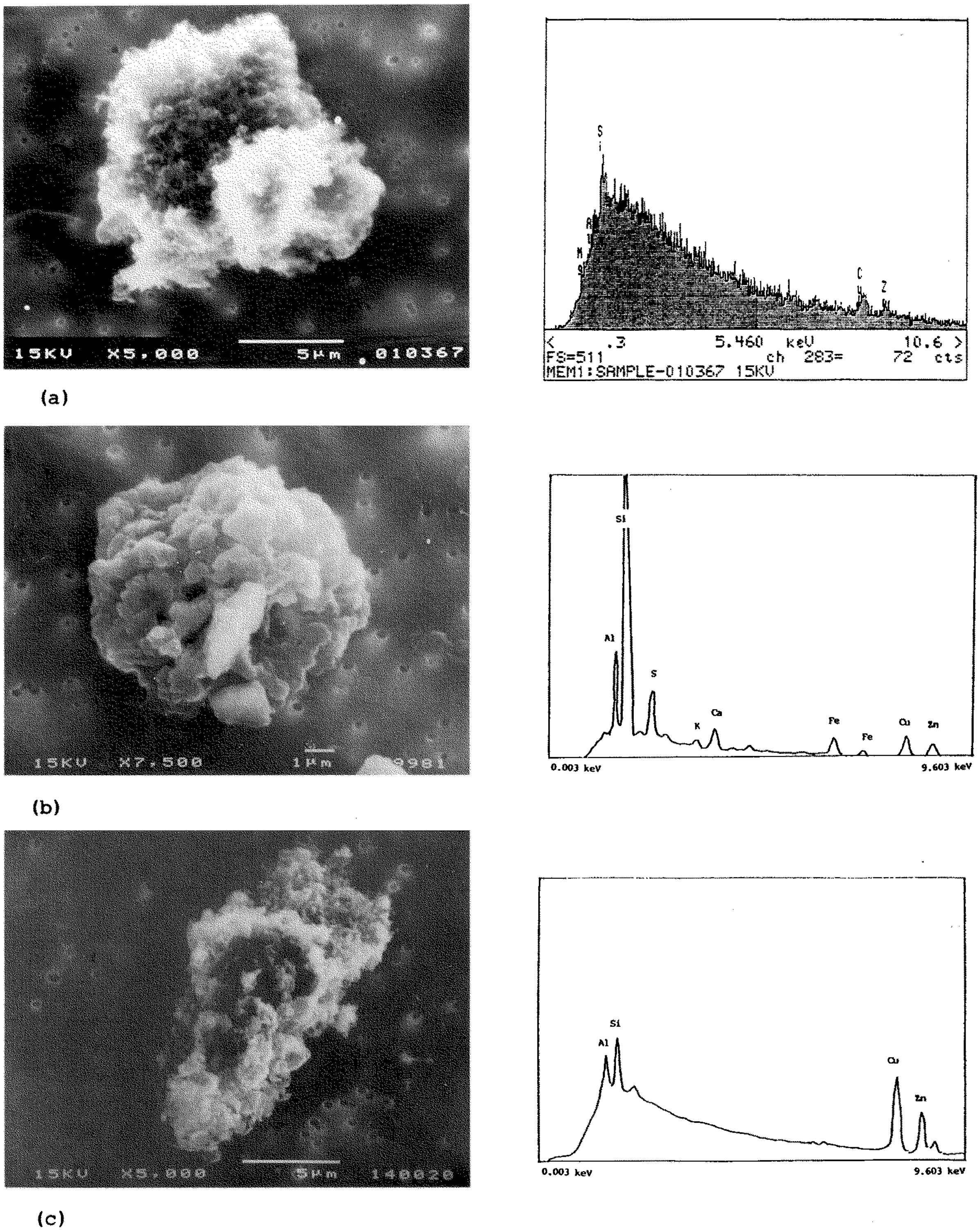


Fig. 7. SEM photographs and EDS of microparticles with the shape of aggregate of minute particulates Ap, (a) 10 m, (b) 40 m, (c) 140 m.

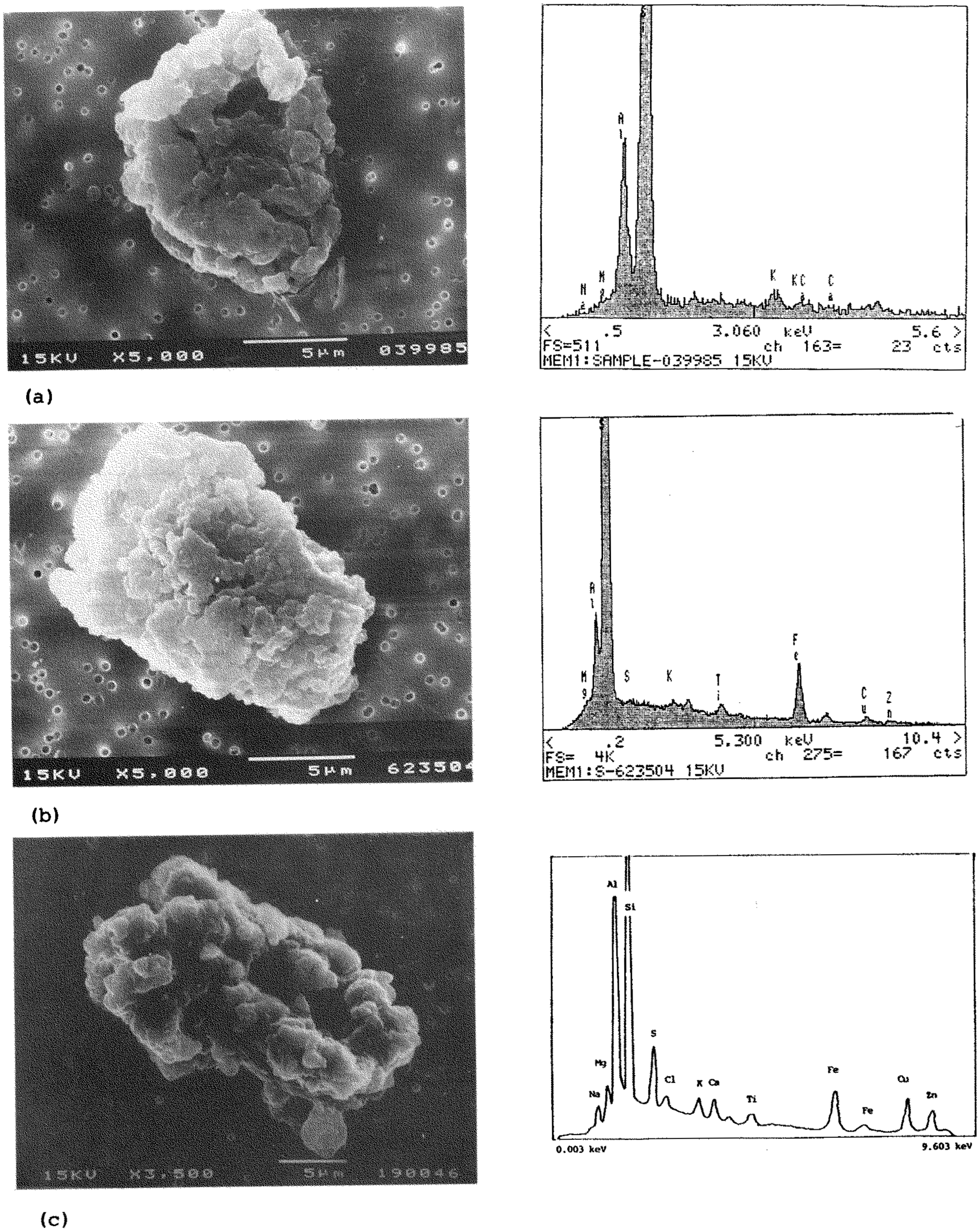


Fig. 8. SEM photographs and EDS of microparticles with the shape of aggregate of flat elements Af, (a) 40 m, (b) 110 m, (c) 190 m.

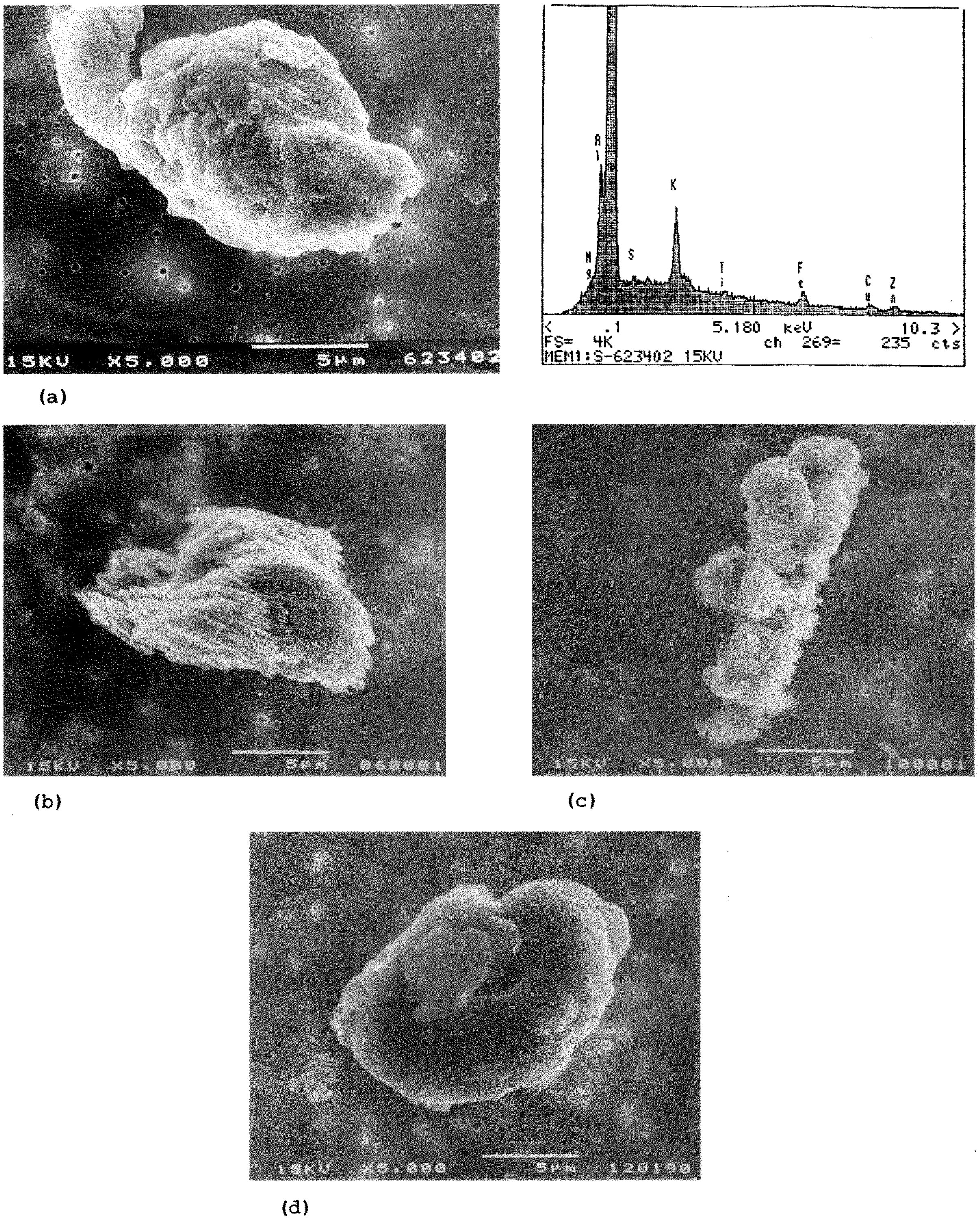


Fig. 9. SEM photographs and EDS of microparticles of the same shape Af as of Fig. 8, (a) 50 m, (b) 60 m, (c) 100 m, (d) 120 m. The last three have no EDS record.

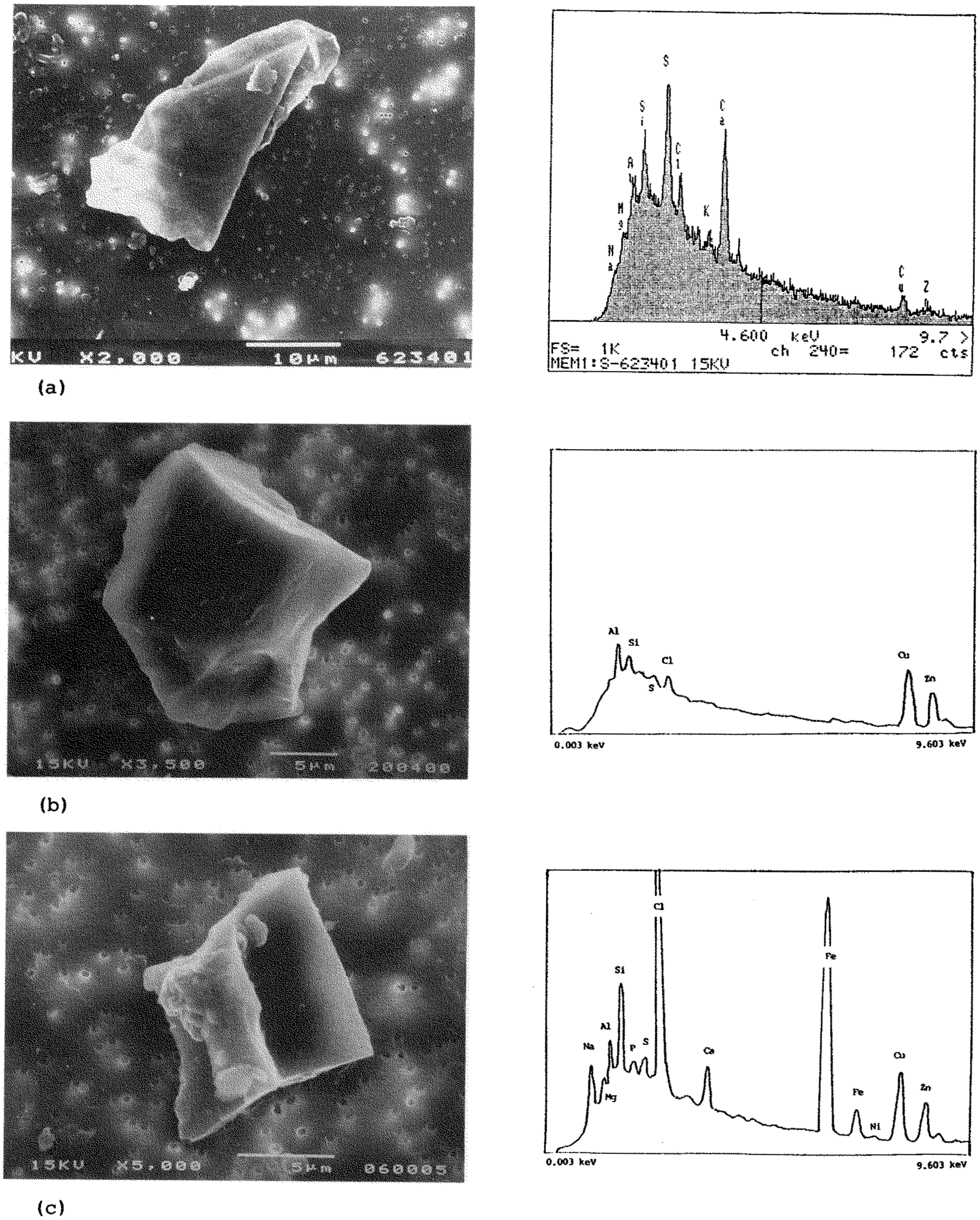
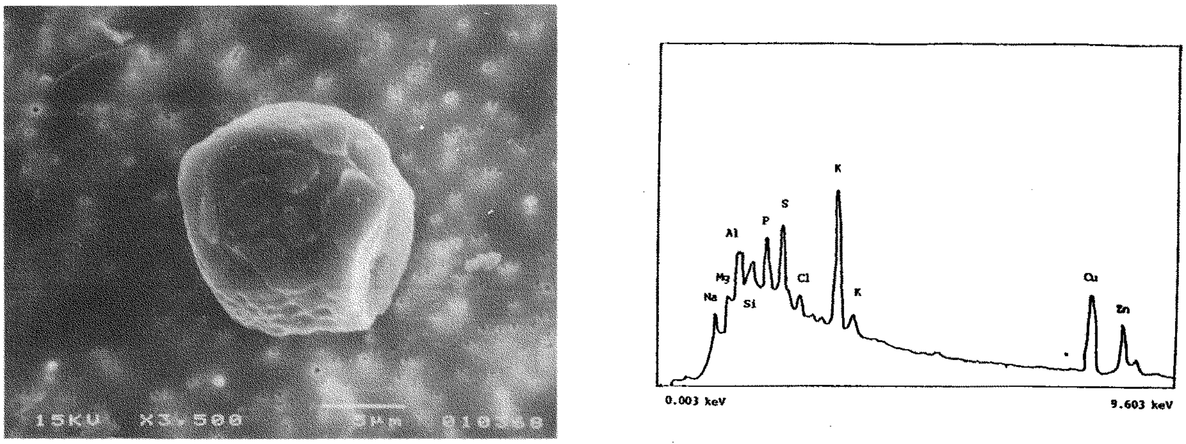
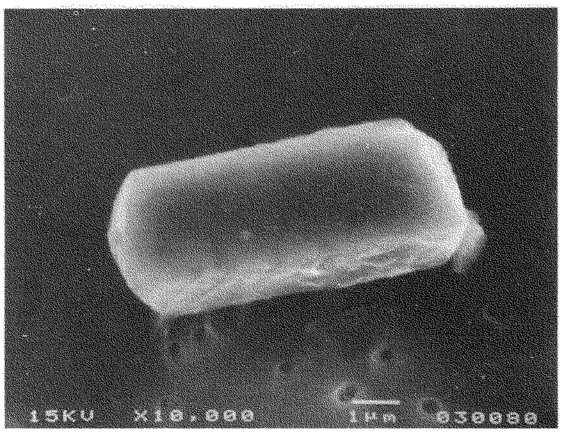


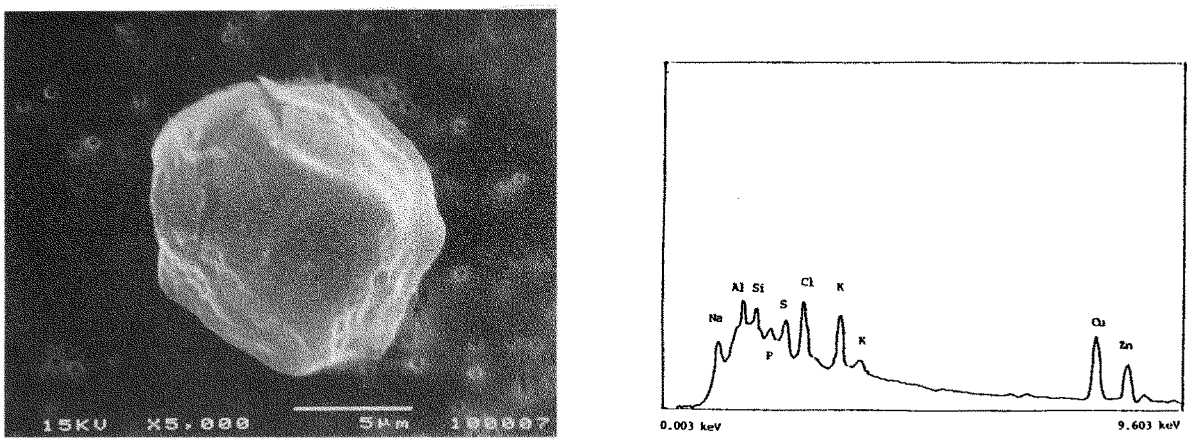
Fig. 10. SEM photographs and EDS of polygonal microparticles with sharp edges M, (a) 50 m, (b) 200 m, (c) 60 m.



(a)



(b)



(c)

Fig. 11. SEM photographs and EDS of microparticles considered as diatoms, (a) 10 m, (b) 30 m, (c) 100 m. No EDS for (b).

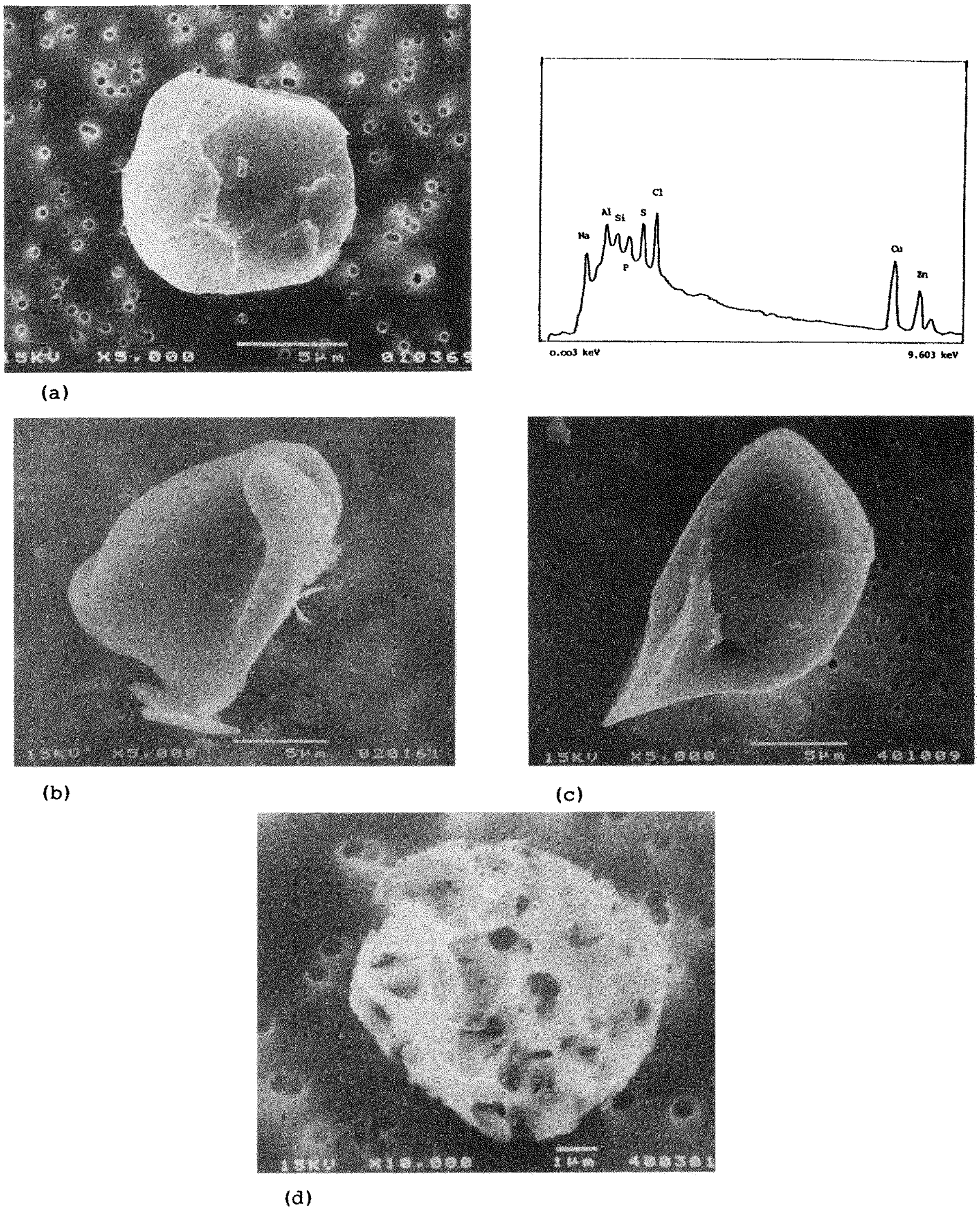


Fig. 12. SEM photographs and EDS of microparticles of special shapes, (a) Cabbage-like, 10 m, (b) drop-like tephra, 20 m, (c) drop-like tephra, 400 m Mizuho, (d) porous tephra, 400 m Mizuho. No EDS spectra were taken with the tephras.

or (c). Sometimes, this type of the aggregate shows fluffy features as can be seen in Fig. 7 (a). In the CDC, many C type particles have morphological features similar to this aggregate. However, judging from the EDS, particles in Fig. 7 are not in C type, but of terrestrial origin.

3.6 Aggregate of flat elements, Af

This type was also often observed in SEM photographs. Particles of sizes 10～20 μm are composed of minute flat elements with sizes of a few μm. Three typical examples, which were found in 40 m, 110 m and 190 m depth ice, are shown in Figs. 8 (a), (b) and (c), respectively. EDS of these particles all exhibit strong Si and Al, with some weak side peaks ; at K in (a), at Fe in (b), and at S, K, Ca and Fe in (c). Strong Si and Al peaks indicate that they are all terrestrial. Microparticles shown in Figs. 9 (a), (b), (c) and (d) are also classified in this category, although particles (a) and (d) seem to be intermediate between Af and N.

3.7 Sharply edged Mineral Fragment, M

Microparticles which have the polygonal shape surrounded by sharp edges were often found in our observations. Typical examples are shown in Figs. 10 (a) and (b), each of which from 50 m and 200 m depth ice respectively. EDS of (a) shows strong peaks of Si, S and Ca, while that of (b) shows no significant peak. Judging from the morphology and the attached EDS data, these particles are inferred to be clay minerals originated from the earth surface. A combined complex of M and Af is shown in Fig. 10 (c). EDS of this particle exhibits strong peaks of Cl and Fe besides Si, with minor peaks of Na, Al, S and Ca. No definitive inferrence on the origin of this particle can be given from either morphology or EDS, but the peaks of Cl and Na in EDS spectrum might be understood as resulted from adhered sea salt on some sort of mineral fragment.

3.8 Diatoms, D

Microparticles showing the die or the rod shape with regular disposition of holes on the surface as shown in Figs. 11 (a), (b) and (c) are occasionally found (10 m, 30 m, 100 m, 180 m). EDS of particle (c) found in 100 m depth ice exhibits many peaks of elements including S, Cl, K and Mg, together with Al and Si. From the similarity of the shape with that found in Greenland ice (Gayley, Ram and Stoermer, 1989), they are identified as diatoms.

3.9 Other Morphological Types

Not often found, but an interesting shape is shown in Fig. 12 (a), which looks like the surface of cabbage. This one was found in 10 m depth ice, and its EDS shows the peaks of Na, Al, Si, P, S and Cl. This might be a sea-salt mixed with mineral oxide or sulfide. A particle in Fig. 12 (b) looks like a drop-like tephra, which can be found in a standard text book of volcanic ash (Heiken and Wohletz, 1985). Particles with similar shapes were also found in a specimen from 402 m depth ice of the Mizuho core, as shown in Fig. 12 (c). Although the tephra of porous structure was not found in any specimen of the AC core, we have observed this type in some specimens of the Mizuho core. A particle in Fig. 12 (d), which is also

Table 3. List of SEM photographs of microparticles collected from ice cores retrieved at AC, East Queen Maud Land, Antarctica.

Depth (m)	Specimen No. (photo No.)	Morphological classification	Approximate size (μm)	Characteristic peaks of EDS
0	000000	N	30	No EDS (Fig. 5)
	000001	Af	25	〃
	000002	N	20	〃 (Fig. 5)
	000003	N	15	〃
	000004	S	12	Fe (Fig. 3)
10	010363	D	30	No EDS
	010365	Ap	15	Al, Si
	010366	S	10	No EDS
	010367	Ap		Al, Si (Fig. 7)
	010368	D		Na, Mg, Al, Si, S, Cl, K (Fig. 11)
	010369	special	10	Na, Al, Si, S, Cl (Fig. 12)

Depth (m)	Specimen No. (photo No.)	Morphological classification	Approximate size (μm)	Characteristic peaks of EDS
20	020161	special	12	No EDS (Fig. 12)
	020165	Af	25	〃
	020166	Af	35	〃
	020167	N	6	〃
	623701	S	10	Al, Si, S, Cl, Ca (Fig. 4)
	623702	M	12	Mg, Al, Si
30	030080	S	7	No EDS
	030081	N	13	Si, Ca (Fig. 6)
	030082	D	8	No EDS
	030083	Ap	30	〃
	030084	N	20	〃
40	039981	Ap	10	Al, Si, S, Ca, Fe (Fig. 7)
	039982	N	20	No EDS
	039984	M	30	〃
	039985	Af	15	Al, Si (Fig. 8)
	623301	M	10	
50	049902	S	11	Fe (Fig. 3)
	049993	Ap, Af	12	No EDS
	049995	Af	9	〃
	049997	special	30	〃
	623401	M	30	Al, Si, S, Cl Ca (Fig. 10)
	623402	Af	16	Al, Si, K, Fe (Fig. 9)
	623403	M	10	Si
	623404	M	10	Fe
60	060001	Af	15	No EDS (F.g. 9)
	060002	Ap	20	〃
	060004	N	15	〃
	060005	M	10	Na, Al, Si, S, Cl, Ca, Fe (Fig. 10)
	060008	Af	25	No EDS
	060009	M	35	〃
70	069804	M	25	No EDS
	069805	N	12	〃
	069806	Af	10	〃
	069807	Af	12	〃
80	080150	M	15	Si
	080151	Af	10	No EDS
	080152	Ap	12	〃
90	090072	Ap fluffy	10	No EDS
	090073	N smooth	12	〃
	090074	special	15	〃
	090075	Af	4	〃
	623901	Af	8	〃

Depth (m)	Specimen No. (photo No.)	Morphological classification	Approximate size (μm)	Characteristic peaks of EDS
100	100001	Af	15	No EDS (Fig. 9)
	100002	Af	10	〃
	100003	Af	11	〃
	100006	M, Af	25	〃
	100007	D	12	Na, Mg, Al, Si, S, Cl, K (Fig. 11)
110	109961	S	9	Fe (Fig. 3)
	109964	special	20	No EDS
	109965	special	10	〃
	109966 (623504)	Af	20	Al, Si, Fe (Fig. 8)
	623502	N	25	S, Fe (Fig. 6)
	623503	N	33	Si, S (Fig. 5)
120	120190	N, Af	13	No EDS (Fig. 9)
	120191	S	10	〃
	120192	Af	12	〃
	120193	Ap fluffy	25	〃
	120194	M	13	〃
	120195	N, M	35	Al, Si, K, Ti, Fe (Fig. 5)
	120196	S	5	Al, Si, Fe (Fig. 4)
130	130110	N, Af	20	No EDS
	130111	S	25	Fe (Fig. 3)
	130113	M, Ap	25	Na, Mg, Al, Si, S, Cl, K, Ca, Fe
	130114	M	30	No EDS
	130115	M	40	Al, Si, Cl
140	140020	Ap	18	Al, Si, (Fig. 7)
	140023	Ap	12	No EDS
	140024	Af	18	〃
	623001	M, Af	25	Al, Si, S, Cl
	623002	N	4	Mg, Al, Si, K, Ti, Fe
150	150200	Af	25	No EDS
	150202	M	8	〃
	150203	M	18	〃
	150204	special	15	〃
160	159910	M	15	No EDS
	159911	N	20	〃
	159912	Af	15	〃
	159913	Ap	9	〃
170	169940	Af	22	No EDS
	169942	S	10	〃
	169943	M	12	〃
	169946	M	12	〃
180	180200	N	15	No EDS
	180201	D	20	〃

Depth (m)	Specimen No. (photo No.)	Morphological classification	Approximate size (μm)	Characteristic peaks of EDS
190	190041	M	20	Al, Si, K, Fe
	190042	Ap	12	No EDS
	190043	Af	35	〃
	190044	M	14	〃
	190045	M	12	〃
	190046	Af	25	Mg, Al, Si, S, Fe (Fig. 8)
200	200400	M	22	Al, Si, Cl (Fig. 10)
	200401	Af, Ap	50	No EDS
	200402	M	12	〃
	200403	S	4	〃
	200404	Af	10	〃

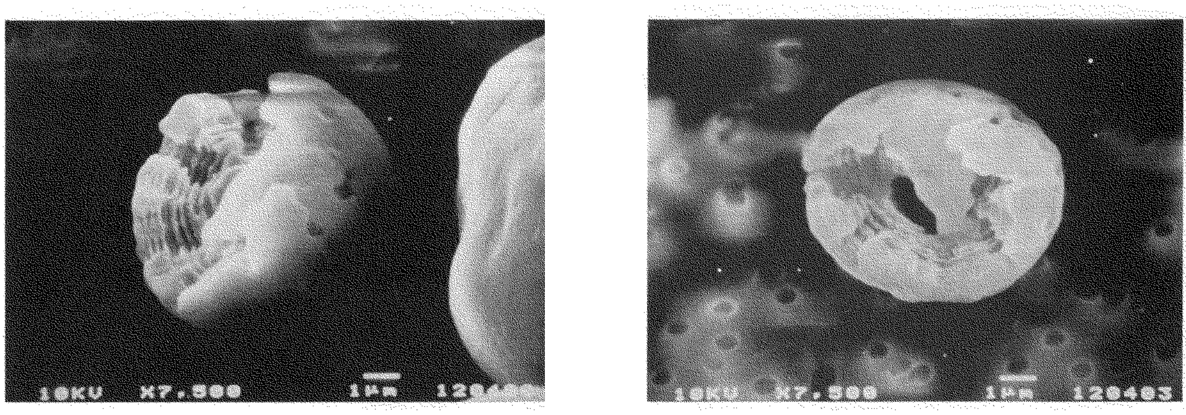


Fig. 13. SEM photographs of a microparticle with inner shell structure, from 400 m Mizuho ice core. Two photographs with different inclination of the sample.

from 402 m depth ice, is an example.

In the last, a microparticle which exhibits the shell structure is shown in Fig. 13. This particle from 402 m depth ice of the Mizuho core was accidentally fractured, showing the layer structure inside. This feature is interesting, because it may give a clue for the growth mechanism of this microparticle, if it was generated by accretion of materials, not by fragmentation of a larger particle.

4. Discussion

As described in the preceding section, microparticles collected from Antarctic ice cores are morphologically classified into several categories. Most of these categories are found in stratospheric microparticles registered in CDC, irrespective whether they are of terrestrial or extraterrestrial origin. In CDC and other astronomical publications, most of the extraterrestrial particles are characterized by chondritic composition in EDS, exhibiting significant peaks of Mg, Si, S and Fe. However, most of our ice core microparticles lack Mg peak in the EDS spectra, even though other conditions are satisfied. Also, most of them exhibit a relatively strong peak of Al, which does not exist or is weak in extraterrestrial particles in CDC. Al-rich silicate particles are common terrestrial minerals. Among several tens of observed microparticles, only one which was shown in Fig. 6 (b) was identified definitely as chondritic.

In addition to a chondritic microparticles in Fig. 6 (b), spherical microparticles as shown in Fig. 3 are possibly of extraterrestrial, Fe-rich siderolite. Although the size range is much larger than our spheres, in the order of a few hundred μm, iron comet spherules found in deep-sea sediments are composed of Fe and Ni (Brownlee, 1985), with more abundance of the latter than the case of particles in Fig. 3. Hypothetical generation process of Fe-rich spherical microparticles is considered as follows. Atmospheric entry of an interplanetary dust particle separates spheroids of molten metal and silicate. The former is composed of FeO melt and Fe-Ni metal (Brownlee *et al.*, 1984). Although the Fe-Ni metal is Ni-rich with such a larger deep-sea sediment spherules, it is plausible to consider that, in the case of smaller spherules like those observed in Fig. 3, Ni escapes during the melting process, supplying Fe-rich siderolite.

Here, we would like to estimate roughly the fall rate of extraterrestrial microparticles on the surface of ice sheet, from the data obtained above. We can say that one chondrite and five Fe-rich siderolites were found in the whole volume of ice examined in 21 samples. Since 5 cm thick sample of ice used for filtering approximately 100 cm^3 melt water should have the horizontal cross sectional area of 22 cm^2=2.2×$10^{-3}m^2$, and the 5 cm of ice corresponds approximately 0.70 year accumulation of snow or ice near the surface at AC (Satake *et al.*, 1986), one extraterrestrial particle out of 21 ice samples of 5 cm corresponds to the fall rate of $9.76 \cdot 10^{-7}m^{-2} \cdot s^{-1}$ by a simple calculation as follows ;

$$1/21 \times 2.2 \cdot 10^{-3} \times 0.7 \times 365 \times 86400 \ m^2 \cdot s$$
$$= 9.76 \cdot 10^{-7} m^{-2} \cdot s^{-1}$$
$$\fallingdotseq 1 \cdot 10^{-6} m^{-2} \cdot s^{-1}.$$

This is one order of magnitude smaller than the value obtained by extrapolating a curve expressing the relationship between the cumulative flux and the size of micro-meteolites (Fig. 1 in Brownlee *et al.*, 1980) to the size of 10 μm. However, if we include the number of Fe-rich spherical microparticles, our estimate of the fall rate increases to the same order of magnitude esimated by Brownlee et al. This coincidence implies that we will be able to find many micrometeorites of which the fall time can be well determined, if we thoroughly inspect whole deep ice cores from inland of Antarctica. For further studies in this respect, we need improved method for sorting microparticles in ice efficiently, and also the correct depth-age relationship of ice at the drilling site.

As was stated at the beginning of this section, most of the microparticles in Antarctic ice cores were determined of terrestrial origin. They should have been nuclei of snow crystals fell on the ice sheet, or dry fallout transported from other continents or small area of bare ground in Antarctica. Depth profile of the number concentration of microparticles measured on SEM photographs (tabulated in Table 1) is shown in Fig. 14. As was stated in Section 3, the concentration is in the order of 1500/0.05 ml in the upper 80 m and it decreases to the order of 500/0.05 ml in the depth deeper than 90 m. Abrupt change of the concentration occuring at 80−90 m depth can be attributed either to the change of snow fall rate or to that of microparticle transportation to Antarctica. At present, we can not determine which is the real cause of this change, because we have no exact depth-age relationship of ice at AC, although the recent accumulation rate at AC is considered almost the same as in Mizuho (Satake *et al.*, 1986).

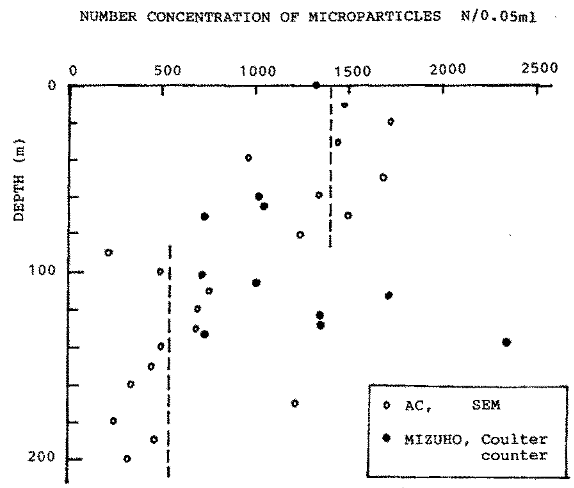


Fig. 14. Depth profile microparticle number concentrations in ice cores at AC by SEM photographic measurement, and in Mizuho ice core by Coulter counter measurements.

Kumai and Langway (1990) pointed out that the concentration of microparticles in firn samples of 1980s was 6.4 times of the mean concentration of particles at depths of 611AD, 45BC and 730BC in Greenland ice cores, according to their SEM observations. This is explained by input of dusts to the firn from modern anthropogenic sources. However, in our data of the AC, Antarctica, no significant differnce was found among samples from 0 m to 80 m depth, as shown in Fig. 14. If the depth-age relationship derived from ice fabric data for Mizuho core (Fig. 4 in Nakawo *et al.*, 1989) is adopted to that for AC ice core, the 80−90 m depth of the abrupt change in the

Table 4. Elemental composition (weight %) of microparticles collected from ice cores retrieved at AC, Queen Maud Land, Antarctica.

Sample No.	Morphology	Fig. No.	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	O
000004	S	3(a)	0	0	0	0.28	0	0	0	0	0	0.32	0.39	58.57	0.38	1.26	0.64	38.3
049902	S	3(b)	0	0	0	0.21	0	0	0	0	0	0.22	0.23	58.48	0.61	1.15	0.93	38.1
623503	N	5(c)	0	0	4.37	13.63	0.42	1.34	0	0	0	0	0	0	0	31.38	16.90	32.0
623502	N	6(b)	0	1.64	2.52	2.35	11.20	3.48	0	0.17	0	0	0	36.51	0	9.40	6.00	26.7
010367	Ap	7(a)	0	0.05	0.08	0.29	0	0	0	0	0	0	0	0	0	0.56	0.36	98.6
039985	Af	8(a)	0	0.09	4.06	16.34	0	0	0.63	0.17	0	0	0	2.56	0	1.15	0.73	74.3
623504	Af	8(b)	0	0.25	2.48	38.0	0.18	0	0.21	0	0.58	0	0	7.05	0	1.37	1.13	48.8
623402	Af	9(a)	0	0.13	2.05	41.5	0.20	0	1.83	0	0.16	0	0	1.13	0	0.92	1.38	50.7
623401	M	10(a)	4.18	2.78	4.98	4.77	11.25	4.42	2.15	14.93	0	0	0	0	0	12.64	6.88	31.0

concentration of particles shown in Fig. 14 is far before the industrial revolution. The difference of cleanness of surface firn on ice sheets between Greenland and Antarctica can be attributed to the difference of distance from industrial area of the world.

Mineralogy of observed microparticles was not made clear yet in this study, partly because of difficulty of obtaining quantitative data of elemental composition from EDS data taken by JED-2000 (shown in figures by unshaded graphs), and partly because of difficulty of approaching vast data of chemical compositions of various rocks and terrestrial dusts. Morphology of particles does not seem to be related with the depth of ice from which the particles were sampled. However, for future references, all observed particles were tabulated in the order of depths, describing the morphological classification, with approximate diameters, referring numbers of figures in this paper (Table 3). A part of quantitative elemental omposition data obtained from the EDS by QX200J are tabulated in Table 4. Information in Tables 3 and 4 will be useful, together with other data to be obtained soon with Mizuho core, for understanding the origin of microparticles on the earth surface.

5. Conclusion

Microparticles included in ice cores retrieved at Mizuho Station and Advance Camp in East Queen Maud Land, Antarctica were examined with a scanning electron microscope and EDS apparatus. Many observed particles, mainly from AC 200 m ice core, were morphologically classified in 5 categories. Comparisons of their EDS data with those of stratospheric particles registered in CDC revealed that most of the observed particles were of terrestrial origin, though their source areas on the earth were not identified.

One extraterrestrial particle of chondritic elemental composition was found from 110 m depth ice, and several spherical particles from various depths were considered to be Fe-rich siderolites. The influx rate of extraterrestrial microparticles with sizes of 10 μm order was roughly estimated from these data, and it coincided well with that derived astronomically.

Depth variation of the number concentration of microparticles does not show any significant modern anthropogenic effect in the firn near the ice sheet surface, as was found in Greenland. However, an abrupt decrease of the concentration is found at a depth 80−90 m in ice, which correspond roughly to the age of 800−900 years BP. This decrease, approximately 1/3, must be caused by climatic changes, either by change of snow fall rate or by that in dust generation and transportation, or by both of them. Importance of ice core studies at inland ice sheet in Antarctica for the study of climate change is now to be recognized, in view of the relative cleaness of ice there as stated above.

Thorough examinations of microparticles in the Mizuho ice core are under way for identifying origins of the particles, and for making clear transpotation and weathering processes of the particles.

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Note added on proof : Cu and Zn peaks appearing on EDS in figures 3−12 are from the brass specimen holder in the SEM.