Electron microscope analysis of aerosols in snow and deep ice cores from Greenland

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Abstract. Electron microscope analysis of aerosols in snow and deep ice cores from Camp Century, Greenland, was carried out to investigate long-term variation of atmospheric dust particles. The aerosols in snow crystals were mainly silicate minerals, sea salt particles, and some unidentified particles. The silicate minerals were 0.05–8 \( \mu \)m in diameter, but most of them were smaller than 1 \( \mu \)m. It is determined that 1 g of snow contained \( 4.9 \times 10^6 \) silicate minerals \( (33.7 \times 10^{-9} \text{ g}) \). The depth of the ice cores selected for this study was 547–1368 m from the surface of the ice sheet. The approximate age of the ice cores was 2000–100 000 years. The aerosols in the cores were mainly silicate minerals and sea salt particles. The concentration of silicate minerals in ice cores of Wisconsin and Sangamon age was higher than that of snow and ice cores of the Holocene age.

INTRODUCTION

Electron microscope analysis of aerosols in snow crystals and deep ice cores from Camp Century, Greenland (77°10'N, 60°08'W, 1885 m a.s.l.) was conducted to investigate long-term variations in the concentration and identification of atmospheric dust particles.

Previously during the summer of 1960, snow crystals had been collected for nuclei identifications at Site 2, located at 2000 m a.s.l. about 320 km east of Thule on the Greenland ice cap, one of the most aerosol-limited places on the earth's surface. The electron microscope study indicated that the natural snow crystals at Site 2 usually developed in supercooled clouds at a temperature between −5 and −20°C, were nucleated mainly by heterogeneous nucleation. By electron diffraction analysis, 85 per cent of the nuclei were identified as clay mineral particles, 0.6 per cent were hygroscopic particles, 10.7 per cent were unidentified mineral particles and 3.7 per cent had no observed nuclei (Kumai and Francis, 1962).

Since the Greenland ice sheet formed by recrystallization of accumulated snow, it is considered possible that atmospheric dust particles of the Holocene, Wisconsin and Sangamon ages can be detected in deep ice cores by electron microscope analysis. During several decades ice core studies have been carried out to determine variations of physical and chemical properties. In 1966 ice core drilling reached the bottom of the Greenland ice sheet at a depth of 1387.4 m (Hansen and Langway, 1966) and the ice at the bottom of this sheet was
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calculated to be 120,000 years old. A 3.55-m-long sub-ice core consisted of frozen till-like material. No pressure melting was observed at the bottom of the ice sheet.

The heavy isotope content of water reflects past and present climatic conditions. Oxygen-18 concentration in the Greenland ice sheet was studied as an indicator of past climate by Dansgaard (1954), Epstein and Sharp (1959), Lorius (1963), and Dansgaard et al. (1969). Stratigraphic analysis of the deep ice core was carried out by Langway (1967).

In this paper, the results of the examination of atmospheric dust particles found in snow crystals and deep ice cores collected at Camp Century during 1965 and 1966 are presented and discussed.

AEROSOLS IN SNOW

Preparation
Precipitation at Camp Century falls generally in the form of snow crystals. The shapes of snow crystals at this site are needle-like, plate-like, dendritic, columnal, irregular, and graupel. The most frequently occurring diameter is 1 mm. Snow crystals were collected directly on collodion-filmed grids for electron microscopy. The sublimation process of the crystals was photographed at temperatures below freezing in an igloo at Camp Century. After the sublimation, the aerosols in snow crystals remained on the grids, and were shadowed by chromium vapour in a vacuum chamber for the electron microscope examination. The Debye-Scherrer pattern of shadowed specimens by chromium was used as a means of identifying the substance of the nucleus.

Measurements
Electron micrographs and electron diffraction patterns of snow crystal nuclei were taken for the identification and measurement of aerosol size and concentration. The nuclei of the snow crystals were found at the centre of the crystals, and minute dust particles were found in the rest of the area. For example, the nucleus [Fig. 1(a)] of a dendritic snow crystal was analysed as a clay mineral by the electron diffraction pattern of a selected area [Fig. 1(b)]. The interplaner distances for the net pattern of this crystal were 2.56 Å for \(d_{200}\) and 4.43 Å for \(d_{020}\), which corresponds to the \(a\)-axis of the unit cell (\(a = 5.12\) Å). Minute silicate minerals were found also in the branches of the crystal.

![FIGURE 1.](image-url) (a) Clay mineral in a snow crystal. (b) Electron diffraction pattern of clay in (a).
An average of about 40 silicate minerals was found in each snow crystal from Camp Century. The size of the silicate minerals ranged from 0.005 to 8 \( \mu \text{m} \) in diameter, but most of them were smaller than 1 \( \mu \text{m} \). Identification of central nuclei of snow crystals revealed that 84 per cent were silicate minerals, 1 per cent were sea salt particles, 10 per cent were unidentified particles and 5 per cent were nonobserved nuclei. The size distribution and concentration of silicate minerals per gram of snow crystals from Camp Century, Greenland are shown in Fig. 2. The size of the snow crystals ranged from 0.5 to 4 mm in diameter, and their mean mass was calculated to be \( 8.22 \times 10^{-6} \text{ g} \) for needle-like, plate-like, dendritic, columnal and irregular shapes. Central nuclei of the crystals were generally larger than 0.1 \( \mu \text{m} \), and silicate minerals found in the rest of the area were generally smaller than 0.1 \( \mu \text{m} \). However, large sea salt particles were sometimes found in the branches of the crystals. It was calculated that 1 g of the snow at Camp Century contained \( 1.22 \times 10^{5} \) snow crystals and \( 4.9 \times 10^{6} \) silicate mineral particles (33.7 \( \times 10^{-9} \text{ g} \)).

**AEROSOLS IN ICE CORES**

**Preparation**

The ice cores obtained at Camp Century were kept at \(-20^\circ \text{C}\) in a refrigerated laboratory at the USA CRREL, Hanover. Experiments were carried out in the laboratory at a temperature of \(-10^\circ \text{C}\).

The depths of the ice cores selected for this study were 547, 1170, 1197, 1224, 1302, 1314, 1322, 1355 and 1368 m from the surface of the ice sheet at Camp Century in 1966. When a thin section of deep ice core is observed under a microscope with slightly cross-polarized filters, grains in the ice are revealed.
The increase of the grain size in deep ice cores shows that a slow rate of growth by recrystallization occurs within the ice sheet. The approximate ages of the cores were 2000–100 000 years.

Every precaution was taken to prevent contamination of the specimens during preparation. All specimens for this study were clear ice with atmospheric air bubbles. Each specimen weighed about 150 g. A known volume of a specimen was sublimed below freezing temperature on collodion-filmed grids for electron microscopy. Aerosols in the core samples remained on the grids, and were shadowed by chromium vapour at an angle of 19°25' in a vacuum chamber, so that the aerosol thickness could later be determined from the length of shadow. The lattice spacing of aerosols in the cores was determined by comparing the aerosols' electron diffraction patterns with those from a standard substance such as gold or sodium chloride.

Measurements
In total, 339 electron micrographs and electron diffraction patterns were taken for the identification and measurement of the size and concentration of aerosols in the ice cores. Similar particles were found in snow crystals. Typical electron micrographs and electron diffraction patterns of atmospheric dust particles in ice cores at each depth are shown in Figs. 3–11. For example, a particle of

![Figure 3](image-url)
FIGURE 4. (a) Clay minerals in the ice core at 1170.15 m depth. (b) Electron diffraction pattern of clay mineral in (a).

FIGURE 5. Clay mineral in the ice core at 1197.6 m depth.

FIGURE 6. Clay mineral in the ice core at 1224 m depth.

FIGURE 7. Clay mineral in the ice core at 1302 m depth.
FIGURE 8. (a) Particle, possibly volcanic ash, in the ice core at 1314.3 m depth. (b) Electron diffraction pattern of the particle in (a).

FIGURE 9. Silicate minerals in the ice core at 1322 m depth.

FIGURE 10. (a) Clay minerals in the ice core at 1355 m depth. (b) Electron diffraction pattern of mineral in (a).
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FIGURE 11. (a) Sea salt particles and clays in the ice core at 1368 m depth. (b) Mica needle in the ice core at 1368 m depth. (c) Electron diffraction pattern of mica in (b).

1.3 μm diameter [Fig. 3(a)] obtained from the ice core at 547 m depth was identified as a silicate mineral. In the same specimen of the core, hygroscopic particles were also found [Fig. 3(b)]. From their electron diffraction patterns [Fig. 3(c)] these particles were identified as sea salt (NaCl with trace of KCl).

Thirty electron micrographs were taken of the core from 547 m to determine the size distribution of silicate minerals for the known mass of the samples at magnifications from × 500 to × 10 000. The size range of the silicate particles was 0.05–8 μm. The concentration of silicate minerals in ice cores was of the same order as that of the present snow cover (3 × 10⁶ particles, 32 × 10⁻⁹ g/g of snow).

Electron micrographs and the electron diffraction patterns of aerosols in ice cores at 1170, 1197, 1224 and 1302 m depth are shown in Figs. 4, 5, 6 and 7, respectively. These aerosols showed hexagonal net patterns as seen in Fig. 4(b), and were identified as silicate minerals. The size distributions of the silicate minerals—ranging from 0.04 to 9 μm—were obtained from electron micrographs of known volume samples at each depth. Sea salt particles were also found in cores at each depth. The age of the core samples ranged from about 13 000 to 17 000 years old (the late Wisconsin age), and the concentration of silicate minerals in these core samples was much higher than that of the present snow cover.
Many particles with sharp edges [Fig. 8(a)] were found in an ice core of the Middle Wisconsin age (about 37 000 years old) at a depth of 1314.3 m. The diffraction pattern of these particles [Fig. 8(b)] consisted of diffused rings and showed amorphous substances, such as volcanic ash. Silicate minerals and their diffraction patterns in cores at 1322 m and 1355 m depth of the Middle Wisconsin are shown in Figs. 9 and 10, respectively. The size range of the silicate minerals was from 0.04 to 8 μm, and the concentration of silicates in this core was much higher than that of the present snow cover.

A brown coloured band of silt, visible to the naked eye, was found in the ice core at 1368 m depth, 19.4 m above the bottom of ice sheet. It is suspected that this band was derived from the frozen till located under the ice mass. A colourless ice core sample 2.5 cm above the silt band was examined. Twenty electron micrographs of aerosols in this clear ice were taken to measure the aerosols' sizes and concentrations. Irregularly shaped minerals in various sizes [Fig. 11(a)] showed ring patterns of electron diffraction, and were identified as NaCl with a trace of KCl. These minerals were considered to be sea salt. A needle-shaped mineral of 4.5 μm length [Fig. 11(b)] showed a diffraction pattern illustrated in Fig. 11(c), and the a-axis of the unit cell was determined to be 5.18 Å. The needle mineral was identified as a fraction of a mica needle by the cell dimension and morphology (Rex, 1966). The concentration of silicate minerals was determined to be $8.3 \times 10^8$ particles ($2.7 \times 10^{-4}$ g) in 1 g of ice. Its size distribution is shown in Fig. 2.

**SUMMARY AND CONCLUSION**

**Aerosols in snow**

1. The atmospheric dust particles in snow crystals were mainly silicate minerals, sea salt particles and some unidentified particles. The nuclei of the snow crystals were found at the central portion of crystals. Eighty-four per cent of the nuclei were identified as clay minerals from the d-spacing by electron diffraction analysis and also by morphology. Minute atmospheric dust particles collected during crystal growth and precipitation were also found in the branches of the crystals.

2. Silicate minerals, 0.02–8 μm in diameter, and an average of $4.9 \times 10^6$ particles ($33.7 \times 10^{-9}$ g) of silicates were found in 1 g of falling snow crystals. The concentration of silicate minerals in snow from Greenland was about double that found at South Pole station, Antarctica (Kumai, 1976).

3. The concentration of silicate minerals in snow cover from 1753 to 1965 at Camp Century was estimated to be $35 \times 10^{-9}$ g per gram of snow cover by Murozumi et al. (1969). The concentration of silicate minerals in the snow cover is of the same order as that in falling snow crystals. This indicates that the dry fallout of silicate minerals at Camp Century is very small.

**Aerosols in ice cores**

1. The nonhygroscopic aerosols in the cores were mainly silicate minerals, and were identified as clay and related minerals by electron diffraction analysis and by analysis of their morphology. The origin of these clay minerals was mainly from the nuclei of snow crystals. The concentrations of silicate minerals in ice cores of Wisconsin age were higher than those of falling snow crystals, of recent snow cover, or of ice cores of Holocene age.

2. The concentration of silicate mineral in a clear ice core near a silt band at 1368 m (Sagamon age) was $8.3 \times 10^8$ particles ($2.7 \times 10^{-4}$ g), and was the maximum particle concentration in this examination.
The hygroscopic aerosol particles in ice cores were identified as sea salt particles by analysis of their electron diffraction patterns. The sea salt particles resembled the hygroscopic nuclei found in sea fog droplets.

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DISCUSSION

Picciotto:
In the last table you showed, what is the meaning of ‘clay concentration’? Is it a value computed from the results of chemical analysis or is it resulting from direct counting of particles?

Kumai:
The concentration of silicate minerals in snow crystals and ice cores from Greenland and Antarctic specimens was calculated directly from their size and thickness obtained by electron microscopy for a known mass of specimens.

Warburton:
Did you ever observe particles of 1 \(\mu\text{m}\) or larger at locations in snow crystals other than at the nucleus?

Kumai:
Yes, but it is very seldom in snow crystals from Greenland and Antarctica.

Warburton:
Were those specific particles composed of minerals normally recognized as ice nucleation minerals?
Kumai:
Yes, they were silicate minerals (= clay), as found at the centre. But such particles were found very seldom. In general, those particles are smaller than 0.1 μm in diameter.

Linkletter:
You report, that most of the centre nuclei are clay particles. Yet, also you report an important contribution to the overall particle content by sea salts. Have you observed any relationship between the amount of riming on snow crystals and the concentration of sea salts in crystals?

Kumai:
Generally, sea salt particles were found in rimed snow crystals. The mass of sea salt particles was between $10^{-12}$ and $10^{-14}$ g for rimed snow crystals from Greenland and Antarctica. However, sometimes sea salt particles were found in non-rimed snow crystals. When the sizes of cloud droplets collected by snow crystals were smaller than 10 μm in diameter, the cloud droplets were possibly spread on the surface of the snow crystals.

Higuchi:
Why do you think that sea salt particles were transported by snow crystals? Such a transportation can occur by formation of rimed crystals. Did you observe enough rimed crystals to explain the amount of sea salt particles? How do you think about dry fallout of sea salt particles?

Kumai:
Many rimed crystals were found in snow crystals from Camp Century and some from South Pole station. Sea salt particles were found in both rimed and non-rimed snow crystals. It is believed that the majority of the sea salt particles was trapped during nucleation, growth and precipitation of the snow crystals. Dry fallout of sea salt is considered to be small at South Pole because of the great distance from the sea coast.