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Article

Elemental Composition, Morphology and Concentration of Particles in Firn and Ice Cores from DYE-3, Greenland

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Abstract

A variety of particles extracted from firn and ice core samples from DYE-3, Greenland, was investigated to characterize the type, nature and concentrations of material. A scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) analyzer were employed to analyze particles in firn samples from three annual layers (1981–1983 A. D.) and ice core samples from depth of 833. 412 m corresponding to 45 B. C. The particles were extracted by filtering the meltwater of each firn or ice sample with a nuclepore membrane filter having 0.4-μm pore diameter.

In the firn samples (1981–1983 A. D.) we found relatively high concentrations of clay and silt particles, and low concentrations of quartz, pine pollen, spores and spherule particles. Some spherules were identified as coal fly ash by SEM and EDX analysis.

In the deep ice core samples from 45 B. C., we found relatively high concentrations of clay and silt particles, and some pine pollen, spores and spherules. Some spherules are possibly of extraterrestrial origin.

The mean concentration of particles in firn samples from 1981–83 was 6.4 times higher than that of ice cores from 611 A. D., 45 B. C. and 730 B. C. The mean concentration of spherules in the firn was 27.3 times higher than that of the ice cores. The increase of spherules in the recent firn is mostly a result of deposition of coal fly ash spherules from modern industrial sources.

1. Introduction

Various categories of atmospherically transported water-soluble and insoluble substances are found in polar glacier ice. The substances in firn and ice cores from the Greenland ice sheet represent a record of wet and dry deposition of atmospheric particles derived from many sources, including soil-derived minerals, volcanic ash, natural and fossil fuel combustion byproducts, sea spray and extraterrestrial materials. The present study was undertaken to identify and characterize the type, elemental composition and concentration levels of the solid aerosol particles deposited in firn and ice cores collected from DYE-3, Greenland (65°11′N, 43°49′W), and to obtain a chronology of wet and dry deposition of atmospheric particles during the present and past.

Dust concentrations in meltwater determined by a light scattering instrument were reported for Holocene and Wisconsin ice samples from DYE-3, Greenland, by Hammer and others (1985) and Steffensen (1985). Clay and related minerals, sea salt nuclei, determined by electron microscopy, and electron diffraction analysis of fresh snow and ice core samples from Camp Century, Greenland, were reported by Kumai (1977). Coal and oil fly ash particles determined by SEM and EDX analysis were reported for new fallen snow samples from Alaska and New Hampshire by Kumai (1985, 1987).

This paper presents the results of an SEM and EDX study of particles in firn and ice core samples from DYE-3, Greenland, including data on elemental composition, morphology, particle concentration and identification of sources.

2. Previous Work

Some results from previous work on snow crystal nuclei, aerosols, fly ash, volcanic ash and extraterrestrial particles in polar firn and ice are summarized in below.

2.1. Snow crystal nuclei

During a period of snowfall at Site 2, Greenland, we collected snow crystals falling into an ice tunnel on grid mesh covered with collodion film. The sublimating image of the snow crystal center was photographed soon after collection with an optical microscope in clean room conditions for later examination of the nucleus by electron microscopy. We collected 356 specimens of snow crystal nuclei in the Site 2 ice tunnel. Images of the snow crystal nuclei were obtained by transmission electron microscopy and the nuclei were identified by electron diffraction analysis. The distribution of snow crystal nuclei found in fresh Greenland snow crystals was 85% clay minerals, 0.6% hygroscopic particles, 10.7% unidentifiable material and 3.7% no nucleus (Kumai and Francis, 1962).

2.2. Aerosol

Aitken nuclei counts in air near the summit of the Greenland ice cap are generally tens to hundreds/cm^3, and $100-200/cm^3$ in the katabatic flow from the ice cap (Flyger and Heidman, 1978). Hogan *et al.* (1984) measured aerosol variation at Barrow, Alaska ; Igloolik, Canada ; and DYE-3, Greenland. The Aitken nuclei count at DYE-3, Greenland, was sometimes near the threshold of detection in the morning and increased slowly to $45/cm^3$ in the evening. The Aitken nuclei count for the period 26 July-18 August 1982 varied from the threshold of detection to thousands/cm^3 during frequent winds shifts and precipitation. Many particles collected by impaction from the air at DYE-3, Greenland, were identified as clay particles from EDX analysis by Hogan *et al.* (1984).

Aitken nuclei counts in maritime air at Barrow, Alaska, varied from 50 to $300/cm^3$ in June 1975. Aerosol particles ($0.01-2.5\ \mu m$ dia.) collected during this experiment and examined by electron microscopy and electron diffraction analysis included 2% sea salt particles, 3% clay minerals, 15% carbon particles, 1% fly ash and 80% unidentified small particles (Kumai, 1978).

2.3. Coal and oil fly ash

Fly ash particles collected near coal-fired electric power plants using Alaskan coal with a high calcium content were spherical or irregular in shape, with a 0.2 to 50 μm diameter, and were rich in calcium, with lesser amount of silicon, aluminum, magnesium, iron, potassium, titanium and sulfur. Calcium-rich spherical coal fly ash particles were found in fresh snow and snow cover samples from Fairbanks, Alaska (Kumai, 1985). However, coal fly ash particles from coal-fired power plants burning coal from the eastern United States were generally richer in silicon with lesser amounts of aluminum, iron, sulfur and calcium. Spherical coal fly ash particles with a high content of silicon were found in fresh snow and snow cover samples from Hanover, New Hampshire (Kumai 1985, 1987).

2.4. Volcanic ash

In 1968 an ice core of 2164 m length was recovered from Byrd station in West Antarctica (80°01'S, 119°31' W). In the Byrd ice cores, Gow and Williamson (1971) found 25 distinct tephra layers and estimated 2000 cloudy layers. The most likely source of these tephra layers was believed to be the volcanoes of Marie Byrd Land. Kyle and Jezek (1978) examined glass shards and lithic particles in the Byrd ice cores and classified the glass as peralkaline trachyte by electron microprobe analysis. They suggested that the probable source was a young volcano, Mount Takahe, located about 450 km from Byrd station. Palais (1985) examined tephra ashes in Byrd ice cores using an SEM and EDX analyser. The tephra ashes were equant, blocky grains with curviplaner surfaces and few vesicles. She concluded that the source of tephra was Mount Takahe in Marie Byrd Land, West Antarctica.

Nishio *et al.* (1985) found tephra in the bare ice from Yamato Mountain, Dronning Maud Land, and also from the Allan Hills, Victoria Land, Antarctica. Tephra from Yamato Mountain had a composition of a tholeiitic andesite and contained crystal fragments such as calcic plagioclase, orthopyroxene and magnetite. A possible source was a volcano in the South Sandwich Islands. Tephra from Allan Hills was composed of glass shards of trachybasaltic composition and contained crystal fragments of titanaugite calcic plagioclase, olivine, rhönite and titanomagnetite. The possible source of the tephra was a young volcano of the McMurdo volcanic group.

2.5. Extraterrestrial particles

The Greenland and Antarctic ice sheets are valuable reservoirs of extraterrestrial particles that are easily identified against the background of terrestrial materials. Langway and Marvin (1964) reported the results of an investigation of the chemical composition, mineralogy, and physical properties of black spherules from Site 2 and Camp Century, northwestern Greenland. The diameters of the Greenland spherules ranged from 5 to 230 μm. A typical spherule consisted mainly of magnetite or magnetite with minor amounts of hematite. One spherule, 65 μm in diameter that was collected from Camp Century, gave an x-ray powder diffraction pattern of olivine. This spherule is probably an ablation product from a stony or stony iron meteorite. Yanai and Kojima (1987), reporting on meteorites found in the Antarctic ice sheet, published individual color photographs of 327 meteorites together with their original weights, type and chemical data for classification.

In an SEM and EDX analysis, microspherules from firn and pack ice collected at the Weddell Sea, Antarctica, were found to be silicon-, titanium-, or iron-rich particles. The silicon- and titanium-rich spherules were similar to particles found in coal fly ash. The iron-rich microspherules were tentatively identified as being of extraterrestrial origin. The concentration of spherules in the firn and ice from the Weddell Sea, Antarctica was three orders of magnitude smaller than that of firn from Greenland (Kumai *et al.*, 1983).

2.6. Concentration of particles in firn and ice cores

The concentration of silicate minerals in firn deposited from 1753 to 1965 at Camp Century, northwestern Greenland, was estimated to be 35×10^{-9} g/g snow by Murosumi *et al.* (1969). Particles in sublimated fresh snow crystals collected at Camp Century, Greenland, examined under the electron microscope ranged from 0.02 to 8 μm in diameter. The concentration of particles in fresh snow was found to be 4.9×10^{6} particles/g snow, and the mass was estimated to be 33.7×10^{-9} g/g snow by Kumai (1977). The concentration of particles in a sublimated clear ice core collected at 1368 m depth (Sangamon age) from Camp Century was found to be 8.3×10^{8} particles/g ice and the mass was estimated to be 2.7×10^{-4} g/g ice by Kumai (1977).

The dust concentration in the core was continuously measured by pumping meltwater from a melted groove along the cleaned ice core surface into a light scattering instrument. The dust concentration in ice cores from DYE-3, Greenland, was estimated by Hammer *et al.* (1985) to be 50×10^{-9} g/g ice for the Holocene age, and $200-3{,}000\times10^{-9}$ g/g ice for the Wisconsin age.

Particle concentrations in firn samples (1970–1975) from the South Pole measured on a Coulter Counter by Mosley-Thompson (1980) varied from 800 to 12,000 particles/g snow for particles larger than 0.8 μm in diameter. Particle concentrations in ice cores for the period 1878–1889 from the South Pole varied from 2×10^{4} to 2.5×10^{5} particles/g ice for particles larger than 0.63 μm in diameter.

The particle concentration in firn and ice core samples obtained at Advance Camp, Queen Maud Land, Antarctica (74°12′S, 35°E) was measured by SEM observation (Higashi *et al.*, 1990). The mean particle concentration in firn and ice core samples from 0–80 m depth was 3×10^{4} particles/g firn or ice for particles larger than 0.6 μm diameter, and that of ice core samples from 90–200 m depth was 1×10^{4} particles/g ice.

3. Firn and Ice Core Samples Used in This Analysis

Firn samples were collected from a 5.4 m-deep pit excavated at DYE-3 (6-B) in southern Greenland by J. Schwander, University of Bern, in the summer of 1983. The firn samples for this study were collected in continuous 5-cm-depth intervals from the pit wall between 17 to 262 cm deep. This profile represents snowfall from January 1981 to the summer of 1983, as determined by the δ^{18}O record (Oeschger, unpublished data).

Ice core samples were obtained by drilling at DYE-3, Greenland, in 1980 (Langway *et al.* 1985). The core samples used for this study were selected from depths of 619.910 m, 833.412 m and 1009.435 m. Each ice core sample was 10 cm thick, and includes less than one year's precipitation. The samples were deposited in 611 A. D. $\pm$ 40, 45 B. C. $\pm$ 60 and 730 B. C. $\pm$ 80 as determined by the δ^{18}O record (Dansgaard *et al.* 1984). The concentration levels and composition of the aerosol particles were investigated for the recent firn and the old ice core samples, using the same analytical technique, to investigate variation in their deposition with time.

4. Experimental Procedure

Firn samples were cut, cleaned by removing surface material, placed in sterile containers and melted in a microwave oven, all under clean room conditions. After cleaning the firn samples for particle study weighed an average of 65 g each. The deep ice core samples wighed about 150 g each, and the ice core samples were cleaned by rinsing in doubly distilled deionized water. The core samples for particle analysis weighed an average of 80 g each after cleaning. The cleaned samples were then placed in sterile containers and melted in a microwave oven under clean room conditions. The meltwater was weighted and then filtered through a 0.4-μm-pore-diameter membrane filter. Particles remaining on the filters were fixed on SEM mounts and dried in a vacuum oven at 30°C. The particles were coated by Au (60%) and Pd (40%) vapor in a vacuum chamber for SEM examination and EDX analysis.

Semi-quantitative analyses of individual particles in the firn and deep ice core samples were conducted using a Hitachi SEM with a Kevex 8000 series Quantex analytical spectrometer. An accelerating voltage of 20 kV and a working distance of 15 mm were used for SEM imaging and EDX analysis. Elemental compositions of the standard materials were calculated and compared with their elemental peak intensities. Elemental compositions of particles are given as weight percents normalized to 100%. Soil-derived minerals, volcanic ash, coal fly ash, pollen, spores and extraterrestrial particles from firn and ice core samples were identified by their characteristic elemental compositions and morphology. The concentrations and size of particles in firn and ice core samples were calculated from SEM images of particles in known masses of samples.

5. Elemental Composition of Particles in Firn

Precipitation at DYE-3, Greenland, generally occurs in the form of snow. In summer ice layers are formed occasionally when solar radiation, warm advection or freezing drizzle melt the surface snow. In the firn samples accumulated from January 1981 to the summer of 1983, we found 11 ice layers ranging in thickness from 1 mm to 12 mm. Nine of these were stratigraphically located in the 1981 annual layer. This indicates that the summer of 1981 was relatively warmer than those of 1982 and 1983. The density of 45 individual firn samples collected from these layers ranged from 410 to 500 kg/m^3; the mean value was 450 kg/m^3.

The particles contained in the firn and deep ice core samples were originally either 1) atmospheric aerosols captured by snow crystals during the processes of ice nucleation, growth and precipitation or 2) dry fallout, which precipitated directly upon the snow surface. In the firn samples we found many kinds of solid particles, such as soil-derived minerals, coal fly ash, possible exraterrestrial particles, pollen and spores. These typical particles are shown and discussed in below.

5.1. Clay and related mineral particles in firn

Mineral particles found in the firn samples were irregular in shape, with diameters ranging from 0.1 to 60 μm. The most frequently observed mineral particles were thin and irregular in shape, with a high Si content and with diameters ranging between 0.1 and 13 μm, with a mean value of 0.5 μm. Clay mineral particles found in these firn samples commonly serve as ice nuclei in the formation of snow crystals within supercooled clouds (Kumai, 1977).

Table 1 shows elemental compositions and size of typical silicate mineral particles (weight %) from 1981–1983 firn samples, DYE-3, Greenland. In the mean elemental concentrations of these silicate minerals, the highest concentration was Si, followed by Al, Ca, Fe, Mg, K, S, Mn and Na.

Typical SEM images and EDX analysis of particles in firn samples are described in below. Figure 1 shows silicate mineral particles extracted from 1983 spring firn. The largest particle is 14.6-μm in diameter, with a rough surface. Many number of clay-size particles surround it (Fig. 1). The elemental composition analysis of the 14.6-μm-diameter particle is shown in Figure 1 and Table 1. Based on its elemental composition, size and morphology, this particle is considered to be originated from a moraine. Ca-rich silicate minerals (Fig. 2) were found less often in the firn samples; they tend to reduce the acidity of snow (Kumai, 1985). Figure 3 shows a quartz particle with a crystal face and its EDX analysis is showing an Si element. A tetragonal bipyramidal crystal (Fig. 4) with Al, Mn, Cr, Fe, Si, Mg and Na elements was found in autumn firn sample of 1981. A rod shaped mineral (Fig. 5) was found in firn from the summer of 1981. The particle is 6.5 μm in diameter and 50 μm long, and consisted of Si, Ca and Al elements. These

Table 1. Elemental composition (weight %) and size of particles in 1981-1983 firn samples from DYE-3, Greenland.

Sample		Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	dia. μ
2365	Fig. 2	1.7	15.5	6.3	10.3	5.7	4.6	0	0	46.1	0.6	0	2.3	2.3	0.6	1.7	0	2.3	8.8
2366	Fig. 1	3.2	5.1	13.8	25.8	0	9.0	8.0	4.8	7.1	4.8	0	3.2	1.3	11.3	0	0	2.6	14.6
2476		1.0	2.9	7.7	77.7	3.9	6.8	0	0	0	0	0	0	0	0	0	0	0	15.8
3062		0	0	5.9	94.1	0	0	0	0	0	0	0	0	0	0	0	0	0	27.1
3063		3.6	4.3	5.8	10.8	0	10.8	7.1	0	57.6	0	0	0	0	0	0	0	0	22.7
3065	Fig. 4	2.0	4.4	31.9	10.8	0	0	0	6.0	4.0	0	5.9	8.0	21.0	6.0	0	0	0	2.9
3513		0	0	4.5	95.5	0	0	0	0	0	0	0	0	0	0	0	0	0	5.2
3515		3.4	8.4	15.2	22.8	0	0	8.0	4.2	2.7	4.9	0	0	3.8	26.6	0	0	0	13.8
3524		2.2	3.9	24.7	62.5	0	0	0	0	6.7	0	0	0	0	0	0	0	0	9.6
3559		4.6	6.9	19.6	47.1	0	0	0	6.8	6.0	4.1	0	0	0	3.2	0	2.7	0	17.8
3561		0	2.4	18.7	57.8	0	0	0	19.3	0	0	0	0	0	1.8	0	0	0	43.8
3599		0	6.6	10.5	56.4	0	0	0	3.3	11.1	3.6	0	0	0	8.5	0	0	0	44.4
3602		2.8	3.2	0	91.6	0	0	0	2.4	0	0	0	0	0	0	0	0	0	5.7
3619		0	3.2	21.5	46.8	0	0	0	6.3	5.1	3.8	0	0	0	13.3	0	0	0	12.0
3634	Fig. 3	0	0	0	100.0	0	0	0	0	0	0	0	0	0	0	0	0	0	12.4
3637	Fig. 5	1.3	1.5	14.1	55.9	0	0	0	0	26.2	1.0	0	0	0	0	0	0	0	6.3
Mean		1.6	4.3	12.5	54.1	0.6	2.0	1.4	3.3	10.7	1.4	0.3	0.8	1.8	4.5	0.1	0.2	0.3	16.4

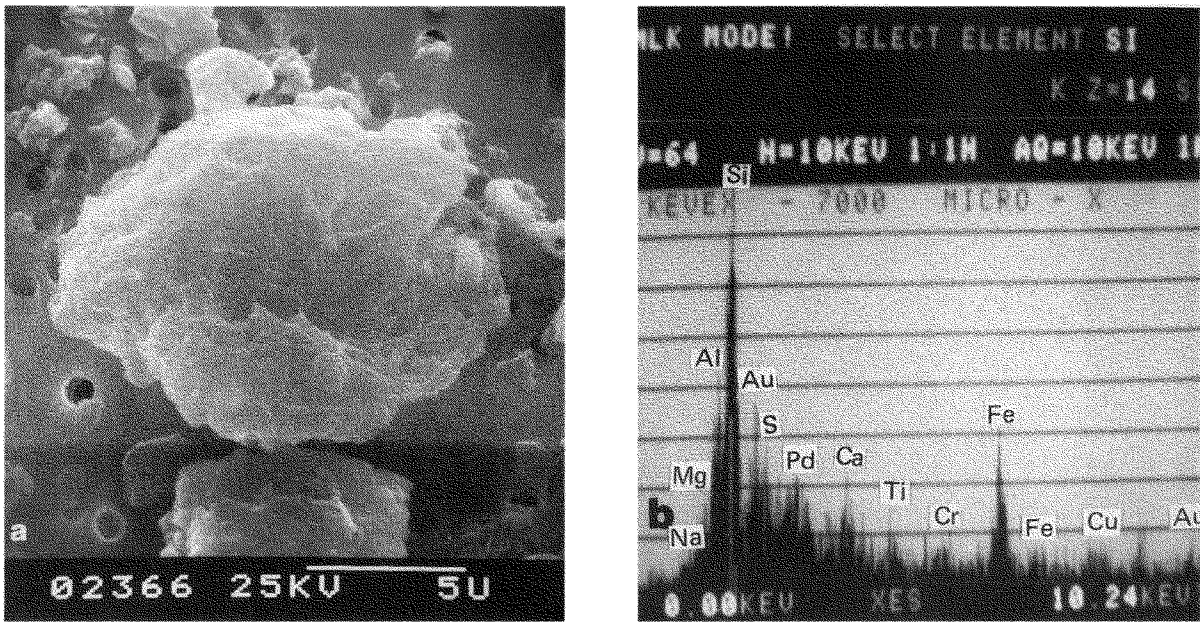


Fig. 1. SEM image of mineral particles from the spring firn layer of 1983, DYE-3, Greenland (a), and the elemental composition of the largest mineral particle (b). (All specimens are coated with Au and Pd.)

silica-rich minerals are possibly derived from terrestrial materials.

5.2. Silicate spherules in firn

The elemental composition and size of typical spherules from 1981–1983 firn samples are shown in Table 2. The diameters of spherules ranged from 0.9 to 13 μm, with a mean value of 3.7 μm. Four types of spherules were found in the firn samples. They included Si-rich (Fig. 6), Fe-rich (Fig. 7), Ca-rich (Fig. 8) and Ti-rich spherules (Fig. 9). A characteristic of these spherules was the minute particles attached to their surfaces. These spherules were similar in nature to coal fly ash particles collected at coal-fired electric power plants and to coal fly ash found in fresh snow samples from Fairbanks, Alaska, and Hanover,

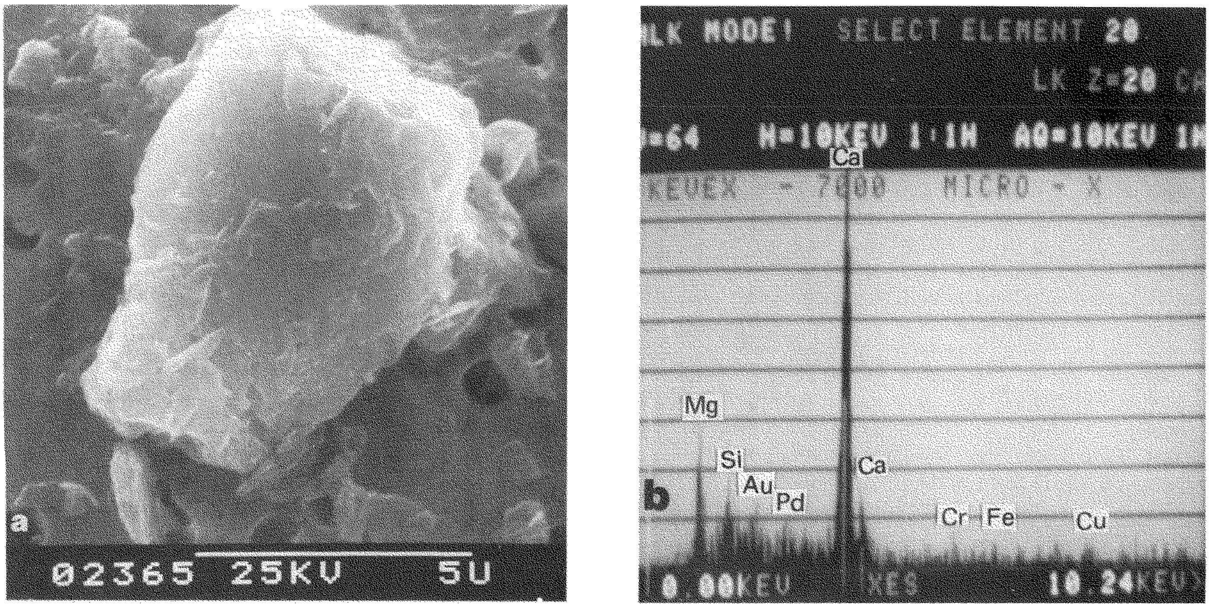


Fig. 2. SEM image of a Ca-rich mineral particle from the spring firn layer of 1983 (a), and its elemental composition (b).

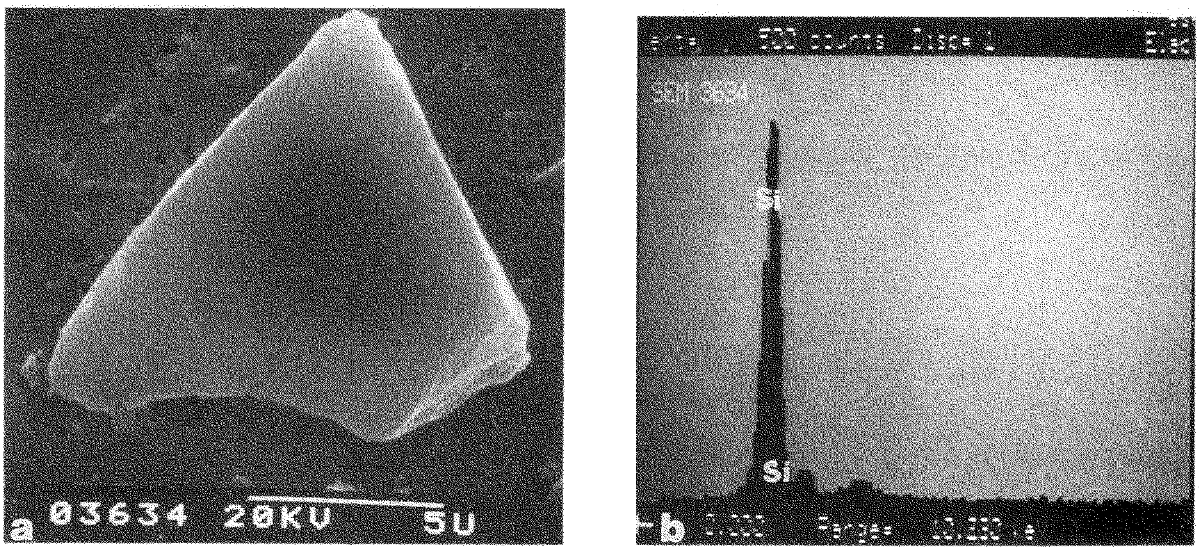


Fig. 3. SEM image of a quartz particle from the autumn firn layer of 1981 (a), and its elemental composition (b).

New Hampshire (Kumai, 1985), and also to coal fly ash from Tennessee valley, Tennessee (Hulett and others 1980). Ti-rich spherules are rare in fly ash from coal-fired plants. Most common spherules found in the firn were Si-rich spherules, and followed by Fe-rich, Ca-rich and Ti-rich spherules.

The majority of spherules in the firn samples are considered to be scavenged from the atmosphere by snow crystals, and some were deposited as dry fallout. However, a spherule 0.2 μm in diameter was found as a nucleus of a single snow crystal from among 356 fresh snow crystals collected at Site 2, northern Greenland. Few spherules appear to act as ice nuclei (Kumai and Francis 1962, Byers 1965).

5.3. Extraterrestrial particle in firn

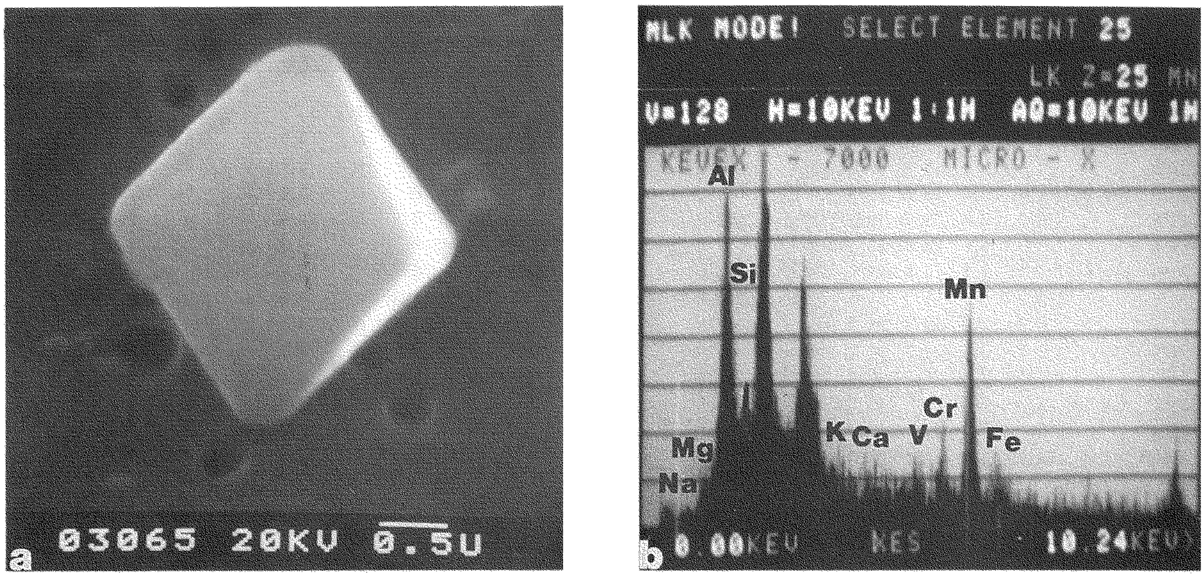


Fig. 4. SEM image of a tetragonal bipyramidal crystal from the autumn firn layer of 1981 (a), and its elemental composition (b).

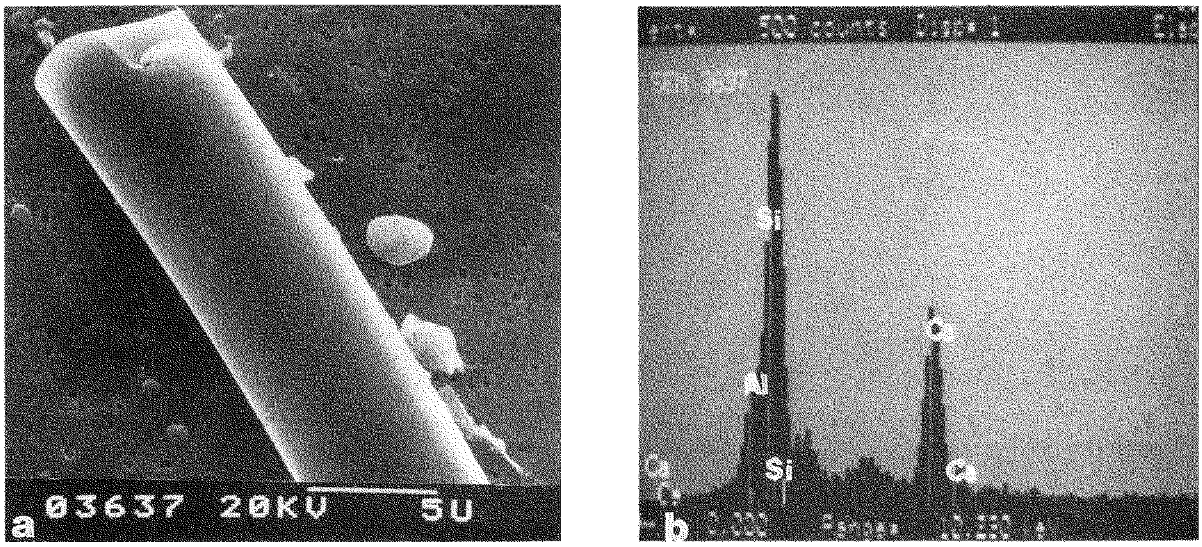


Fig. 5. SEM image of a rod shape mineral particle from the summer firn layer of 1981 (a), and its elemental composition (b).

Some spherules in the firn samples possessed smooth surfaces. Minute particles are not attached to these surfaces. A spherule with a smooth surface (Fig. 10) measured 2.2 μm in diameter, and contained the elements Si, Al, Fe and K. This spherule is different morphologically from coal and oil flyash particles from Fairbanks, Alaska, Tennessee valley, Tennessee, and Hanover, New hampshire. It may be of extraterrestrial origin.

5.4. Pollens and spores in firn

Pollens and spores were found in the firn samples. They were identified on the basis of morphological characteristics and size, and from elemental compositions obtained by EDX analysis. Pollens found in the firn samples included those from pine and maple.

Table 2. Elemental composition (weight %) and size of spherules in 1981–1983 firn from DYE-3, Greenland.

Sample		Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Dia. μ
2367	Fig. 6	0	2.7	26.9	43.0	0	4.3	0	8.1	2.2	4.3	1.1	1.5	0	4.3	0	0	1.6	4.0
2371	Fig. 7	0	1.0	2.9	3.8	0	2.9	0	2.8	2.9	2.8	0	1.0	1.9	76.2	0	0	1.8	13.0
2374		0	3.2	23.3	51.8	0	5.2	0	6.5	1.9	2.3	0	0	0	4.5	0	0	1.3	2.3
2375		2.5	3.4	10.9	67.2	3.4	5.0	0	0	0	0	0	0	0	4.2	0	0	3.4	3.6
2376	Fig. 9	1.0	3.6	18.2	19.9	0	0	0	4.2	3.1	41.7	0	0	0	5.7	0	0	2.6	8.9
2378		0	2.8	5.6	9.3	0	2.8	0	0.9	0	1.0	0	0	0	74.8	0	0	2.8	3.2
2380		3.3	6.6	29.8	33.1	0	0	0	0	4.1	9.9	0	0	0	8.3	0	0	4.9	1.0
2383	Fig. 8	1.2	3.1	16.8	20.7	0	2.0	0	2.3	31.3	18.8	0	0	0	2.3	0	0	1.5	4.1
2472		2.0	5.3	11.3	53.3	0	8.7	0	6.7	5.4	0	0	1.3	0	4.0	0	0	2.0	1.6
2475		0.5	2.9	38.3	38.9	0	5.3	0	5.8	2.9	0.5	0	1.0	0	3.9	0	0	0	3.3
2479		2.1	3.6	32.3	41.7	0	0	0	9.4	4.7	2.1	0	0	0	4.1	0	0	0	1.7
2480		2.1	2.6	27.5	42.4	0	5.3	0	4.2	8.5	0	0	0	0	7.4	0	0	0	1.9
3604	Fig. 10	0	1.5	22.3	65.4	0	0	0	8.5	0	0	0	0	0	2.3	0	0	0	2.2
3606		0	2.7	30.1	51.2	0	0	0	7.8	1.8	2.7	0	0	0	3.7	0	0	0	0.9
Mean		1.1	3.2	20.4	38.6	0.2	2.9	0	4.8	4.9	6.1	0.1	0.3	0.1	15.8	0	0	1.5	3.7

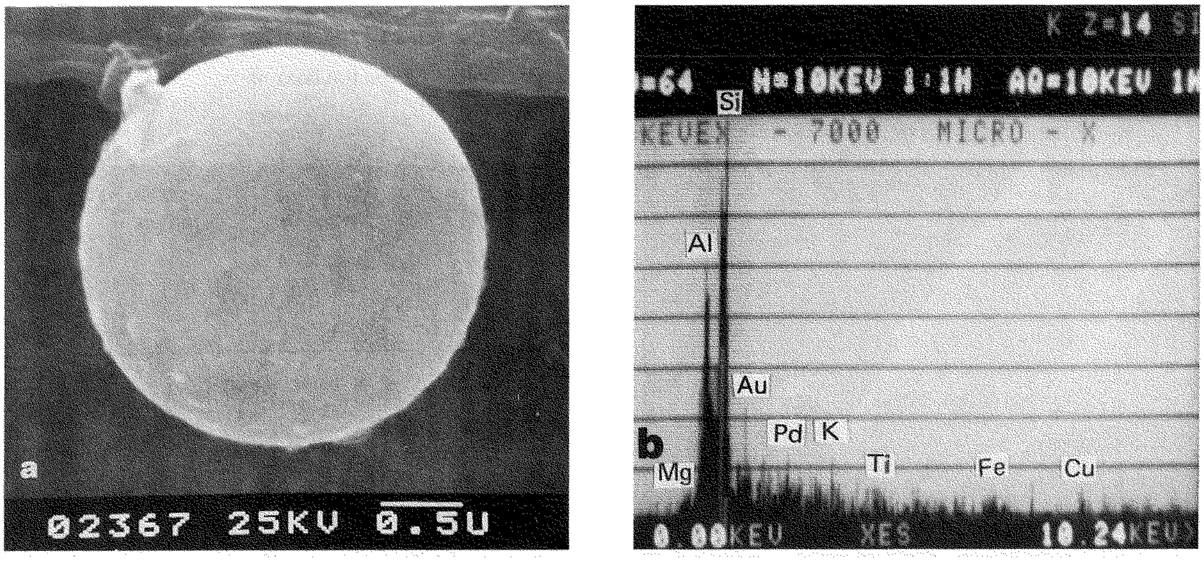


Fig. 6. SEM image of a Si-rich coal fly ash particle from the spring firn layer of 1981 (a), and its elemental composition (b).

Figure 11 shows a pine pollen grain measuring 46.8 μm in diameter that was found in the spring firn layer of 1982. The EDX analysis of the pine pollen shows the presence of trace elements of Si and Ca. Au and Pd, in Figure 11b, are coated materials for SEM specimen preparation. The pine pollen has an oval body with two attached bladders. All type of pine pollen grains vary from about 45 to 110 μm in diameter (McCrone and Delly 1973). Figure 12 shows a maple pollen grain measuring 30 μm in diameter found in the 1981 autumn firn layer. The maple pollens have the shape of oblate spheroids with one or two folds. The EDX analysis of maple pollen shows the presence of trace elements of Si, K, Ca and Al.

Two kinds of spores were found in the firn samples. One is a wheat smut spore shown in Figure 13, which was found in the 1981 autumn firn layer. The spore measured 9.2 μm in diameter with a random array of hemispherical bumps, 0.2–0.3 μm in diameter, and averaging about 0.6 μm from center to center. The spore diameters varied from 5 to 10 μm. Another example is a mushroom spores (*Coprinus comatus*) with a diameter of 7.3 μm, which was also found in the 1981 autumn firn layer. The morphology of the mushroom spore is similar in size and shape to that of a human red cell. According to McCrone and Delly

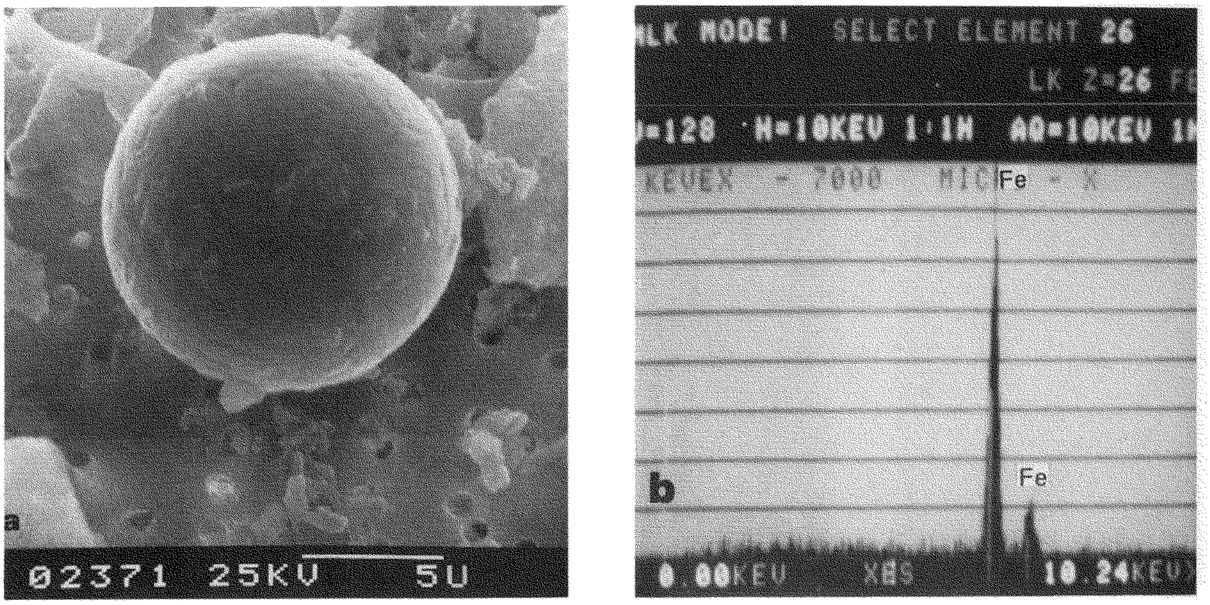


Fig. 7. SEM image of an Fe-rich coal fly ash particle from the spring firn layer of 1983 (a), and its elemental composition (b).

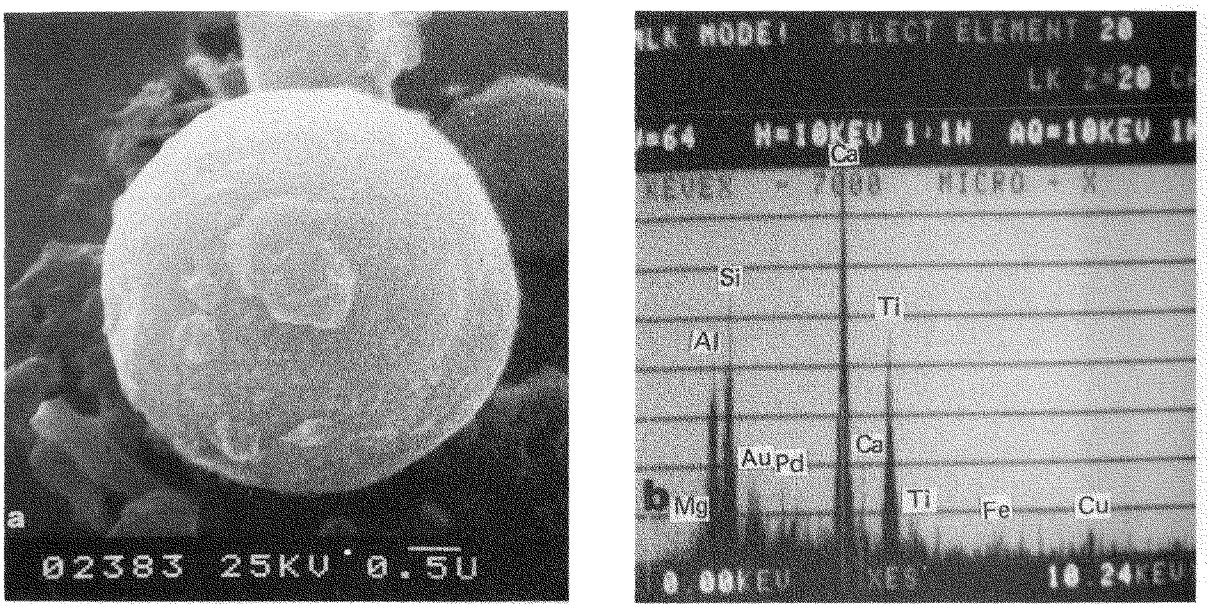


Fig. 8. SEM image of a Ca-rich coal fly ash particle from the summer firn layer of 1982 (a), and its elemental composition (b).

(1973) the spore is smooth surfaced, with diameters ranging between 7 and 11 μm.

6. Elemental Composition of Particles in Ice Cores

Particles in the deep ice core from DYE-3, Greenland, were investigated to analyze the past atmospheric particles. The particles were originally deposited as a result of both wet and dry deposition.

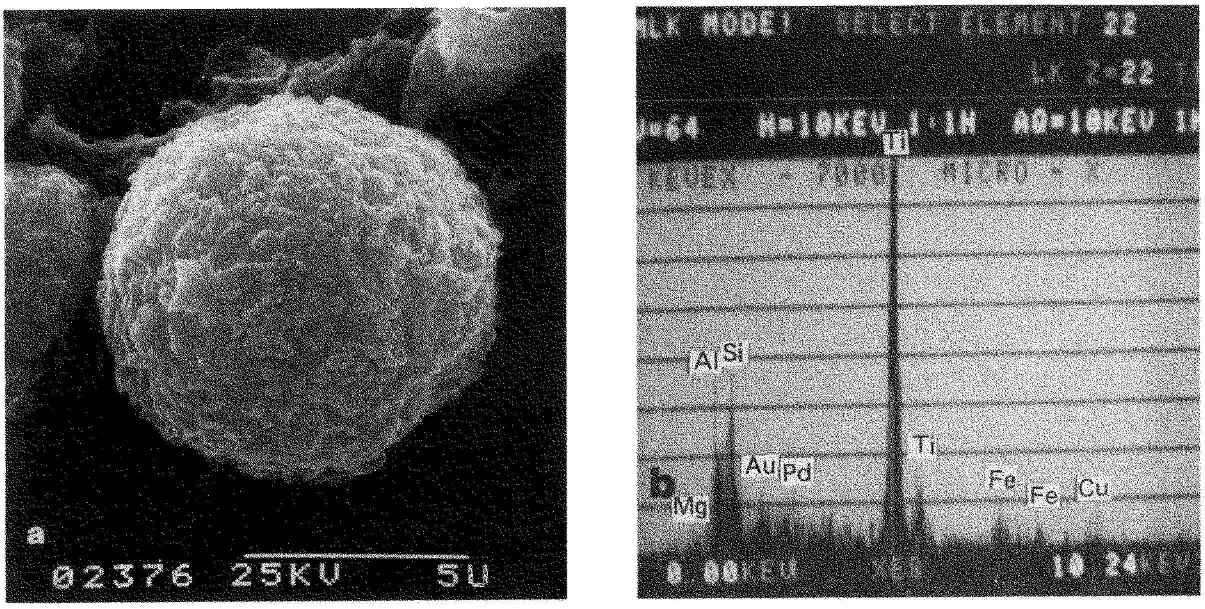


Fig. 9. SEM image of a Ti-rich spherule from the spring firn layer of 1983 (a), and its elemental composition (b).

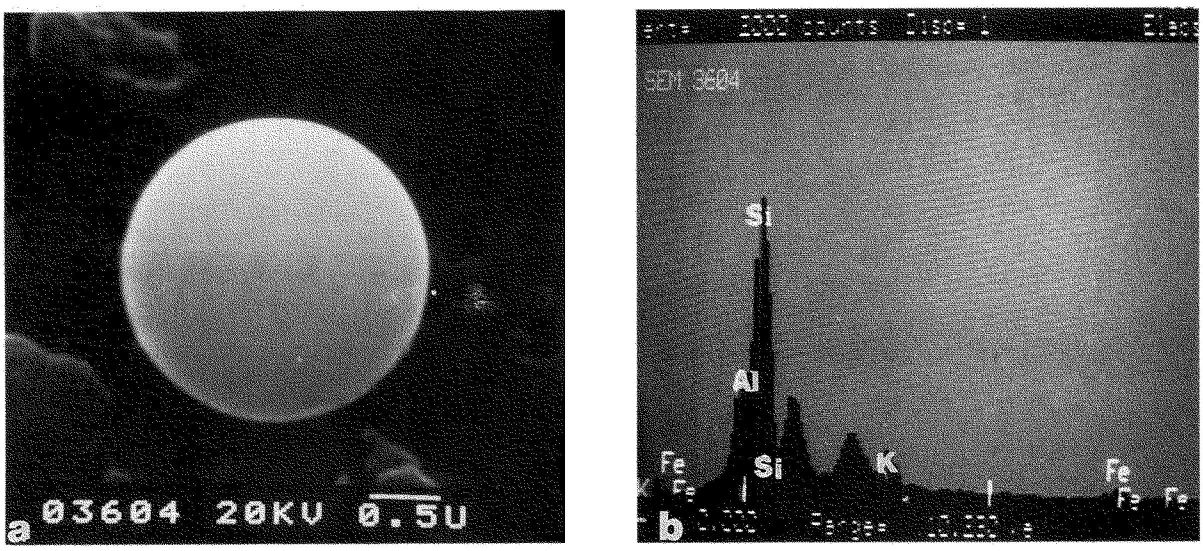


Fig. 10. SEM image of a Si-rich spherule with a smooth surface from the autumn firn layer of 1981 (a), and its elemental composition (b).

The ice sample examined in this study was less than one year in thickness and represents the period 45 B. C. ± 60, as determined by Dansgaard *et al.* (1984). Thus, the particles found in the ice core were deposited by precipitation and dry fallout around the year 45 B. C. We found many clay and related mineral particles, some microspherules, pollen grains and spores in the ice core sample. Typical examples of particles found in the ice core are shown in Figures 14–19.

6.1. Silicate mineral particles in ice core

Many mineral particles less than 2 μm in diameter were found in the ice core. Elemental compositions and sizes of typical silicate particles are shown

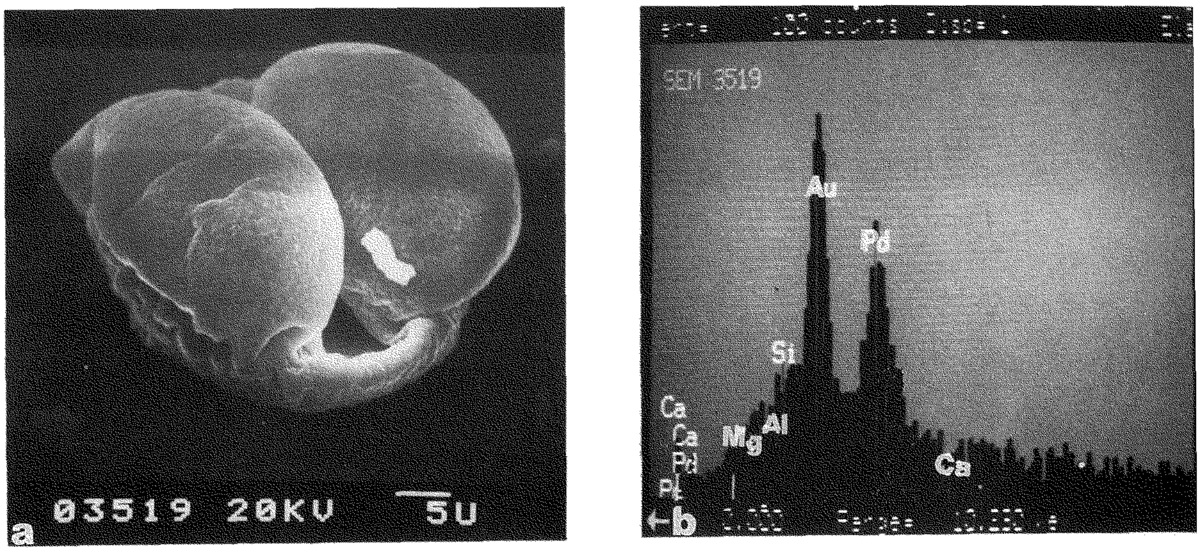


Fig. 11. SEM image of a pine pollen grain from the spring firn layer of 1982 (a), and its elemental composition (b).

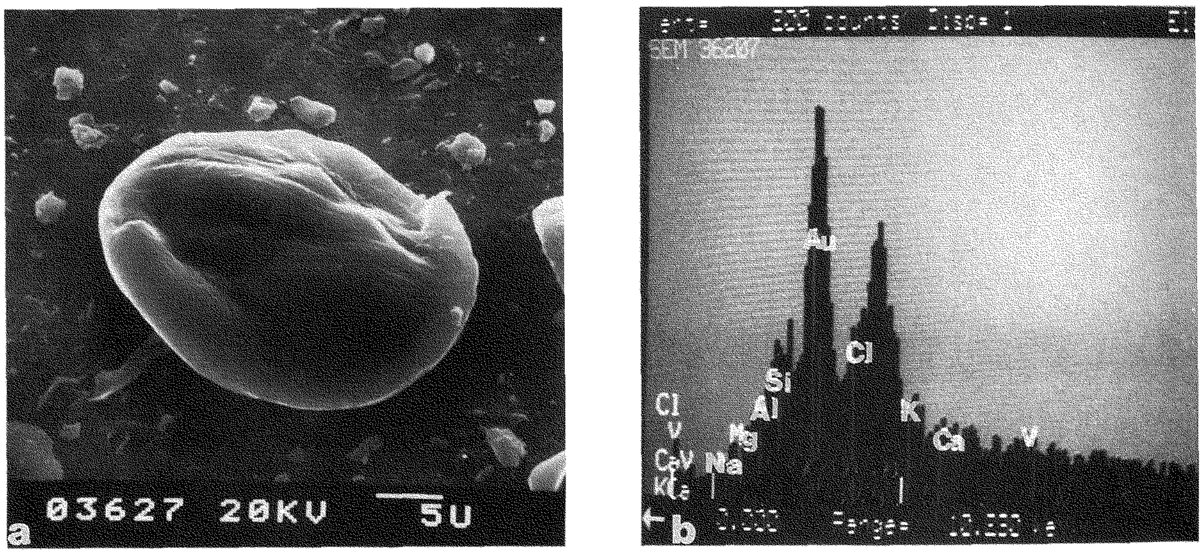
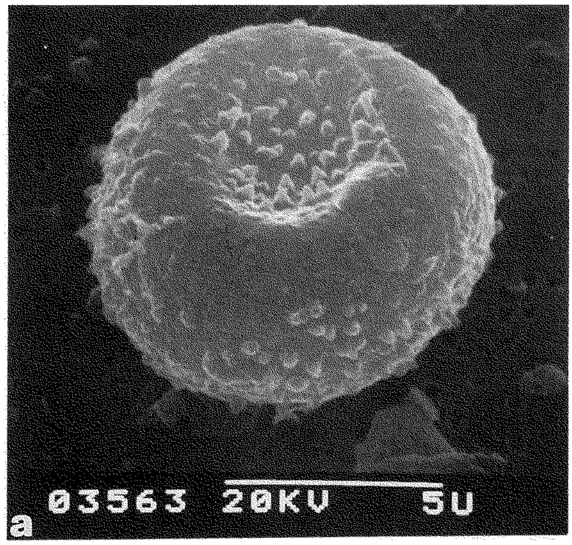


Fig. 12. SEM image of a maple pollen grain from the autumn firn layer of 1981 (a), and its elemental composition (b).

in Table 3. In the mean elemental compositions of the minerals, the element of maximum concentration was Si, followed by Al, Ca, Fe, Mg, K, Ti, Cu, Cr, Co and Na. The diameters of mineral particles varied from 3.9 to 25.9 μm, with a mean value of 12.8 μm. An SEM image of a representative clay mineral particle, together with its elemental composition, is shown in Figure 14. The particle measured 8.1 μm in diameter and contained the major elements Si, Al, K, Fe, Ti, Ca, Mg and Cr. The shape, size and elemental compositions are similar to that of an illite particle (Kerr and others, 1950). The morphology, size and lattice spacings of the clay mineral particles are similar also to some snow crystal nuclei found at Site 2, Greenland (Kumai and Francis, 1962).

Another type of silicate mineral grains consisting of many particles aggregated together is shown in Figure 15. The morphology of the silicate mineral



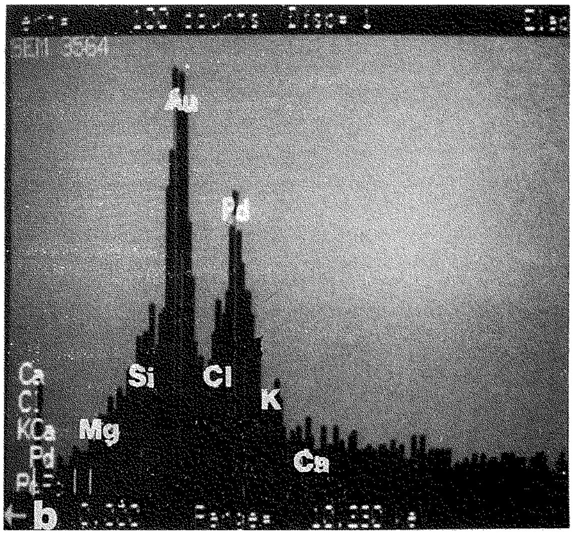


Fig. 13. SEM image of a wheat smut spore from the autumn firn layer of 1981 (a), and its elemental composition (b).

Table 3. Elemental composition (weight %) and size of silicate minerals in 45 B.C. ice core from DYE-3, Greenland.

Sample	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Dia. μ
3386	0	9.3	16.9	46.4	0	0	0	5.0	4.6	3.8	0	2.5	0	6.8	1.3	0	3.4	25.9
3389	0	2.9	17.8	26.4	0	0	0	0	46.0	0	0	0	0	5.2	0	0	1.7	12.2
3390	0	0	8.5	91.5	0	0	0	0	0	0	0	0	0	0	0	0	0	3.6
3405	0	0	33.6	51.9	0	0	0	4.3	4.0	1.7	0	0	0	2.7	0	0	1.8	20.0
3406	0	10.2	23.0	41.2	0	0	0	2.2	4.4	5.7	0	0	0	10.1	0	0	3.1	3.9
3408	0	3.7	21.3	59.6	0	0	0	4.3	3.2	1.1	0	0	0	4.2	0	0	2.6	5.3
3409	0	3.6	23.3	57.0	0	0	0	3.7	3.1	1.0	0	0	0	6.7	0	0	1.6	17.3
3410	1.0	10.5	17.1	50.3	0	0	0	8.0	0	2.5	0	0	0	10.6	0	0	0	16.2
4067	0	8.2	16.4	45.2	0	0	0	3.4	8.9	4.2	0	4.1	0	4.8	1.4	0	3.4	9.3
4068 Fig. 14	0	1.5	27.7	52.8	0	0	0	8.2	2.1	2.6	0	1.0	0	4.1	0	0	0	8.1
4073 Fig. 15	0	2.1	29.4	57.7	0	0	0	3.4	2.5	1.5	0	1.0	0	2.4	0	0	0	19.7
Mean	0.1	4.7	21.4	52.7	0	0	0	3.9	7.2	2.2	0	0.8	0	5.2	0.2	0	1.6	12.8

grain (Fig. 15) is similar to a morainic soils from glacier (Kumai and others, 1978).

6.2. Spherules in ice core

Silicate spherules were also found in the 45 B. C. ice core. The elemental compositions and sizes of typical spherules are shown in Table 4. The mean elemental compositions of the spherules showed that Si was the most abundant, followed by Ca, Al, Fe, Ti, Mg and Cu. Spherule diameters varied from 0.5 to 9.1 μm with a mean value of 4.2 μm. Figure 16 shows a spherule measuring 9.1 μm in diameter. It contained the elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, as shown in Table 4. Another silicate spherule with a smooth surface is shown in Figure 17 along with its elemental composition. These two spherules differ in elemental composition from industrial spherules, such as coal fly ash, and they may be of extraterrestrial origin.

6.3. Pollens and spores in ice core

Both pollens and spores were found in the 45 B. C. ice core sample. EDX analysis revealed only trace elements of Si, Al, Mg, Na, Cl and Ca in the pollens and spores. A pine pollen measuring 42.0 μm in diameter is shown in Figure 18. It had an oval body with two attached bladers. This SEM image of pine pollen (Fig. 18) is the inverted image of pine pollen shown in Figure 11. The spores in the ice core ranged in size from 8.9 to 9.7 μm in diameter. The surfaces of the spores were smooth, but were broken by strong electron beam irradiation. An oval-shaped spore is

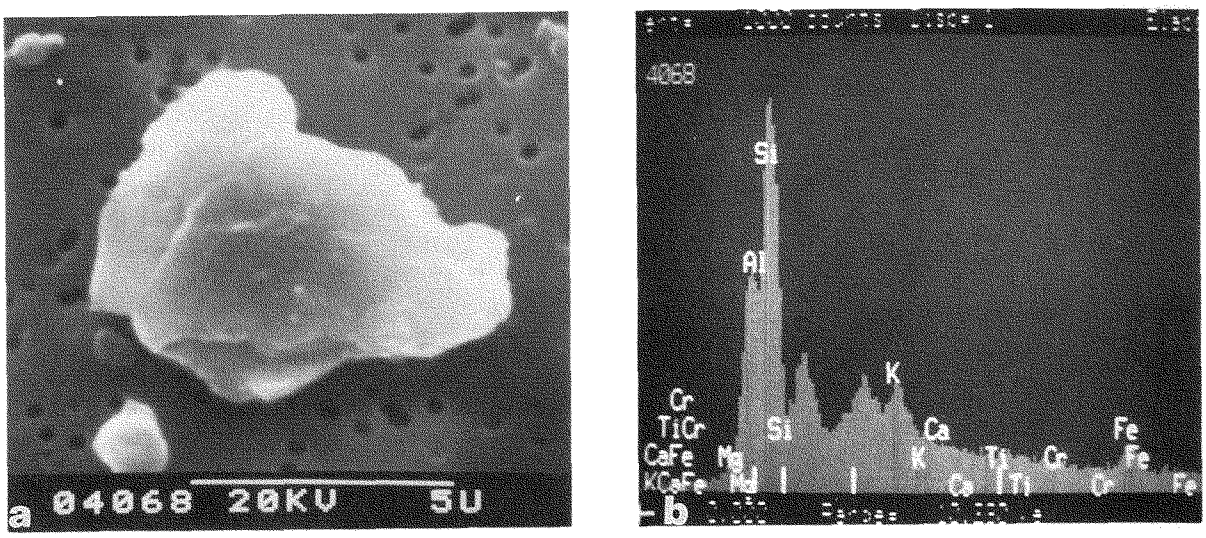


Fig. 14. SEM image of a mineral particle from the 45 B. C. ice core (a), and its elemental composition (b).

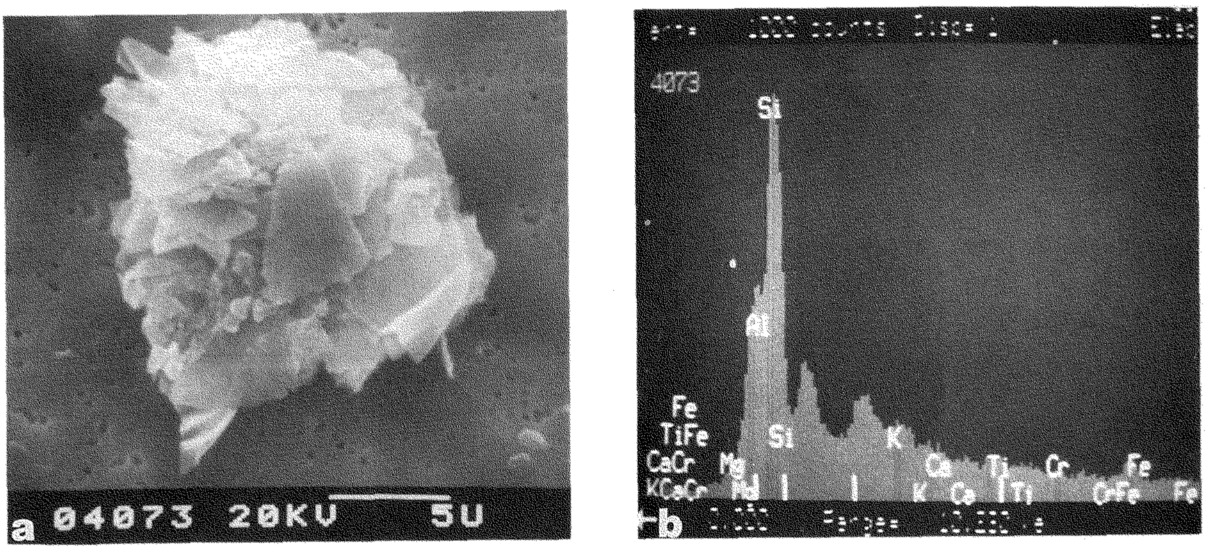


Fig. 15. SEM image of a silicate mineral particle consisting of many grains from the 45 B. C. ice core (a), and its elemental composition (b).

Table 4. Elemental composition (weight %) and size of spherules in 45 B.C. ice core from DYE-3, Greenland.

Sample		Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Dia. μ
2421	Fig. 16	5.2	6.3	8.7	12.5	9.9	12.4	7.5	5.2	4.7	3.8	3.5	2.5	2.3	2.5	2.5	2.3	5.2	3.2	9.1
3442		0	0	0	100.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.1
3448		0	8.6	19.3	24.9	0	0	0	10.7	6.4	3.0	0	0	0	21.0	0	0	6.0	0	0.5
4063		1.2	3.7	9.9	23.7	0	0	0	9.1	45.5	1.2	0	0	0	3.7	0.8	1.2	0	0	8.0
4093		1.6	2.7	24.3	51.7	0	0	0	9.7	2.2	1.6	0	0	0	4.3	0	0	1.9	0	2.6
4094	Fig. 17	0	4.9	0	61.8	0	0	0	5.6	7.4	4.9	0	0	0	14.2	0	1.2	0	0	2.9
Mean		1.3	4.4	10.4	45.8	1.6	2.0	1.3	6.7	11.0	2.4	0.6	0.4	0.4	7.6	0.6	0.8	2.2	0.5	4.2

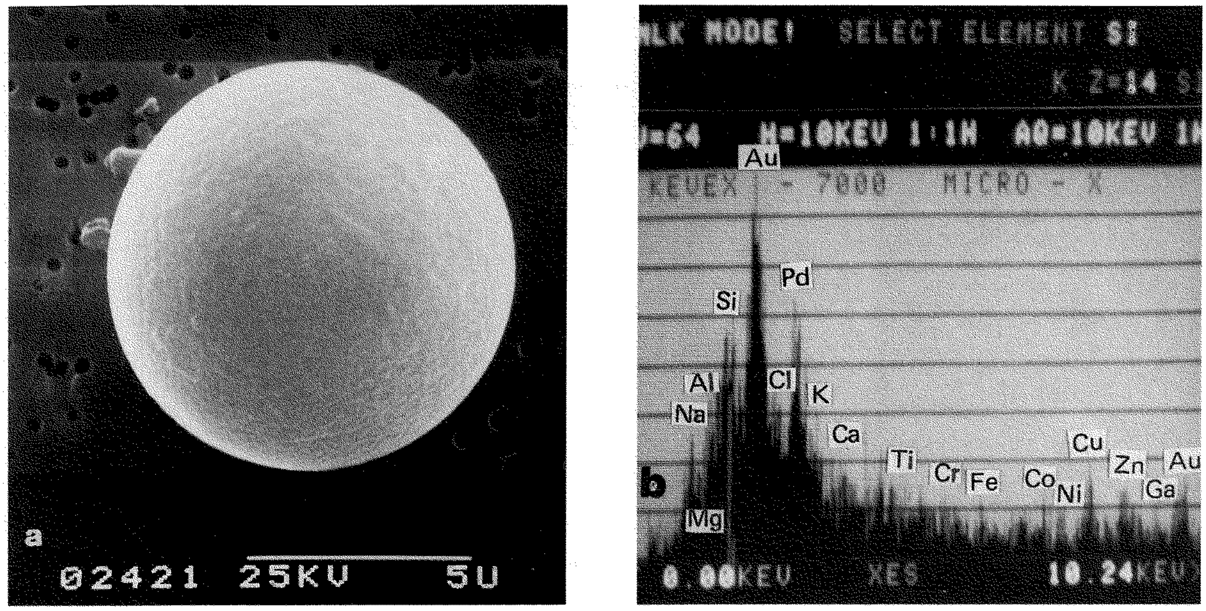


Fig. 16. SEM image of a spherule containing many elements from the 45 B. C. ice core (a), and its elemental composition (b).

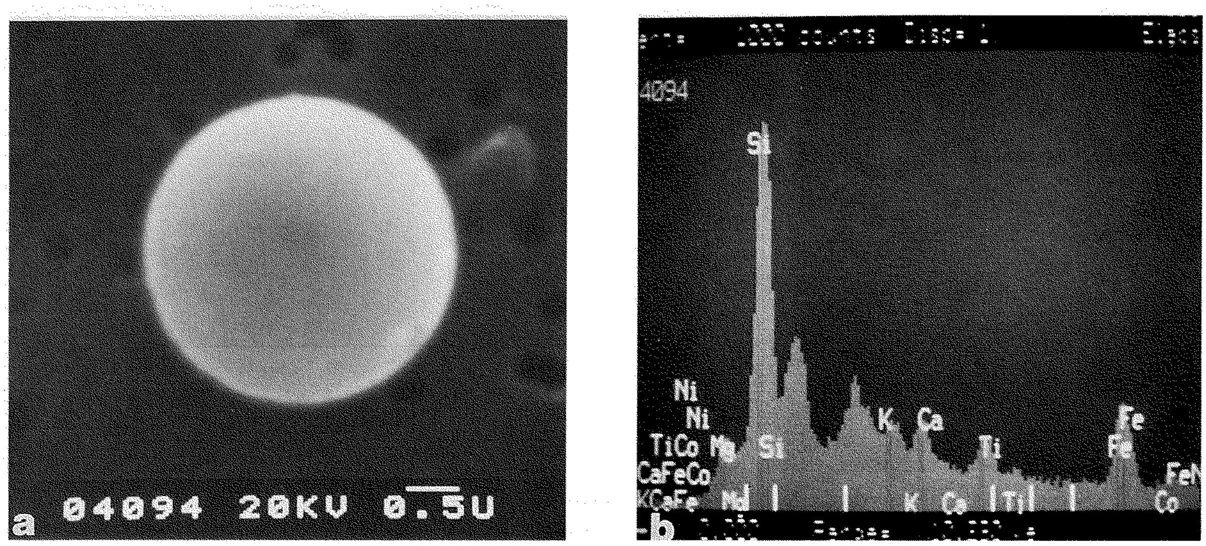


Fig. 17. SEM image of a Si-rich spherule with smooth surface from the 45 B. C. ice core (a), and its elemental composition (b).

shown in Figure 19, together with its elemental composition. However, the species of this spore could not be identified from the particle atlas of spores (McCrone and Delly, 1973).

7. Particle Size and Concentration

The concentrations and sizes of particles in firn and ice core samples were measured from the SEM images of particles for the known mass of samples in order to compare the levels of concentration before and after the industrial revolution. Two kinds of spherules were found in particles from firn and ice

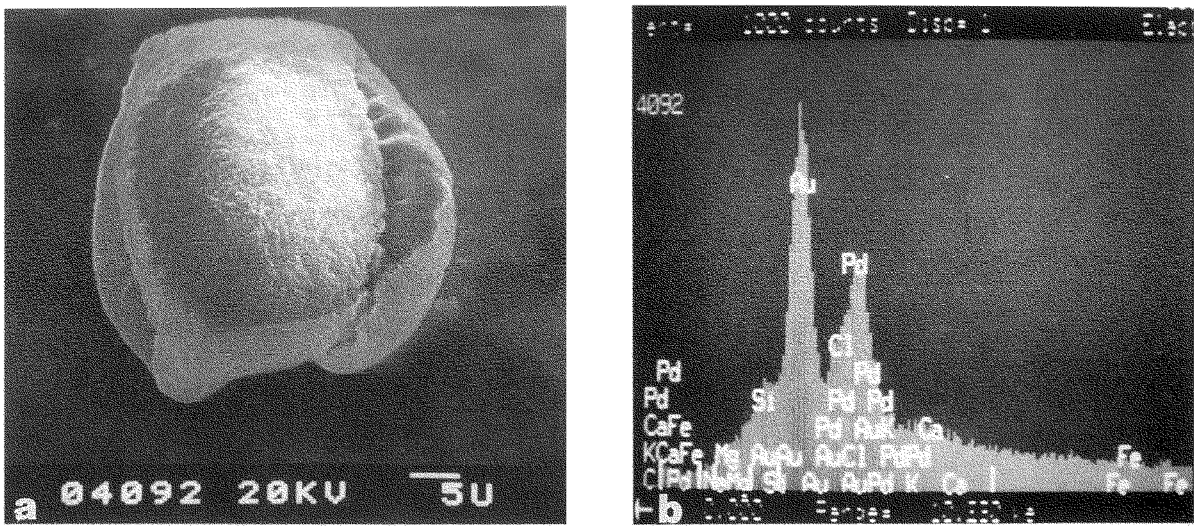


Fig. 18. SEM image of a pine pollen grain from the 45 B. C. ice core (a), and its elemental composition (b).

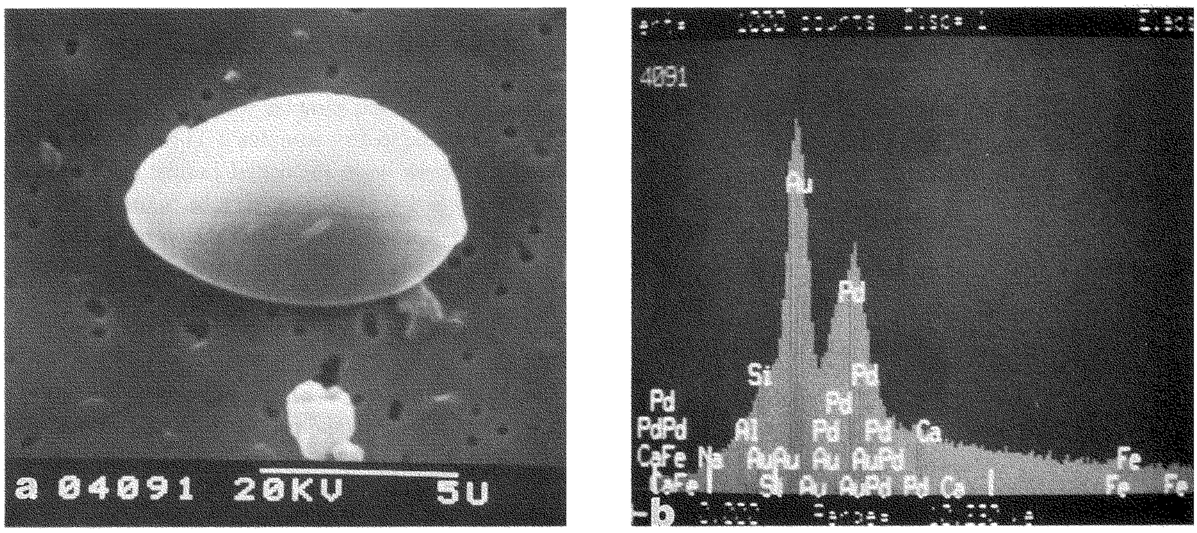


Fig. 19. SEM image of a spore from the 45 B. C. ice core (a), and its elemental composition (b).

core samples : either inorganic or organic, according to EDX analysis. The inorganic spherules may be of both terrestrial and extraterrestrial origin. It is well known that very large amounts of inorganic spherules are produced from coal-fired power and heating plants throughout the world. The organic spherules were identified as spores on the basis of size and morphology. Organic spherules have been identified previously in snow crystal nuclei from Site 2, Greenland, from observations with the transmission electron microscope and from electron diffraction analysis (Kumai and Francis, 1962 ; Byers, 1965).

7.1. Particle size and concentration in firn samples

To measure the size and concentration of particles in firn samples, six firn samples were selected from the firn samples from the wall of a pit at DYE-3, Greenland. The firn samples represent snow deposition during the winter and summer of 1981–83. Filters with a 0.4-μm-diameter pore size were used for

Table 5. Concentration and size of particles in firn and ice core samples from Dye 3, Greenland.

Time of snowfall	Particles/g firn	Size range, Dia. μm
July 1983	1.30×10^5	0.2–43.6
Jan. 1983	9.54×10^5	0.5–30.0
July 1982	1.33×10^5	0.1–28.2
Jan. 1982	1.06×10^5	0.2–47.5
July 1981	1.95×10^5	0.1–45.0
Jan 1981	1.47×10^5	0.1–60.0
Mean	2.78×10^5	
611 A.D.	6.32×10^4	0.1–42.5
45 B.C.	2.72×10^4	0.4–37.5
730 B.C.	4.10×10^4	0.2–31.2
Mean	4.36×10^4	

Table 6. Concentration and size of spherules and spores in firn and ice core samples from Dye 3, Greenland.

Time of snowfall	Spherule/g firn or ice	Spherule Range, μm	Spherule Mean dia. μm	Spore/g firn or ice
July 1983	18.2	1.4–13.6	3.7	2.4
Jan. 1983	15.3	1.0– 2.6	1.7	23.8
July 1982	54.3	0.7– 2.8	1.3	6.3
Jan. 1982	10.1	0.7– 7.4	2.4	10.0
July 1981	23.6	0.6– 2.7	1.6	26.6
Jan. 1981	27.1	1.0– 1.7	1.4	8.1
Mean	24.8		2.0	12.9
611 A.D.	1.1	0.7– 2.3	1.1	1.4
45 B.C.	0.6	0.5– 9.1	4.2	0.6
730 B.C.	0.9	1.0– 9.2	3.4	1.4
Mean	0.9		2.9	1.1

filtering firn and ice core samples for SEM sample preparation. Although most particles smaller than 0.4 μm passed through the filter during sample preparation, some particles smaller than the pore diameter were observed on the filter, as shown in Figure 14.

The concentrations and sizes of particles larger than 0.4 μm diameter obtained from winter (January) and summer (July) firn samples during 1981–83 from DYE-3, Greenland, are shown in Table 5. The maximum particle concentration was 9.54×10^5/g firn for the January 1983 sample and the minimum was 1.30×10^5/g firn for the July 1983 sample. The mean was 2.78×10^5/g firn for all the 1981–83 samples. Particle diameters varied from 0.1 to 60.0 μm in 1981–83 firn samples.

Concentrations of spherules and spores in firn samples from DYE-3, Greenland, are shown in Table 6. The concentrations of spherules varied from 10.1/g firn to 54.3/g firn during 1981–83, with the mean at 24.8/g firn. The majority of spherules were identified as coal fly ash on the bases of elemental composition and morphology. As shown in Table 6, the concentrations of spores in firn samples varied from 2.4/g firn to 26.6/g firn during 1981–83 ; the mean was 12.9/g firn.

7.2. Particle size and concentration in ice core samples

Concentrations and size of particles larger than 0.4-μm-diameter in the ice core samples, dated at 611 A. D., 45 B. C. and 730 B. C., respectively, were measured from SEM images for samples of known mass. The results are shown in Table 5. Particle concentration was 6.32×10^4/g ice for 611 A. D., 2.72×10^4/g ice for 45 B. C. and 4.10×10^4/g ice for 730 B. C. The mean concentration of particles in ice cores was 4.36×10^4/g ice, about 1/6.4 of that of firn samples. This result shows that the concentration of solid particles in firn samples from 1981–83 was 6.4 times higher than that found in ice cores from 611 A. D., 45 B. C. and 730 B. C. at DYE-3, Greenland.

The spherule concentration in ice cores was 1.1/g ice for 611 A. D., 0.62/g ice for 45 B. C. and 0.93/g ice for 730 B. C. (Table 6). The mean concentration of spherules in ice core samples was 0.9/g ice, about 1/27.6 of that found in firn samples. The spherules in the deep ice cores were deposited before the industrial revolution and are considered to be mainly of natural origin, for example, volcanic eruption or cosmic dust. The size of spherule diameters varied from 0.5 to 9.2 μm. This result shows that the concentration of atmospheric spherules in firn from 1981–83 was 27.6 times higher than that of ice cores from 611 A. D., 45 B. C. and 730 B. C. The large increase of spherules in firn samples deposited during 1981–83 is attributed to coal fly ash input from modern industrial sources over the natural aerosols and dry fallout.

The spore concentrations in ice core samples varied from 0.6/g ice to 1.4/g ice. The mean concentration was 1.1/g ice, and it was 1/11.7 of that of firn samples from 1981–83. The pollen concentrations in firn samples were several times higher than those of ice core samples. The increase of pollen and spore concentration in the firn samples may be related to precipitation rates and temperature increases at higher latitudes in the northern hemisphere (Dansgaard *et al.*, 1984).

8. Conclusions

The particles in the firn samples from DYE-3, southern Greenland were identified to be both natural and anthropogenic in origin, including silicate mineral particles, coal fly ash, pollen grains and spores. Some silicate spherules differed apparently from those of industrial origin and are considered to be of extraterrestrial origin. Some organic particles were identified as pine pollen, maple pollen and mushroom spores. There is an increase of 6.4 times for particle concentration in firn from 1981–83 in comparison with that of ice cores from 611 A. D., 45 B. C., and 730 B. C. The increase of particle concentration in firn samples can be explained partly by inputs from modern anthropogenic sources.

In the ice cores we found silicate mineral particles, silicate spherules, pollen grains and spores. Some silicate spherules in the ice cores differed significantly in elemental composition and morphology from those of industrial origin, and they may be of an extraterrestrial origin. Organic particles in ice cores were identified as pine pollen and spores.

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