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Scientific note

210-year ice core records of dust storms, volcanic eruptions and acidification at Site-J, Greenland

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Abstract: 210-year records of dust concentration, electrical conductivity, acidity (pH), non-sea salt sulfate (nss sulfate) and nitrate concentrations were obtained for an ice core from Site-J, Greenland. The ice core was well dated by counting annual cycles of the $\delta^{18}O$ profile and by tuning with time markers established for tritium peaks and the Laki 1783 eruption signal. Dust records in both ice cores from Site-J and Crête suggest that dust storms occurred in 1818, 1900, 1919, 1936 and 1943 over Greenland. Electrical conductivity shows remarkable peaks probably due to volcanic eruptions with VEI larger than 4. The anthropogenic effect on precipitation chemistry started in *ca.* 1860, 40 years earlier than the time previously reported. Nss sulfate increased remarkably, much more than nitrate, because of the rapid increase in solid fossil fuel combustion, but by the early 1970's, the nitrate concentration exceeded the nss sulfate concentration due to the intense increase in liquid fossil fuel combustion since the 1950's. The decrease in sulfate and nitrate concentrations started in the early 1970's. This is attributed to the spread of suppression facilities for anthropogenic pollutants emitted by the combustion of solid and liquid fossil fuels.

1. Introduction

As the Greenland Ice Sheet has much snow accumulation, the original stable oxygen isotope profile at the time of deposition is well preserved even though it has been smoothed by diffusive processes (*e.g.* Dansgaard *et al.*, 1973). Greenland ice cores, therefore, provide detailed climate and environment records over the past thousand years (*e.g.* Johnsen *et al.*, 1972; Mayewski *et al.*, 1990; Clausen *et al.*, 1998). There have been many works done on the climate and environment changes in the past with Greenland ice cores, but not many works on detailed environment changes in dust storms, volcanic eruptions and acidification during the past hundred years since the pre-Industrial Era. These signals in an ice core are well associated with atmospheric loading of aerosols, which play an important role in the climate system because of their direct or indirect interaction with solar and terrestrial radiation.

We present changes in dust concentration, electrical conductivity, acidity and major ions, and discuss dust storms, volcanic eruptions and anthropogenic acidification during the

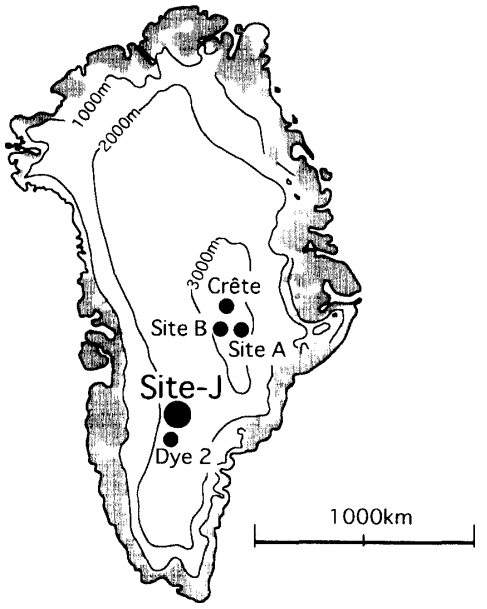

Fig. 1. Location of Site-J, Greenland. Ice core drilling sites referred to in this study are shown by small solid circles.

past 210 years on the basis of analyses of an ice core from Site-J (66°51.9′N, 46°15.9′W and 2030 m a.s.l.; Fig. 1) in southern Greenland. The place is far from any local anthropogenic sources and is thought to be ideal to evaluate the anthropogenic effect on the background level of atmospheric chemistry in the Arctic.

2. Ice core drilling and sample procedure

In 1989, we obtained a 205.15 m deep ice core at Site-J (Watanabe and Fujii, 1990), 50 km north from a previously drilling location, Dye 2 (66.2°N, 46.1°W; Langway *et al.*, 1985), with an electro-mechanical drill. After stratigraphic observation and electrical conductivity measurement (ECM), we cut the ice core at every 10 cm in depth to a depth of 168 m to obtain seasonal variation of $\delta^{18}O$ assuming the annual accumulation rate of 40 cm of ice at Site-J, referring to the rate of 37.4 cm at Dye-2 (Clausen and Hammer, 1988).

After removing the outer contaminated part, 5 mm thick, with a cleaned knife, we melted each ice sample in a Teflon container with a microwave oven in a science trench at the drilling site. We measured *in-situ* electrical conductivity of the melted samples and mixed samples prepared by mixing 10 successive samples, namely 1-meter long melted samples. These melted samples, and the frozen ice core deeper than 168 m, were brought back to Japan.

We carefully analyzed the melted samples in a class 1000 clean room to avoid contamination during processing and analyzing. The numbers of samples analyzed are 950 10-cm long samples continuously to 104 m in depth and 205 1-m long mixed samples to 205 m in depth.

3. Ice core dating

The ice core was precisely dated by counting annual cycles of the $\delta^{18}O$ profile to a

depth of 104 m as shown in Fig. 2. Tritium profile (Fujii, 1991) in the depth range from 15 to 23 m is also shown in Fig. 2, indicating reference horizons of 1959, 1963 and 1964 which are also obtained in other Greenland ice cores (*e.g.* Koide *et al.*, 1982). These tritium reference horizons are used to crosscheck the $\delta^{18}O$ dating for the upper 21-m layer where the $\delta^{18}O$ annual cycles are somewhat complicated.

The dating below this depth was achieved without many complications and high

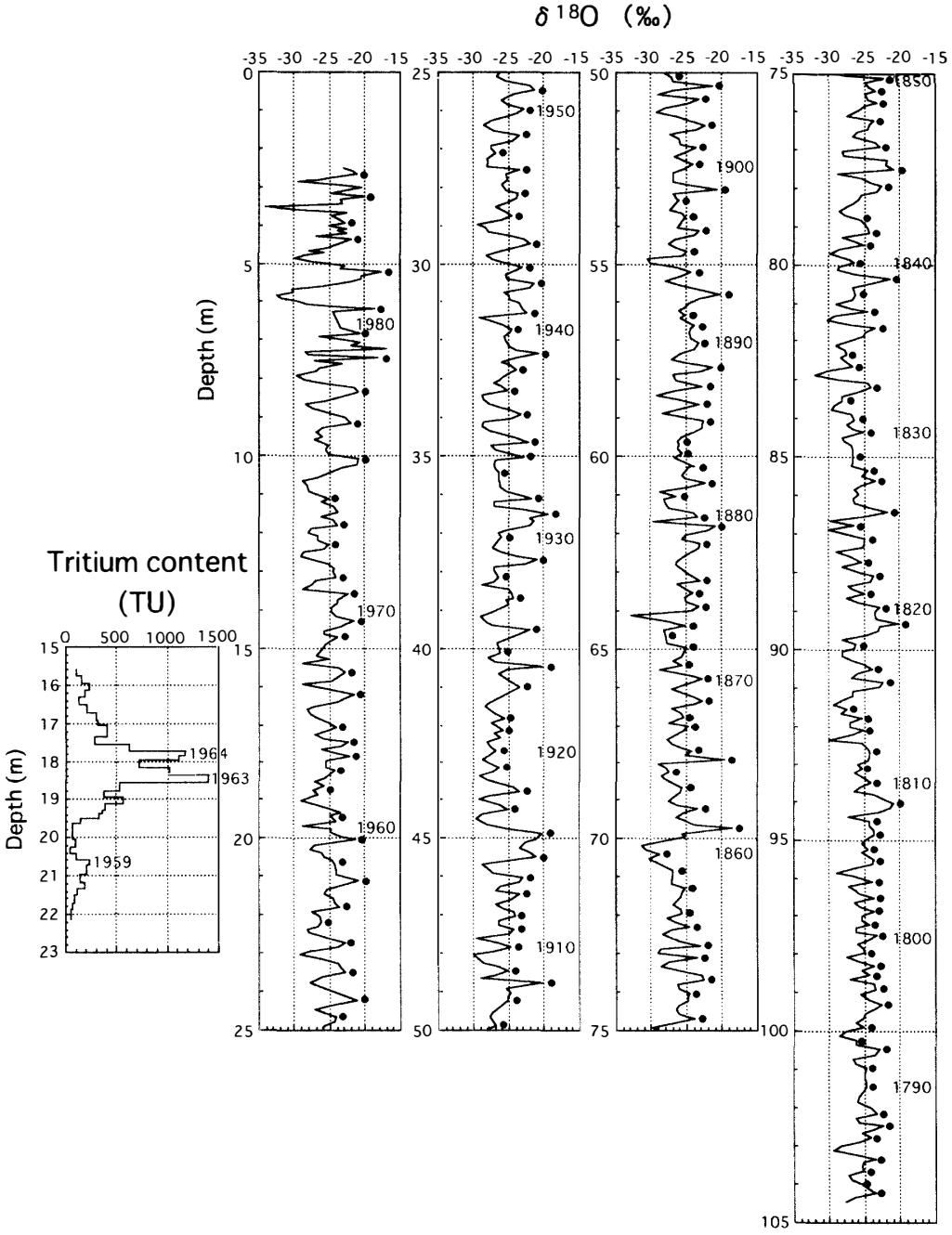

Fig. 2. Profiles of $\delta^{18}O$ and tritium content. Ice core dating was done by counting summer $\delta^{18}O$ peaks shown by black dots, and was crosschecked by tritium time markers.

precision was obtained to a depth of 104 m. The most distinct signal peak in ECM measurement observed at 103.63 m in depth is considered to be the Laki eruption in 1783 (Shoji *et al.*, 1991), which is the useful reference horizon in dating ice cores from Greenland (Clausen and Hammer, 1988). The dating by counting $\delta^{18}O$ annual cycles was tuned to be 1783 AD at this depth and estimation error is ± 2 years between these time markers.

4. Results and discussion

4.1. Acidity enhancement

To clarify formation of ice layers and change in acidity in the surface snow layer

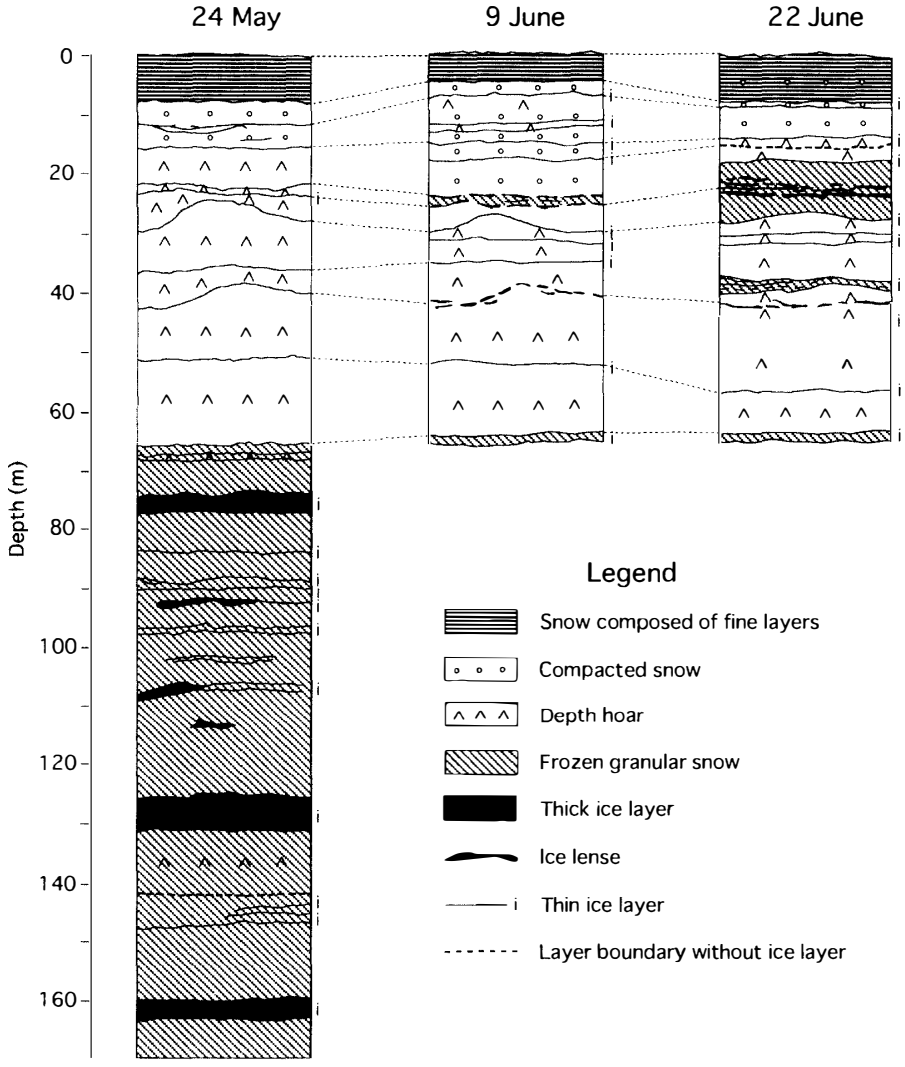

Fig. 3. Sequence of surface snow stratification at Site-J in early summer, 1989. The development process of thick ice layer is seen at around 25 cm in depth. Thick ice layers, seen at around 75, 130 and 160 cm in depth in the surface pit of 24 May, are the summer reference horizons. The surface of previous melting season appears at 65 cm in depth as the top of frozen granular snow.

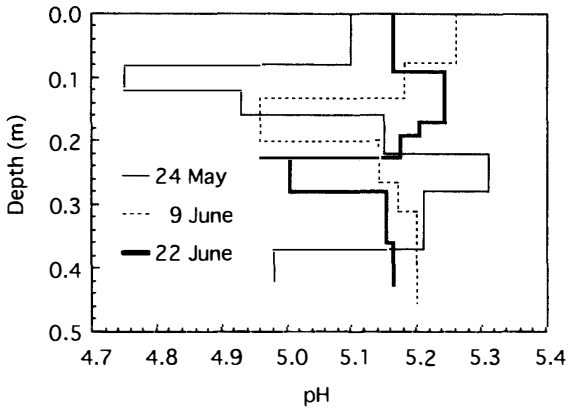

Fig. 4. Downward movement of high acidity layer observed in surface pit in early summer due to high acidic meltwater percolation.

during snow melt season, pit works were conducted on 24 May, and 9 and 22 June, near the drilling site. Figure 3 shows the sequential changes in stratification of the surface snow layer.

On the pit wall of 24 May, layers below 65 cm in depth were composed of frozen granular snow involving thick ice layers. The thick ice layers probably indicate summer horizons of each previous year. Development of frozen granular snow below 65 cm in depth suggests that some summer meltwater percolated into the snow layer deposited, at least in the previous year. The top of the frozen layer, therefore, indicates the end of the snow melt season of 1988.

Figure 4 shows the change in acidity in the surface 40 cm layer. As snow melted, the high acidity level at around 10 cm in depth moved downward and a thick high acidity ice layer developed at around 25 cm in depth by the middle of June. The high acidity in a thick ice layer is the result of concentration of acid in the surface snow layer by percolation of acidic meltwater.

4.2. Dust events

The bulk of the insoluble dust in the polar ice core is of continental origin (Hammer, 1977; Biscaye *et al.*, 1997). It has been transported over Greenland through the mid- and high troposphere and is considered to be a tropospheric background aerosol of continental origin (Hammer *et al.*, 1978; Svensson *et al.*, 2000).

Concentration and size distribution of dust in melted samples were analyzed for particles larger than 0.63 μm in diameter with a Coulter Counter TA-II in a clean room. This diameter is the minimum diameter measurable with the device. The result measured to a depth of 104 m is shown in Fig. 5. Peaks of dust concentration, which exceeds 3000 per 0.05 m*l*, are shown in this figure with the ages.

Steffensen (1988) analyzed dust concentration in two ice cores from central Greenland, that is, Site A and Site B, and discussed the detailed seasonal variations together with $\delta^{18}O$ and major anions. He showed these profiles in the period from 1890 to 1910, indicating a high dust concentration peak in 1899 in this period. Furthermore, Hammer (1989) showed the dust concentration profile in the Crête core, Greenland in the period 1815–1972. According to it, high dust peaks occurred in 1819, 1835, 1861, 1862, 1868, 1870, 1899, 1919, 1936 and 1942.

These studies suggest that dust storms appeared over Greenland at least in 1818 (or 1819), 1835, 1860 (or 1861), 1867 (or 1868), 1900 (or 1899), 1919 and 1936, during the past 210 years.

The source of the dust deposited on the Greenland ice sheet during the past several hundred years has not been studied yet. Steffensen (1988), however, suggested it to be continental origin from where vigorous atmospheric circulation, associated with the northward movement of the polar front, causes both horizontal and vertical transport of dust into the mid- and high troposphere of the Arctic in spring. Recent studies on mineralogy and Sr, Nd, and Pb isotope composition of dust in the Greenland deep ice core from GISP2 show that the most probable source area of the dust within marine isotope stage 2, between 23340 and 26180 calendar years BP, was in eastern Asia (Biscaye *et al.*, 1997). These studies suggest that the recent dust source is in eastern Asia as well. But there is a possibility of a local source, the western Greenland coast, where we saw a dust storm delay aircraft operation in spring.

4.3. Volcanic events

Many studies have revealed volcanic eruption signals in Greenland ice cores (*e.g.* Hammer *et al.*, 1980; Clausen and Hammer, 1988; Zielinski *et al.*, 1998; Clausen *et al.*, 1998).

Figure 6 shows the electrical conductivity profile to a depth of 104 m in the Site-J ice core. The electrical conductivity gradually increased with time due to anthropogenic acidification as discussed in the next section. There are many distinct peaks, which considerably exceed the background level as shown in Fig. 7. The layers that shows high electrical conductivity levels above the 2σ threshold value from the average are candidates of volcanic signals (Langway *et al.*, 1995). Taking into account the effect of anthropogenic acidification on the electrical conductivity, we take 2σ threshold values of 0.90 and 2.2 μS cm^{-1} and the averages of 1.4 and 2.3 μS cm^{-1} for the periods before and after 1950 AD from when pH used to drop to 5.1, respectively. With the help of precise dating of the core, probable volcanic eruptions with VEI (Volcanic Explosivity Index; Newhall and Self, 1982) larger than 4 are identified as shown in Fig. 6.

All of the explosive eruptions with VEI larger than 5 are identified here for volcanic eruptions located north of 8°S, except for eruption of Westdahl volcano in the Aleutian Islands in 1795. The largest signal is of Laki 1783, Iceland as revealed in other Greenland ice cores as mentioned above.

The second largest signal is seen in 1986 when two volcanic eruptions with VEI=4 took place at Augustine in Alaska and Chikurachki in the Kuril Islands (Simkin and Sibert, 1994). Such signals with high electrical conductivity are seen in the upper 20 m firn layer, formed from snow deposited with high anthropogenic acid content since early 1960's as described in the next section. Furthermore, these signals are the results of the enhancement of acidity by percolation of meltwater of high acid snow.

The Tambora eruption in Indonesia in 1815 was the most explosive with VEI=7, during the past 500 years (Simkin and Sibert, 1994). The signal is found in all Greenland and Antarctic ice cores (Clausen *et al.*, 1998). The Tambora 1815 signal is characterized by the double peaks of 1816 and 1817 as shown in Fig. 6, reaching the polar regions after one and two year delays following the eruption because of the southern hemisphere

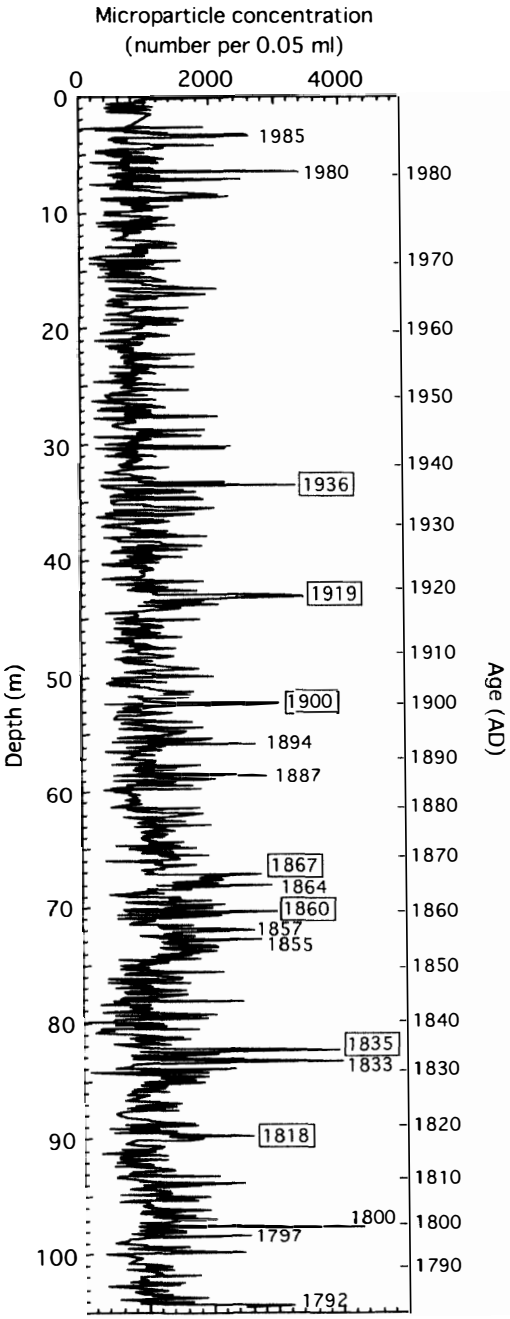

Fig. 5. Profile of total number of microparticles larger than 0.63 μm in diameter per 0.05 ml. High dust concentration peaks are shown with the age. Dust peaks indicated by dates in rectangles are found in other ice core, Greenland, suggesting that dust storms occurred over Greenland.

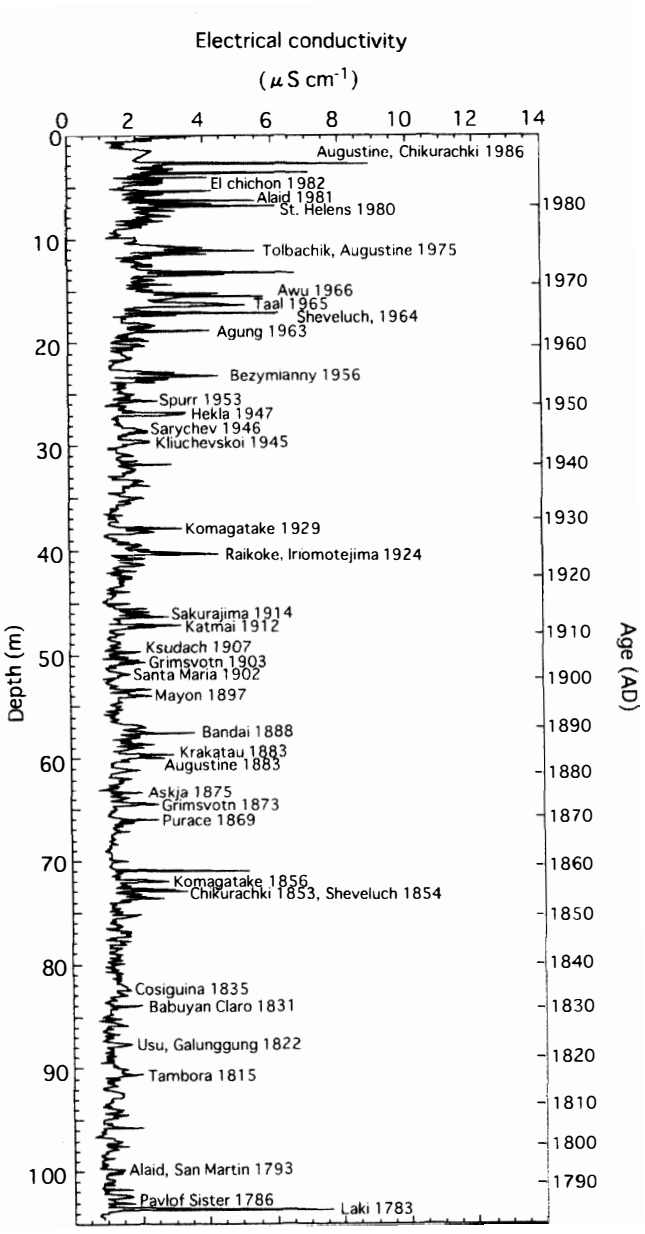

Fig. 6. Electrical conductivity profile. The distinct peaks are well associated with explosive volcanic eruptions with VEI larger than 4 in the equatorial region and the Northern Hemisphere.

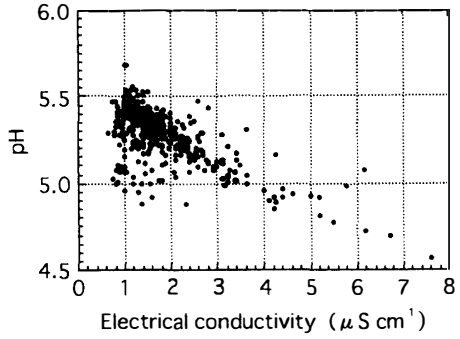

Fig. 7. Relation between pH and electrical conductivity. High electrical conductivity is well correlated with acidity, suggesting the effect of volcanic eruptions.

location of the volcano.

Although Katmai is located in Alaska, windward of Greenland, and the eruption in 1912 had a high VEI value of 6, the signal is not so distinct in the Site-J ice core. Clausen *et al.* (1998) pointed out that the signal is found in ice cores in central and northern Greenland but is barely detectable in ECM records of ice cores from the Dye 3, southern Greenland region. This suggests that the trajectory of volcanic clouds from the eruption may have shifted from central to northern Greenland. As Site-J is located in southern Greenland, the signal is not distinct in the ice core.

4.4. Acidification

To clarify the trend of anthropogenic acidification in Greenland since the Industrial Era, sulfate, nitrate, electrical conductivity and pH were analyzed for 1 m mixed samples. The results are shown in Fig. 8.

Prior to *ca.* 1860, the Site-J core records indicate no apparent trends for nss sulfate, electrical conductivity or pH, except for some perturbations due to volcanic events such as Laki in 1783 and Tambora in 1815. Nitrate shows a different trend from these trends. Its concentration remained at the 70–90 ppb level until *ca.* 1860. The principal sources of nitrate are biomass burning, lightning, NH_3 and N_2O oxidation, and NO exhalation (Mayewski *et al.*, 1990; Finkel and Langway, 1986; Clausen and Langway, 1989; Herron, 1982; Steffensen, 1988; Neftel *et al.*, 1985). But it is uncertain whether any of these sources varied or not.

After *ca.* 1860, increase in nss sulfate, electrical conductivity and acidity (pH) in Greenland precipitation started, though previous works reported *ca.* 1900 (Mayewski *et al.*, 1990; Finkel and Langway, 1986), suggesting that acidity increase is associated with anthropogenic pollutants transported from East Eurasia and North America.

Probable sources of Greenland sulfate are well documented (Mayewski *et al.*, 1990; Finkel and Langway, 1989; Clausen and Langway, 1989; Herron, 1982; Steffensen, 1988; Neftel *et al.*, 1985; Whung, 1994) with contributions from sea salt, biogenic emissions (dimethyl sulfide emissions on sea surface) and volcanic events as well as anthropogenic activity. The nss sulfate concentration after *ca.* 1860 shows good correlation with global solid fossil fuel (coal and lignite) production (Keeling, 1973; Boden *et al.*, 1990) until *ca.* 1960, suggesting that post-1860 acidification to *ca.* 1960 is mainly due to the increase in atmospheric Sox emitted by solid fossil fuel combustion (Fig. 9).

The depression in nss sulfate around 1930 (a similar trend was shown by Neftel *et al.*

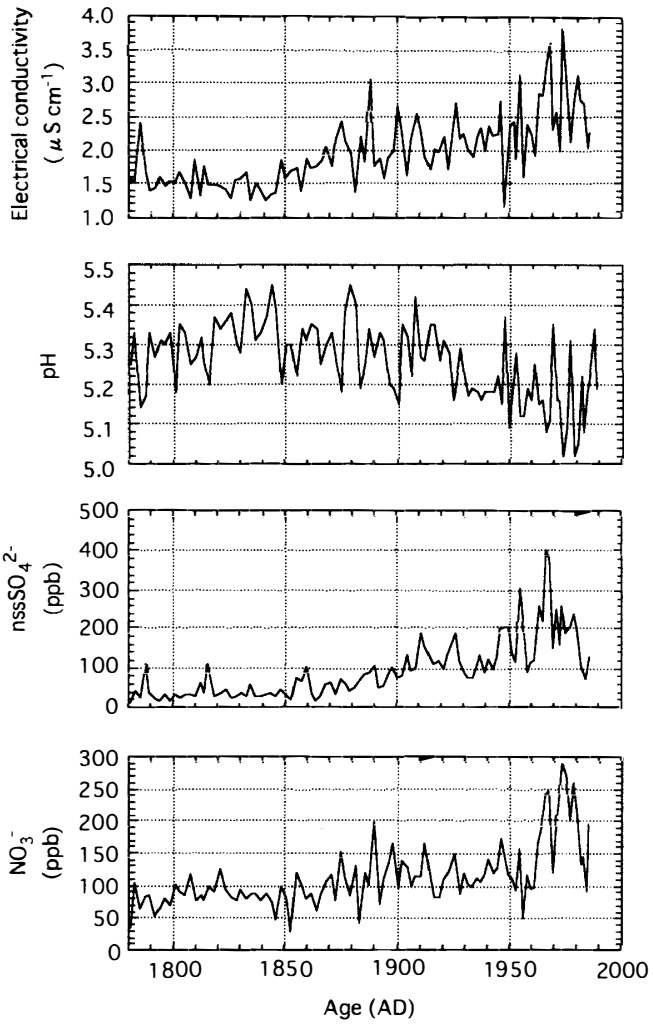

Fig. 8. Time series of the past 210 years of acidity (pH), electrical conductivity, nss sulfate and nitrate, showing acidification progress since ca. 1860, 40 years earlier than the time previously reported.

(1985) is probably associated with decrease in solid fossil fuel consumption during the economic depression. The background trend seems to have reached a maximum in the late 1960's as shown in the figure by Neftel *et al.* (1985). After the late 1960's, the nss sulfate concentration seems to have decreased or to have been stationary, even though fossil fuel consumption increased (Fig. 9). This is probably due to the increased use of sulfur removal equipment.

The background concentration of nitrate rose to 110–120 ppb from 80–90 ppb in *ca.* 1860 and remained at that level until *ca.* 1960. As there is no documented evidence of increases in lightning, NH_3 oxidation or NO-exhalation source strengths, we suggest that increase in anthropogenic biomass combustion is the most probable cause for the nitrate rise *ca.* 1860. After 1960, the concentration significantly increased from 100 ppb in 1960 to 290 ppb in the early 1970's due to the increase of fossil liquid fuel consumption (Fig. 9), followed by a clear decrease probably due to the spread of nitrogen removal equipment.

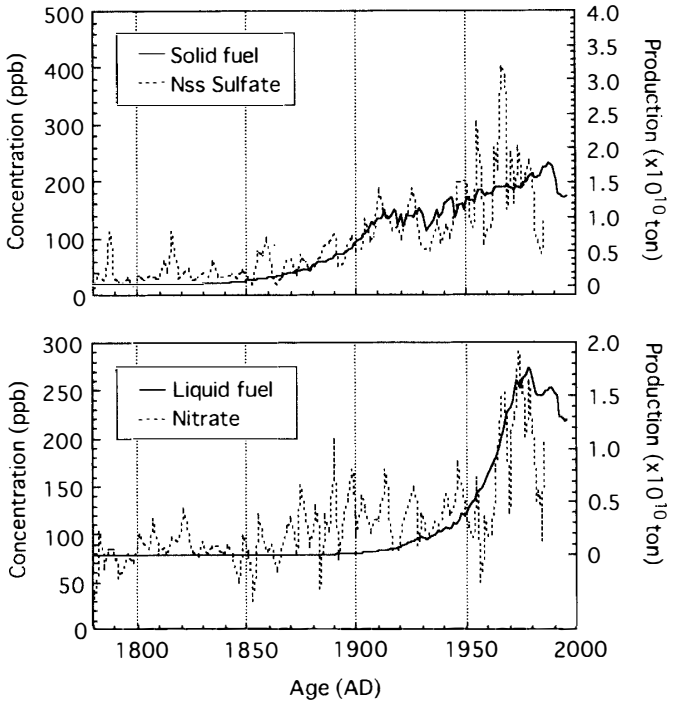

Fig. 9. Relation between major acid ions and fossil fuel production in America and Europe. Nss sulfate and solid fossil fuel production (above) and nitrate and liquid (thin dashed line) fossil fuels (below). These figures show acidification since ca. 1860, which is associated with anthropogenic pollutants emitted by the combustion of solid and liquid fossil fuels.

As reported by Mayewski *et al.* (1990), nss sulfate levels exceeded nitrate levels at the turn of the nineteenth century, reflecting the more intense increases in the emissions of anthropogenic SO_2 due to solid fossil fuel consumption, but nitrate levels again exceeded nss sulfate levels in the early 1970's in response to drastic increase in the emissions of NOx pollutants, probably due to liquid fossil fuel combustion (Fig. 9).

Nss sulfate (including volcanic origin) and nitrate concentrations increased by factors of 5.3 and 2.9 respectively from the period before *ca.* 1860 to recent decades.

5. Conclusions

On the basis of analyses done for pit samples and an ice core from Site-J, Greenland, we obtained the following results.

1) Acid in the surface snow layer percolates downward with meltwater and forms a high acid ice layer during the summer melting season.

2) Dust records in ice cores both from Site-J and Crête suggest that dust storms occurred in 1818 (or 1819), 1900 (or 1899), 1919, 1936 and 1942 over Greenland.

3) All the explosive eruptions with VEI larger than 5 from volcanos located north of 8°S are well identified in the electrical conductivity profiles.

4) Anthropogenic pollutants emitted by the combustion of solid and liquid fossil fuels have affected the sulfur and nitrogen cycles in the Arctic since *ca.* 1860. The mean

background levels of nss sulfate and nitrate concentrations were 45 ppb and 75 ppb, started to increase *ca.* 1860 and reached 400 ppb and 290 ppb in the late 1960's and early 1970's, respectively. Nss sulfate (including volcanic origin) and nitrate concentrations increased by factors of 5.3 and 2.9, respectively, from the period before *ca.* 1860 to recent decades.

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