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Studies on microparticles contained in medium-depth ice cores retrieved from east Dronning Maud Land, Antarctica

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ABSTRACT. SEM observations of microparticles in ice-core samples retrieved by the Japanese Antarctic Research Expedition in east Dronning Maud Land have been carried out since 1987. Morphology and elemental composition by EDS of many microparticles taken from various depths of the 700 m Mizuho ice core were compared with each other and with those of stratospheric microparticles in NASA Cosmic Dust Catalogs and microparticles hitherto found in deep ice cores retrieved in Antarctica. Number concentrations of microparticles were measured on all samples throughout the 700 m Mizuho ice core. Remarkable fluctuations found in the depth profile of the concentration seem to coincide with cold climates indicated by $\delta^{18}O$ of the same core. Compositional analysis of volcanic ash at a depth of 500.7 m in the Mizuho ice core, dated at approximately 6000 years BP, indicates that the ash originated from the South Sandwich Islands.

INTRODUCTION

The Antarctic continent, which is far from aerosol dust sources and mostly covered by snow and ice, is considered to be an ideal site for studying the background of global dustfall and the long-range transport processes by aerosols. It is known that microparticle concentrations in deep ice cores increased during the last glacial period, and this increase is considered to have resulted from the paleoclimate conditions of the ice age characterized by an increase in arid regions and more vigorous atmospheric circulation (Briat and others, 1982). Studies of the volcanic ash occasionally found in ice cores are important for understanding global volcanic activity in the past and also for comparison of the chronology of ice cores at different sites (Palais and others, 1987).

In the present study, microparticles collected at 10 m depth intervals throughout the 700 m Mizuho ice core were observed using a scanning electron microscope (SEM). Simultaneously, elemental composition analysis was carried out for each observed particle by the method of energy-dispersive X-ray spectroscopy (EDS). Comparing morphological characteristics and quantitative compositions by EDS (spectra shown in the recording chart illustrated here) with each other and with other microparticles found in various publications, the true characteristics and origins of the particles were investigated. The literature includes NASA's *Cosmic dust catalogs* (CDC) (e.g. NASA, 1992), *Volcanic ash* by Heiken and Wohletz (1985) and many other papers which are listed in the References. The number concentration of particles in the ice every 10 m was evaluated by counting numbers in low-magnification SEM photographs of specimens. The depth profile of the concentration shows a good correlation between the long-range increase of microparticles and the cold climate in the Holocene.

Ice cores used for the study were retrieved at Mizuho Station (70°12′ S, 44°22′ E, altitude 2230 m) and at Advance Camp '85 (74°12′ S, 34°59′ E, altitude 3200 m). Although the Mizuho 700 m core was retrieved in the two austral winters of 1983 and 1984, earlier than the AC 200 m core retrieved in the austral summer of 1985, complete examinations of the former were not carried out till later than those of the latter, the results of which were published in our earlier paper (Higashi and others, 1990). Several volcanic ash particles collected from a visible ash layer found at 500.7 m depth in the Mizuho core (Fujii and Watanabe, 1988) were semi-quantitatively analysed by EDS. From the results of the analyses, we have concluded that the ash, dated at approximately 6000 year BP, originated in the South Sandwich Islands, as is discussed below.

METHODS

Samples

Details of the sampling of microparticles from ice cores

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have been given in our earlier paper (Higashi and others, 1990). Ice samples of approximately 5 cm length (corresponding approximately to a little less than 1 year) were taken from vertically half-cut ice cores at approximately 10 m intervals (covering approximately ~100–120 years according to the analysis by Nakawo and others (1989)).

Meltwater of the inner part of every individual sample was filtered through a Nucleo filter (0.6 μm pore size) using a vacuum suction funnel. The sampling and filtering procedures were carried out in a cold room and a class-1000 clean chemistry laboratory at the National Institute of Polar Research, Tokyo, Japan, where the ice cores had been stored.

SEM observations and EDS analyses

The filters on which microparticles were deposited were transported to the electron-microscope laboratory of the International Christian University (ICU), Tokyo. A square-shaped piece of approximately 50 mm^2 was cut from each Nucleo filter so that it covered equal parts of the center and the periphery. Then, it was stuck to a specimen holder and coated with evaporated carbon in a vacuum. The SEM is a JSM-T220, JEOL attached to a QX-200J, Link for the EDS analysis. For the quantitative elemental analysis using EDS, a cobalt standard and ZAF4 program were used. Since the specimen holder was made of brass, artifact peaks of Zn and Cu appear in the EDS spectra.

The number concentration of microparticles was evaluated from counted numbers of particles on low (~100–200) magnification SEM photographs covering whole areas of the filter examined, by a conversion equation as follows:

$$N = 0.05mS/s\nu \quad (1)$$

where m is the number of particles on a photograph of the examined area s, and S is the area of Nucleo filter through which ν ml of meltwater was filtered. The unit adopted here for the concentration is the number of particles in 0.05 ml of water, the same unit customarily used for the Coulter-counter measurement. For comparison with the number concentration thus obtained, measurements by a Coulter counter of particles larger than 0.63 μm were carried out on the same sample.

RESULTS OF OBSERVATIONS

Number concentration of microparticles

A depth profile of the number concentration of microparticles larger than 1 μm in diameter counted on SEM photographs at every 10 m depth interval is shown by solid circles in Figure 1. Results of the Coulter-counter measurements on the same sample (shown by horizontal bars in Figure 1) generally coincide with results of direct counting on SEM photographs. As can be seen in the figure, the average particle concentration is of the order of 200/0.05 ml meltwater throughout the 700 m depth. However, there appear to be some higher values at

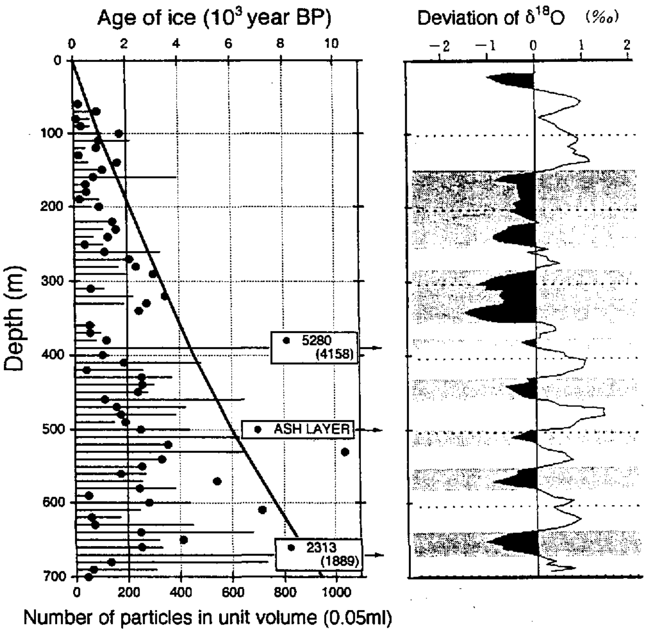

Fig. 1. Depth profile of the observed number concentration of microparticles (expressed by solid circles) in the Mizuho 700 m ice core, with a curve representing the depth–age relationship of the ice derived by Nakawo and others (1989). Data of the Coulter-counter measurements are expressed by horizontal bars at each depth. The righthand side of the figure is the depth profile of the deviation $\Delta\delta^{18}O$ from a smoothed curve of the depth profile of $\delta^{18}O$ (Fujii and Watanabe, 1992).

certain depth ranges: 260–340, 430–450, 500–550, 570, 610 and 640–670 m. Large single fluctuations occur at 390 m (5280/0.05 ml) and 670 m (2313/0.05 ml) depths, which correspond exactly to a large fluctuation in the microparticle concentration measured by the Coulter counter (4158/0.05 ml and 1889/0.05 ml, respectively). In addition, there is a visible volcanic ash layer at a depth of 500.7 m, just between our 500 and 510 m sampling depths.

Morphology and EDS analysis

In our earlier paper (Higashi and others, 1990), the morphology of observed microparticles was tentatively classified in six primary categories: spherical particles (S), micro-nodules (N), aggregates of minute particles (Ap), aggregates of flat particles (Af), sharp-edged mineral fragments (M) and diatoms (D). By taking many SEM photographs accompanied by EDS charts, we have noticed that many particles categorized N, Ap and Af were almost the same in elemental composition, despite the variation in their morphology. Although the morphology itself often tells little about the origin of the observed microparticles, we will give here some interesting examples.

A relatively large number of spherical particles (S) was found at various depths. There are two kinds of sphere: one with a characteristic surface feature as shown in Figure 2a, which is a reproduction of figure 3b of our previous paper mentioned above. It is characterized by a single strong peak of Fe in the EDS chart. Judging from comparisons

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a

b

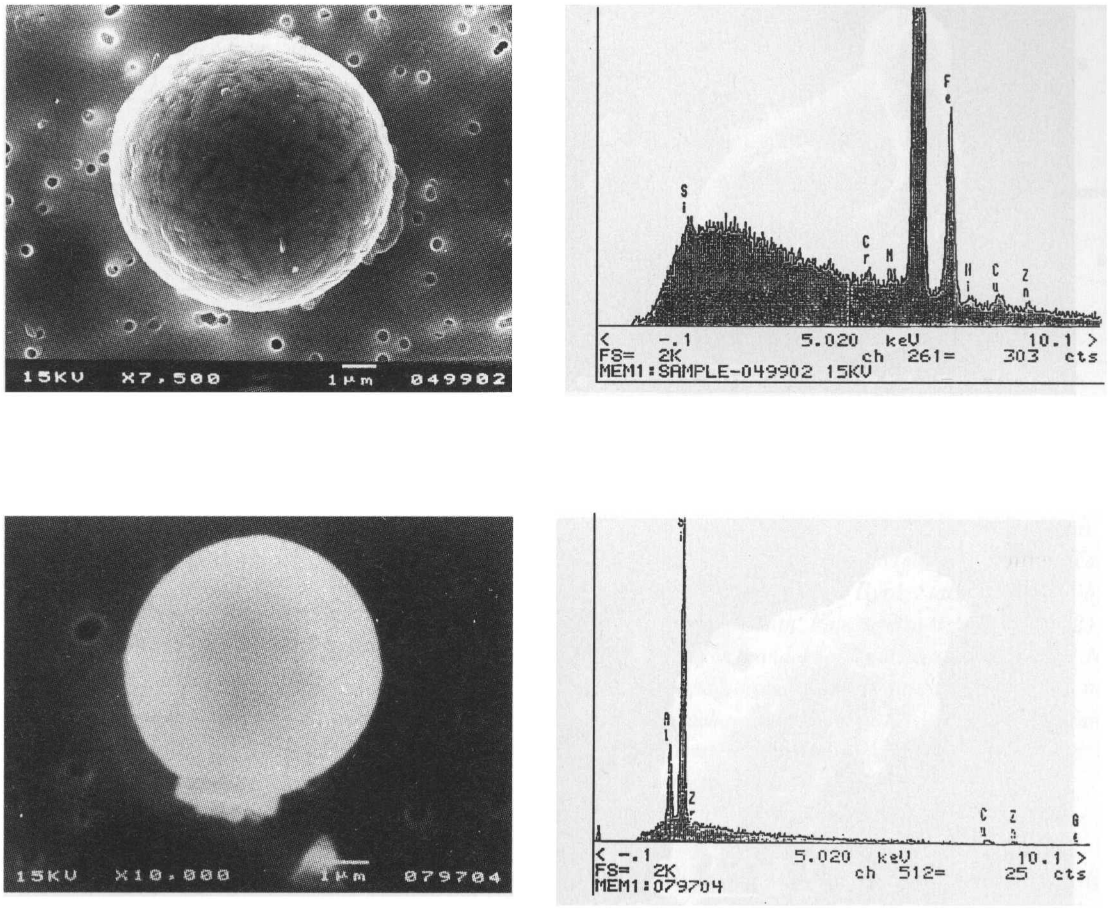

Fig. 2. SEM photographs, with EDS charts, of spherical particles. a. An iron micrometeorite found at 50 m depth in AC core (approximately 560 year BP); b. A Si-rich spherical particle found at 520 m depth in the Mizuho ice core (approximately 6400 year BP).

with many spherical microparticles catalogued in the *Cosmic dust catalog, Volume 13* (NASA, 1992), it is concluded that such iron spheres are iron micro-meteorites.

Another kind of spherical particle has a smooth surface with a high peak of Si in the EDS chart, as shown in Figure 2b. This particle was obtained from 520 m depth of the Mizuho ice core, and an identical one was obtained from 450 m. The origin of these particles is not clear at present.

Common elemental compositions seen in the EDS chart of various microparticles categorized N, Ap and Af are as shown in Figure 3a and b. The particle in Figure 3a from 510 m depth in the Mizuho core has a peculiar convolute shape, while the particle in Figure 3b from 570 m depth looks like an aggregate of minute particles. Both EDS spectra exhibit high peaks at Al and Si with side peaks at S and Cl, but Figure 3a lacks Ca which appears in Figure 3b. We often see a K peak instead of or as well as a Ca peak in the spectra. The most likely mineral of this composition is feldspar. Differences in morphology must be due to differences in their origin.

Our SEM photographs show particles which are similar to tephra from Byrd Station, South Pole and Vostok ice cores described by Palais (1985) and Palais and others (1987, 1992). Two examples of particles which look like volcanic glass shards are shown in Figure 4a and b. The former is from 220 m depth and the latter from 410 m depth, both from the Mizuho ice core. Both EDS charts show Na and K peaks beside the main strong peaks of Si and Al, as an expected characteristic of volcanic ash. Other examples of the volcanic ash will be given in the next sub-section.

Diatoms and sponge spicules were often found in the Mizuho ice core, and particles which look like spores and pollen were found in both the Mizuho ice core and in the surface snow. Details of these particles are not presented here because of limited space in this paper.

Volcanic ash at 500.7 m depth in the Mizuho ice core

A visible volcanic ash layer was found at approximately 500.7 m depth in the Mizuho ice core (Fujii and Watanabe, 1988). The 50 cm ice-core sample which contained the ash layer was not included in the preliminary quantitative analyses of $\delta^{18}O$, microparticles by Coulter counter, electrical conductivity, pH and major ions, of which 50 cm length samples were taken at 2 m intervals all through the core (Watanabe and others, 1992). Most of the ash layer has been kept for detailed analyses using more sophisticated techniques in the near future. Preliminary analyses of the ash by SEM and EDS have been made and are presented here.

Several grams of ice were taken from a depth of 500.665–500.700 m, where the concentration of ash was visually thick. The sample was cut and melted in the same way as our other samples. Volcanic ash particles were filtered on to a Nucleo filter and examined by SEM. Two examples of ash particles, which look like vesicular

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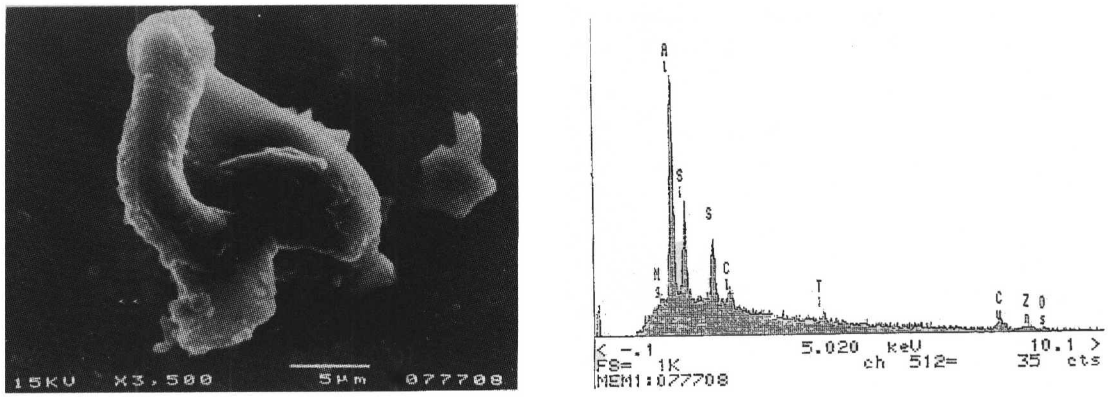
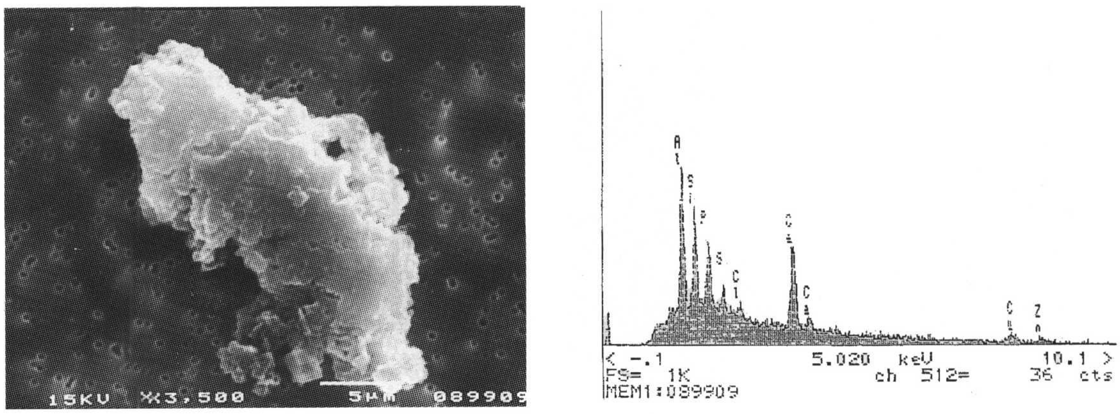
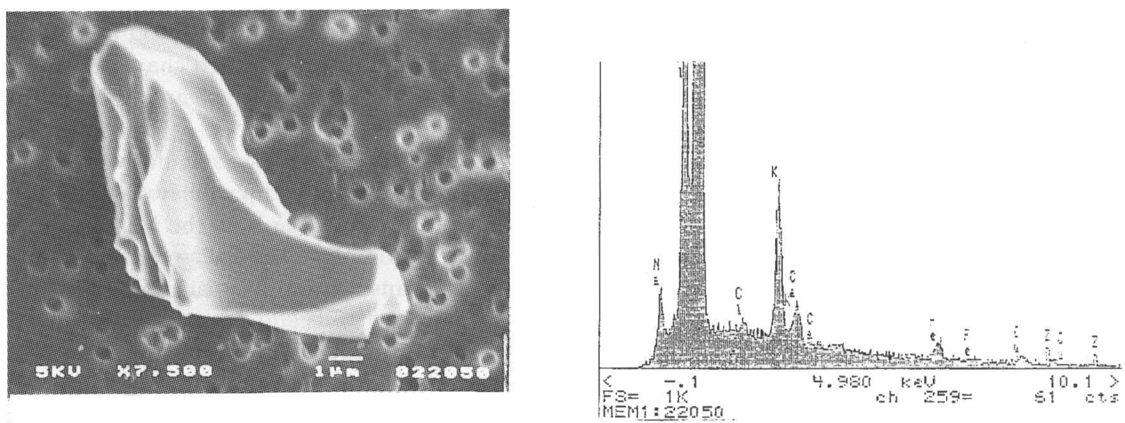


a

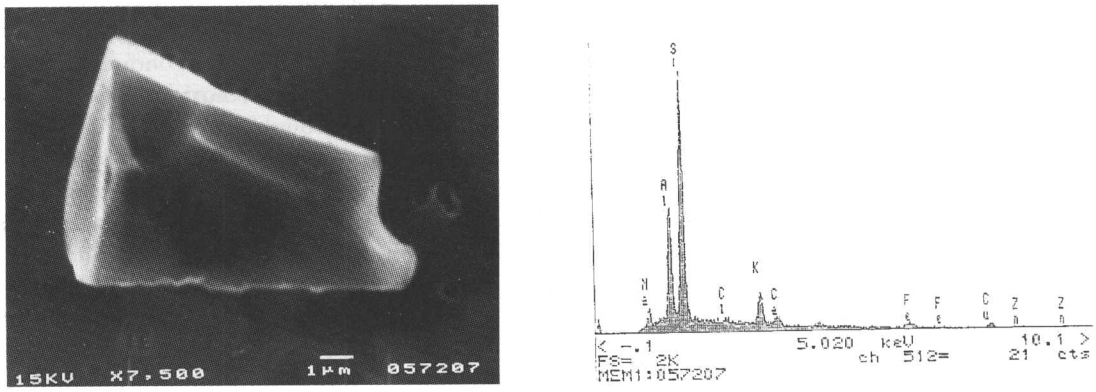


b

Fig. 3. Varieties of microparticle with EDS charts. a. A particle of convolute shape from 510 m depth in the Mizuho ice core (approximately 6200 year BP); b. Ap-type particle from 570 m depth in the Mizuho ice core (approximately 7250 year BP).



a



b

Fig. 4. Particles which look like volcanic ash (glass shards). a. From 220 m (approximately 2400 year BP); b. From 420 m depth (approximately 4700 year BP), both from the Mizuho ice core.

Table 1. Semi-quantitative analyses of oxides contained in individual volcanic ash samples from 500.7 m depth in the Mizuho ice core (wt %)

Particle No.	505	507	508	509
Morphology	V	V	G	V
SiO_2	56.06	51.89	50.57	48.30
TiO_2	0.52	1.47	1.43	1.46
Al_2O_3	12.99	16.86	15.97	17.62
FeO	16.59	13.29	16.17	15.54
MgO	11.47	4.86	4.22	4.64
CaO	2.18	9.29	10.11	10.46
Na_2O	0.32	2.19	1.01	1.41
K_2O	0.05	0.52	0.47	0.50

Morphology, G: glass shard; V: vesicular particle.

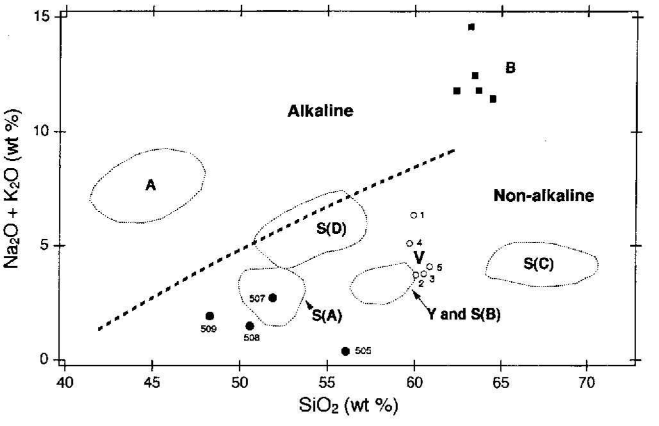


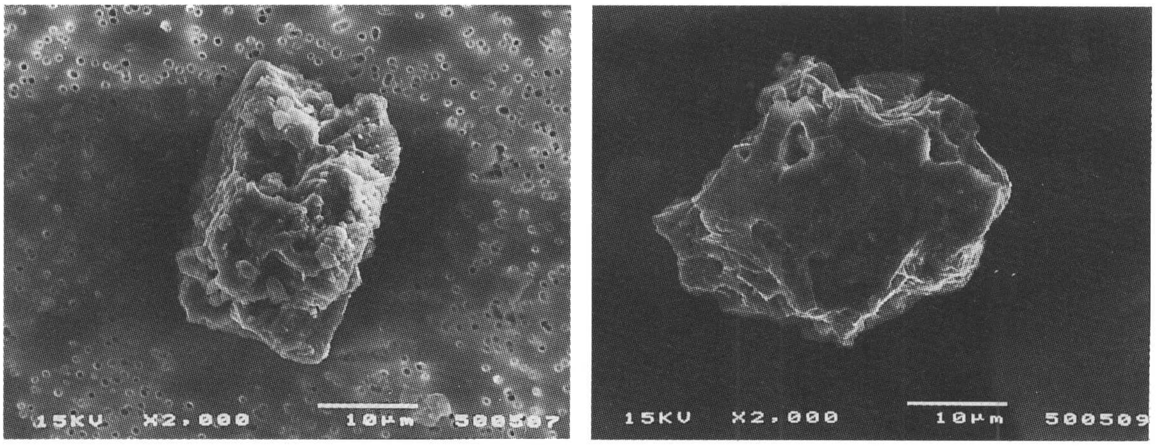
Fig. 6. $Na_2O + K_2O$ vs SiO_2 diagram of analyzed volcanic ash particles sampled from the 500.7 m depth ash layer (●), with other data of Antarctic volcanic ash: A, Allan Hills; Y, Yamato Mountains (from Katsushima and others, 1984); B, Byrd Station ice core by Palais (1985); V, South Pole tephra (Nos 1 and 2), Vostok tephra (Nos 3 and 4), Candlemas Island lava (No. 5) by Palais and others (1987); and S, Sør-Rondane mountains by Naraoka and others (1991); A, B, C and D in parentheses indicate different locations around the Sør-Rondane mountains.

tephra, are shown in Figure 5a and b. They correspond to particle No. 507 and No. 509 in Table 1. Among several particles which were analyzed quantitatively by EDS, two of them exhibited compositions similar to that of feldspars. Results of analyses tabulated in Table 1 should be considered as semi-quantitative analyses, because of the limited numbers of samples and absence of the reproducibility test.

Computed data for oxides in ash particles from the semi-quantitative analyses tabulated in Table 1 are plotted on a diagram of $Na_2O + K_2O$ vs SiO_2 (Fig. 6) with other data previously obtained on Antarctic volcanic ash. This figure indicates that this volcanic ash belongs to the non-alkaline area with less SiO_2 than any ash in dirt layers found at bare-ice areas in the Yamato Mountains (Katsushima and others, 1984) and near the Sør-Rondane mountains (Naraoka and others, 1991). Results of the oxide concentration in tephra found in South Pole and Vostok ice cores and lava from Candlemas Island (Palais and others, 1987) are also plotted in Figure 6. Ternary plots for $Na_2O + K_2O$, FeO and MgO were made from the data in Table 1 and are shown in Figure 7. This also includes other data as mentioned above and it indicates that the ash at 500.7 m depth is different from any other volcanic ash in Antarctica previously investigated.

DISCUSSION AND CONCLUSIONS

As has been mentioned in the preceding section, there appear to be increasing fluctuations in the number concentration of microparticles at certain depth ranges shown in Figure 1. These depth ranges are compared with $\delta^{18}O$ records of the Mizuho ice core (Fujii and Watanabe, 1988, 1992). $\Delta\delta^{18}O$ in Figure 1 is defined as the deviation of $\delta^{18}O$ values at every 5 m in the ice core from the smoothed curve of the depth profile as shown in figure 5 of the paper by Higashi and others (1988). This is an index



a **b**

Fig. 5. Examples of volcanic ash particles from the 500.7 m (approximately 6000 year BP) ash layer in the Mizuho ice core; a. Corresponds to particle No. 507; b. Corresponds to particle No. 509, both as analyzed in Table 1.

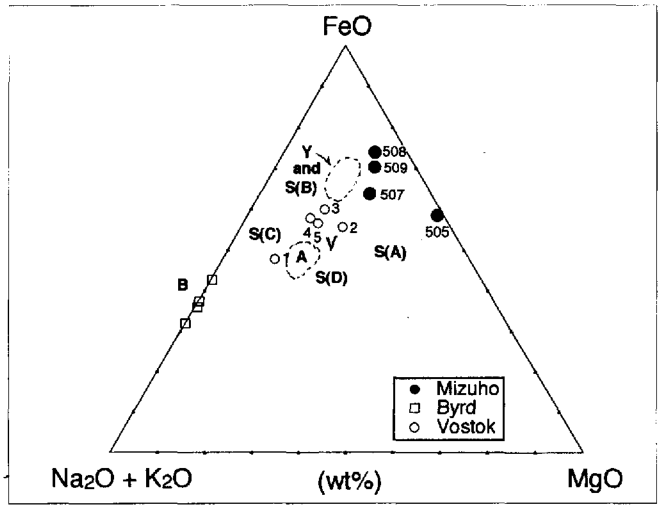


Fig. 7. Ternary diagram of $Na_2O + K_2O$, FeO and MgO for the 500.7 m volcanic ash particles (●) with other data cited in Figure 6.

expressing colder (minus value of $\Delta\delta^{18}O$) or warmer temperatures (plus value of $\Delta\delta^{18}O$) than the average in the Holocene. The curve shown on the righthand side of Figure 1 was obtained by taking the running mean of every five successive values of $\Delta\delta^{18}O$ for obtaining a long-term trend of climate change. Some cold periods, shown by dark bands at minus deviations, coincide with the depth ranges (e.g. 260–340, 430–450 and 640–670 m) of increased concentration of microparticles shown on the left of the figure. This coincidence may be interpreted in terms of stronger dust inputs appearing to occur in a relatively colder climate even during the Holocene, as occurred more severely in the Last Glacial Maximum (De Angelis and others, 1992).

Although no mineralogical survey was carried out using observed microparticles, elemental compositions shown in EDS charts in the present study indicate that most of the particles belong to minerals such as feldspar, quartz and clay minerals. Since local sources of particles are limited mainly to "dry valleys", arid areas of the Southern Hemisphere located in Australia, South America and southern Africa have been considered as potential long-range continental sources for dust accumulated in the Antarctic ice sheet (Gaudichet and others, 1988). Increase of the dust input in a colder climate, as shown in Figure 1, implies that dust blown from continental sources increased as a result of enhanced aridity and wind activity, both of which are believed to prevail in cold climates.

Volcanic ash found at 500.7 m depth in the Mizuho ice core was analyzed to identify its origin. As shown in Figure 6, the ash occurs in the lower SiO_2 part of the non-alkaline region of the $Na_2O + K_2O$ vs SiO_2 diagram, where the ash found at 100.8 m depth in the Vostok core and at 303.44 m depth in the South Pole core (Palais and others, 1987), and also that found in bare-ice areas in the Yamato and Sør-Rondane mountains occurred (Katsushima and others, 1984; Naraoka and others, 1991). Palais and others (1987) concluded that the volcanic ash both at 100.8 m depth at Vostok and at 303.44 m depth in the South Pole ice core originated from Candlemas Island in the South Sandwich Islands, based on a very close similarity of oxide ratios. They estimated the age as 3200 year BP from the accumulation rates and concluded that they can be correlated. Katsushima and others (1984) concluded that the ash found in bare-ice areas near the Yamato Mountains originated from a volcano in the South Sandwich Islands, judging from the $Na_2O + K_2O$ vs SiO_2 diagram.

Our estimate for the age of the ash is approximately 6000 years, as can be seen from the curve of depth–age relationship shown in Figure 1. The relationship was derived by Nakawo and others (1989) by a new method using a relationship between depth and total strain, which was derived from fabric data of the ice core. This method gave several per cent younger ages than those calculated by a steady-flow model. Judging from Figure 6 and the age estimate, it is concluded that the ash of 500.7 m depth in the Mizuho ice core originated from the South Sandwich Islands, approximately 6000 years ago. Differences in the composition of the present ash from others that originated from the South Sandwich Islands may be attributed to the different times of eruption.

Extra-terrestrial or cosmic microparticles contained in ice are interesting and useful for the understanding of meteorite fall on the Earth. Although iron micrometeorites have often been found, only one micro-chondrite was found at 110 m ice depth in the AC core, as was reported in our previous paper (Higashi and others, 1990). Particles of biological origin will be useful in determining routes of transport of the particles, if the species are identified. This is indeed a subject of future interest.

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