HISTORICAL RECORDS OF FATTY ACIDS IN AN ICE CORE FROM SITE-J, GREENLAND

Kimitaka Kawamura[1], Ikuko Suzuki[1], Yoshiyuki Fujii[2] and Okitsugu Watanabe[2]

[1]*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1-1, Minami-Ohsawa, Hachioji-shi, Tokyo 192-03*
[2]*National Institute of Polar Research, 9-10, Kaga 1-chome, Itabashi-ku, Tokyo 173*

Abstract: Homologs of normal and branched chain saturated fatty acids, as well as unsaturated fatty acids, were determined in an ice core (205 m long) taken from Site-J, Greenland using capillary gas chromatography and mass spectrometry. Molecular distributions of normal saturated fatty acids (C_8–C_{32}) were characterized by an even carbon number predominance with two maxima at C_{16} and C_{24} or C_{22}, suggesting that they are transported long range through the atmosphere over Greenland from both marine and continental biological sources. Unsaturated fatty acids (C_{14}–C_{22}) were abundantly detected in the ice samples with oleic acid ($C_{18:1}$) being predominant. This is in contrast to the remote marine aerosols in which unsaturated fatty acids are depleted due to photochemical oxidation, suggesting that the fatty acids settled down in the Greenland ice sheet without serious photochemical degradation during atmospheric transport. Concentrations of the fatty acids (C_{12}–C_{32}) in the ice core fluctuated in the range of 3.9–104 μg/kg-ice with higher values at around 1800, 1900–1950, and 1980 AD. Relative abundances of the higher molecular weight fatty acids (C_{20}–C_{32}) were higher (10–30% of total fatty acids) in 1700–1850 AD, and lower (5–8%) in 1920–1950 AD. These results suggest that atmospheric transport of continentally derived materials over Greenland was relatively enhanced in 1700–1850 AD, whereas the transport of marine derived organic matter was significantly intensified in 1920–1950 AD.

1. Introduction

Fatty acids (FAs) have been reported as major lipid class compounds in atmospheric samples such as continental and marine aerosols (Simoneit *et al.*, 1977; Simoneit and Mazurek, 1982; Peltzer and Gagosian, 1989), rain and snow (Kawamura and Kaplan, 1986; Mazurek and Simoneit, 1986). They originate from terrestrial higher plant waxes, soil particles and marine organisms (Gagosian, 1986; Saliot *et al.*, 1991; Kawamura, 1995). Chain length distributions of fatty acids have been successfully used as biological tracers to demonstrate long range atmospheric transport of terrigenous materials over the Pacific and Atlantic Oceans (Simoneit *et al.*, 1977; Gagosian *et al.*, 1981; Gagosian, 1986; Kawamura, 1995) and to evaluate the biogenic contribution to urban aerosols and rainwaters (Mazurek and Simoneit, 1986; Kawamura and Kaplan, 1986, 1991; Simoneit *et al.*, 1991).

In the preliminary study of ice core samples, we detected a homologous series of fatty acids including normal saturated, unsaturated and branched chain acids (Kawa-

Mura and Suzuki, 1991). The molecular distributions of the fatty acids indicated contributions from both marine and terrestrial organic matter to the Greenland ice and suggested that the ice core samples should contain information over the last 450 years on the sea-to-air flux of the marine organic matter and land-to-air flux of terrestrial higher plant waxes as well as bacteria; these are coupled with long range atmospheric transport.

In this study, we analyzed forty three ice sections taken from a 205 m long ice core (Site-J, Greenland) for the determination of fatty acids using capillary gas chromatography (GC) and GC-mass spectrometry. Here, we report the molecular distribution of the fatty acids and their historical trends in the ice core, which will be discussed in terms of past changes in the source strength from marine and terrestrial organic matter, and long range atmospheric transport over the Greenland ice sheet. A potential response of the fatty acids to climate changes in the last 450 years is also discussed.

2. Samples and Analytical Procedures

The ice core samples (205 m long) were collected from Site-J, Greenland (66°51.9′ N, 46°15.9′ W, altitude: 2030 m) in 1989 with a mechanical shallow drill by the Japanese Arctic Glaciological Expedition 1989 (Watanabe and Fujii, 1990). The ice layer chronology was determined by electrical conductivity and volcanic eruption records: the 205 m layer was estimated to be *ca.* 450 yr old (Shoji *et al.*, 1991). The ages of the surface layers were confirmed by the detection of a tritium signal from nuclear bomb tests (Izumi, personal communication, 1991). Forty three sections were collected from the ice core and handled as described in Kawamura *et al.* (1994). The length of each section was 0.2–1.5 m, which corresponds to less than one half year to 4 years. Most of the ice sections were less than the average annual accumulation rate (42 cm of ice or 38 cm of water, Shoji *et al.*, 1991).

A melted water sample (*ca.* 350 m*l*) was acidified with 6 M HCl (5 m*l*) and then extracted with a methylene chloride/ethyl acetate (2:1) mixture (70+40+40 m*l*). Extracts were then saponified with a 0.5 M KOH/methanol solution (10 m*l*) containing 20% water in a glass ampule at 100°C for 60 min. The methanol in the saponified fraction was removed by using a rotary evaporator under a vacuum and then pure water was added. After neutral components were removed by extraction with an n-hexane/ methylene chloride (2:1) mixture, the saponified fraction was acidified (pH 1) with 6M HCl. Carboxylic acids were isolated by extraction with methylene chloride and were methylated with 14% BF₃ in methanol. The methyl esters were divided into three sub-fractions on a silica gel (Bio-Sil A, 200–400 mesh) column by eluting with an n-hexane/methylene chloride (1:2) mixture (A-1: monocarboxylic acid methyl esters), methylene chloride/ethyl acetate (98:2) mixture (A-2: dicarboxylic acid dimethyl esters) and methylene chloride/methanol (95:5) mixture (A-3: hydroxyacid methyl esters).

The monocarboxylic acid methyl ester fraction was concentrated, dissolved in 50 µ*l* n-hexane, and injected to a Carlo Erba gas chromatogram (VEGA 6000) with a Grob-type cool-on-column injector, a fused silica capillary column (HP-5, 0.3 mm×25 m×0.5 µm) and an FID detector installed. Hydrogen was used as the carrier gas. Data were processed using a Shimadzu Chromatopac C-R7A. The GC peak was identified by

comparing the retention times with those of authentic standards. Identification of the compounds was confirmed using GC-mass spectrometry (Finnigan-MAT ITS-40). Recovery of fatty acids (C_{16}, C_{18} and C_{24}), which were spiked to pure water, was 80%. Duplicate analyses of ice samples showed that analytical error was within 15% in the procedures used. Concentrations of fatty acids are corrected for the procedural blanks, which showed negligibly small peaks of C_{14}, C_{16} and C_{18} acids.

All the organic solvents used were re-distilled prior to use. Reagents were also treated with appropriate organic solvents to remove potential contamination.

3. Results and Discussion

3.1. Distribution, origin and transport process of fatty acids in ice core

Figure 1 presents a capillary gas chromatogram of fatty acid methyl esters isolated from the Greenland ice core. A homologous series of straight chain saturated fatty acids were detected in the range of C_8–C_{32}. Their distribution is characterized by a strong even carbon number predominance with two maxima at C_{16} and C_{22} or C_{24}, except for C_9 acid which is often more abundant than C_8 and C_{10}. Chain length distributions of n-saturated fatty acids are similar to those reported in continental rain and snow from mid-latitude (KAWAMURA and KAPLAN, 1986; MAZUREK and SIMONEIT, 1986) and remote marine
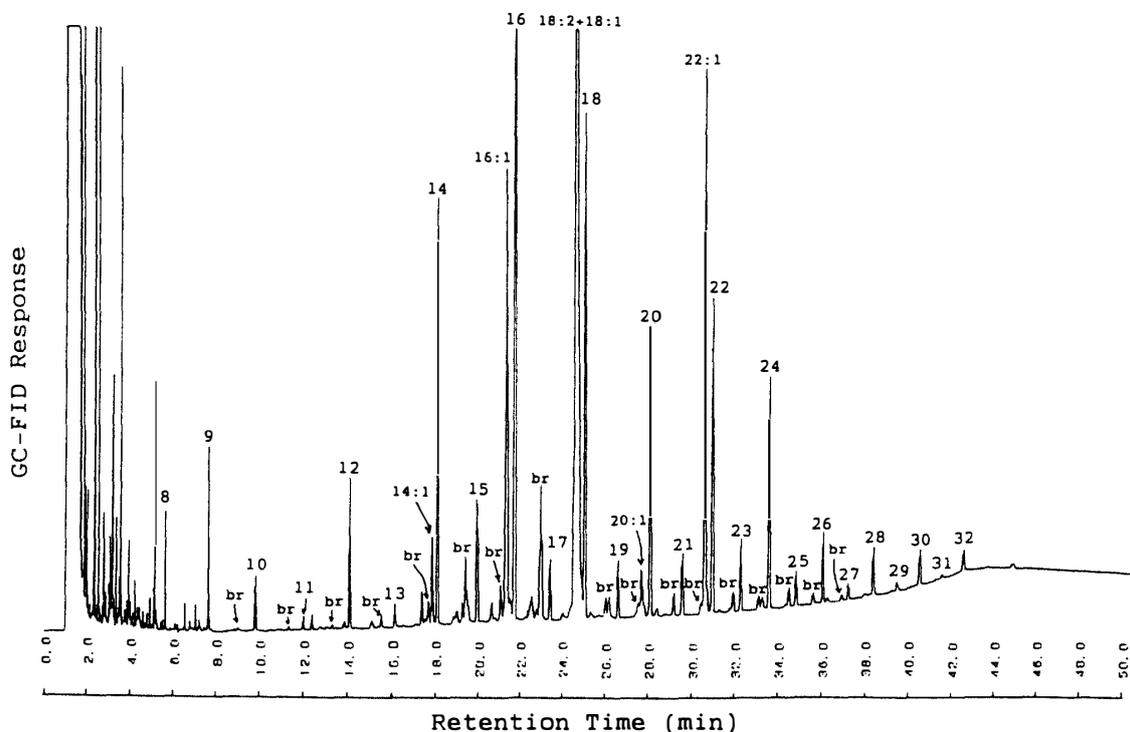
Fig. 1. A typical gas chromatogram of the fatty acid methyl ester fraction isolated from the Greenland ice core sample (#185, 99.5 m depth, 1794 AD).

The number (x) is the carbon number of a saturated fatty acid. Numbers (x:y) mean the carbon numbers (x) and numbers of double bonds (y) of unsaturated fatty acids. br means branched chain fatty acid, which appears just before the corresponding normal fatty acid on the gas chromatogram.

aerosols from the western North Pacific (KAWAMURA, 1995) and Atlantic (SIMONEIT *et al.*, 1977), suggesting that they are of both marine and terrestrial plant origin (GAGOSIAN, 1986). The relatively abundant presence of C_9 acid has been reported in the marine aerosols (KAWAMURA and GAGOSIAN, 1990) and considered to be produced by the photochemical oxidation of unsaturated FAs such as oleic acid (KAWAMURA and GAGOSIAN, 1987). The lower molecular weight FAs (LFAs: C_{12}–C_{19}) are for the most part derived from marine microorganisms whereas higher molecular weight FAs (HFAs: C_{20}–C_{32}) are originated from terrestrial higher plants and soil particles (GAGOSIAN, 1986; KAWAMURA and GAGOSIAN, 1990).

Branched chain saturated fatty acids were also detected in the range of C_{10}–C_{32}. Their distribution showed an odd carbon number predominance with C_{17} being dominant, followed by C_{15}. Branched chain fatty acids have been reported in bacterial cell walls (KANEDA, 1967) and used as bacterial tracers in sediments (CRANWELL, 1982). Although they were in general less abundant than normal fatty acids, branched chain C_{15} and C_{17} fatty acids were often more abundant than the corresponding normal fatty acids, suggesting that ice core fatty acids are influenced by bacterial lipids.

On the other hand, even carbon number unsaturated fatty acids, which are present as dominant lipid constituents in living higher plant leaves and micro algae (HITCHCOCK and NICHOLS, 1971; KOLATTUKUDY, 1976), were detected as major fatty acids in the ice core samples in the range of C_{14}–C_{22} (see Fig. 1). Dominant unsaturated FAs include $C_{18:1}$ (oleic), $C_{18:2}$ (linoleic), $C_{16:1}$ and $C_{22:1}$. Predominance of the *cis* configuration (such as oleic and linoleic acids) which is common in organisms, was observed in all the samples studied, although the *trans* configuration (*trans* $C_{18:1}$, elaidic acid) was also detected as only a minor species. Unsaturated fatty acids were generally more abundant than corresponding saturated fatty acids. This is in contrast to the marine aerosol samples in which unsaturated fatty acids are relatively less abundant (SIMONEIT, 1977). The depletion of unsaturated fatty acids in the marine atmosphere has been considered to be a result of photochemical degradation of a double bond which exists at the C-9 position of the acids (SIMONEIT, 1977). A preferential degradation of unsaturated fatty acids has later been substantiated by the finding of the reaction intermediates such as C_9 dicarboxylic acid and C_9 ω-oxocarboxylic acid in marine aerosols (KAWAMURA and GAGOSIAN, 1987).

Abundant presence of unsaturated LFAs in the ice core suggests that marine-derived organic materials are long range atmospheric transported over Greenland and settled down on the ice sheet without severe photochemical degradation. Depressed photochemical oxidation of unsaturated fatty acids may be associated with the meteorological conditions during atmospheric transport of organic matter, that is, low pressure systems may often develop over the ocean before snowfall events in Greenland and accelerate sea-to-air emission of organic materials enriched in sea surface microlayers through bubble bursting mechanisms (GARRETT, 1967; MARTY *et al.*, 1979). Under such a meteorological condition, long range atmospheric transport of the marine derived organic materials should occur under cloudy conditions and thus decreased solar radiation. Thus, organic aerosols containing abundant unsaturated fatty acids are scavenged over the Greenland ice sheet by wet deposition before serious photochemical degradation occurs.

Table 1. Concentrations (μg/kg-ice) of fatty acids in the ice core samples taken from Site-J, Greenland.

Sample No.	Depth (m)	Years	TOC (mgC/kg)	n-SFAs (C_{12}–C_{32})	br-SFAs (C_{12}–C_{32})	UFAs (C_{14}–C_{22})	Total FAs (C_{12}–C_{32})
#8	5.9	1982	1.29	9.6	5.6	23.3	38.5
#9	6.5	1981	1.47	6.7	1.9	14.7	23.4
#10	6.9	1980	1.06	30.3	12.2	62.4	104.9
#21	12.6	1973	0.94	5.5	1.6	10.3	17.4
#29	15.1	1969	2.41	15.2	5.1	29.6	49.9
#34	16.7	1966	1.00	7.6	2.6	24.6	34.7
#42	19.8	1961	0.73	5.3	1.3	10.1	16.8
#49	22.6	1956	1.08	7.4	2.1	12.1	21.7
#58	26.4	1950	0.80	5.9	2.1	13.4	21.4
#61	27.8	1947	1.18	10.4	3.5	12.7	26.5
#A66	30.3	1943	0.88	17.3	6.1	32.1	55.5
#A67–A69	31.8	1941	2.14	8.4	1.8	8.4	18.6
#74	35.2	1934	2.59	25.6	5.6	16.7	47.9
#A77	37.5	1930	1.22	18.8	4.9	35.9	59.6
#79	38.3	1928	1.36	13.5	2.5	23.5	39.5
#89	47.4	1910	1.82	3.9	1.2	8.4	13.5
#116–117	61.8	1880	2.28	3.2	0.5	1.7	5.4
#126	66.8	1869	1.06	4.2	0.7	10.7	15.6
#130	68.9	1865	3.21	4.0	1.0	8.8	13.8
#139	73.7	1854	0.70	2.1	0.5	5.8	8.4
#151	79.9	1840	1.04	1.5	0.2	5.2	6.9
#163	85.6	1827	1.00	2.5	0.5	4.7	7.6
#A173–A175	91.4	1811	2.00	2.3	0.4	1.8	4.4
#A176	93.2	1808	2.21	6.1	1.5	13.0	20.6
#B185	99.5	1794	2.40	5.3	0.8	8.4	14.4
#194	104.6	1781	0.88	2.6	0.5	5.1	8.2
#203	109.3	1771	1.52	3.3	0.5	8.1	11.9
#222	118.5	1750	1.26	1.2	0.2	0.5	1.9
#A231	125.5	1733	1.01	1.8	0.3	3.8	5.9
#B245	135.6	1710	2.30	5.5	1.2	11.5	18.1
#B252	140.4	1699	0.85	1.3	0.2	1.3	2.8
#C255	143.1	1692	1.42	1.8	0.4	2.9	5.1
#B259	146.3	1685	4.93	2.9	1.0	6.2	10.2
#A264	150.5	1676	2.56	2.6	0.7	4.8	8.1
#A266–A267	152.4	1671	3.44	2.4	0.5	3.2	6.1
#A277	160.4	1652	2.06	4.4	0.7	5.9	11.0
#C286	168.1	1634	5.74	2.7	0.6	5.0	8.3
#A303	179.4	1607	2.17	2.2	0.6	5.4	8.2
#D305–A306	181.8	1602	0.73	2.1	0.3	5.3	7.7
#C318	190.0	1583	1.53	3.0	0.5	5.6	9.1
#A327	195.2	1570	1.22	7.0	1.2	12.8	21.1
#B328	196.3	1568	2.07	1.8	0.3	1.9	4.0
#C343	204.1	1550	1.07	2.6	0.6	5.4	8.5

n-SFAs: normal saturated fatty acids, br-SFAs: branched saturated fatty acids, UFAs: unsaturated fatty acids. TOC data: from KAWAMURA et al. (1992).

Table 1 summarizes the concentrations of normal saturated and branched saturated fatty acids and unsaturated fatty acids as well as total organic carbon (TOC) in the Greenland ice core samples. The total fatty acids largely fluctuated in the ice core with a concentration range of 1.9–105 μg/kg-ice (mean, 20 μg/kg-ice). The concentration ranges of total normal saturated (C_8–C_{32}), branched chain (C_{10}–C_{32}), and unsaturated fatty acids (even numbered C_{14}–C_{22}) were 1.2–30 μg/kg-ice (mean: 6.3 μg/kg-ice), 0.21 –12.2 μg/kg-ice (mean: 1.8 μg/kg-ice), and 0.46–62 μg/kg-ice (mean, 11.6 μg/kg-ice), respectively. These concentration levels are comparable to those reported for rain and snow samples from southern California (Kawamura and Kaplan, 1986); however, some ice core sections showed that fatty acids are more than 5 times more abundant than mountain snow samples from mid-latitude (5–17 μg/kg-snow), indicating that the Greenland ice core samples are enriched with fatty acids. The total fatty acids in the ice samples were found to account for 0.14–9.9% (mean, 1.7%) of the TOC contents (0.7 –5.7 mg/kg-ice, Kawamura et al., 1992). Although a major portion of the TOC has not been characterized, fatty acids are one of the most abundant organic compound classes studied in the Greenland ice sheet.

3.2. Vertical profile of fatty acids in the Greenland ice core

Figure 2a gives historical records of total fatty acid concentrations in the Green-
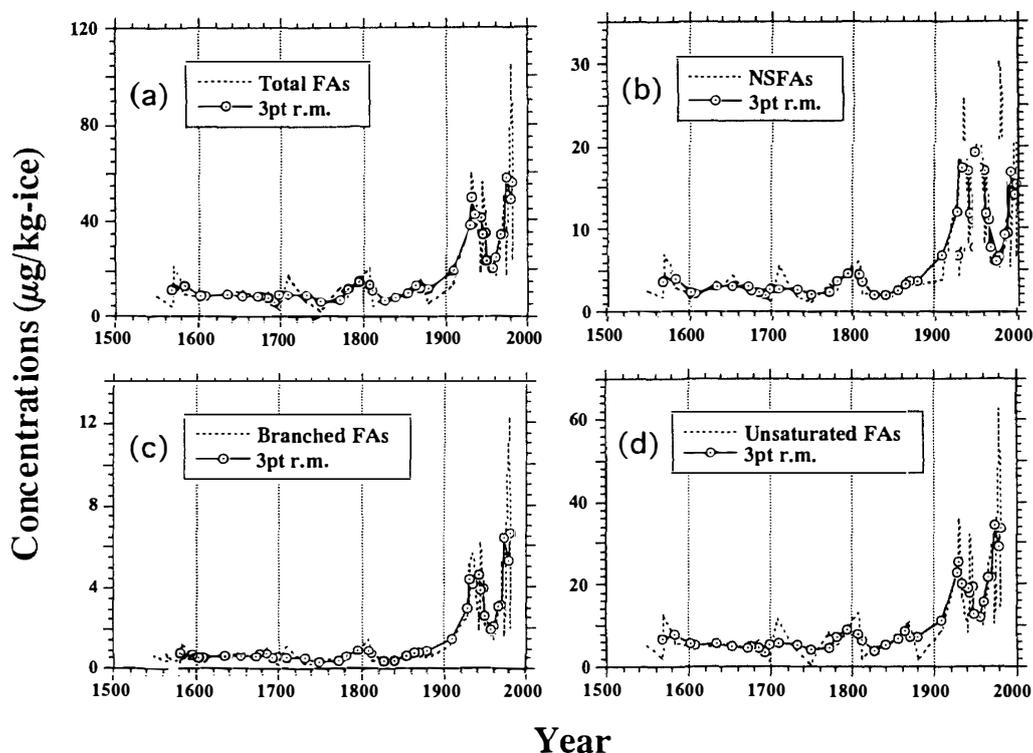
Fig. 2. Historical records of concentrations of fatty acids in the Greenland ice core and their three point running means. (a) total fatty acids (C_{12}–C_{32}), (b) normal saturated fatty acids (C_{12}–C_{32}), (c) branched chain fatty acids (C_{12}–C_{32}), and (d) unsaturated fatty acids (C_{14}–C_{22}).

land ice core and their three point running mean. Concentrations of total FAs stayed constant in the 1500s to the mid 1800s at levels of *ca.* 10 μg/g-kg-ice, although higher concentrations were observed in 1780–1810 AD. After the early 1900s, their concentrations started to increase significantly, showed a maximum at around 1940 AD, and then decreased toward the 1960s. Interestingly, the concentration levels (*ca.* 6 μg/kg-ice) in 1950–1960 AD are still higher than the averaged concentration (*ca.* 3 μg/kg-ice) of the 1500s–1800s. Beyond the minimum observed in 1950–1960 AD, the total FAs again increased and reached the highest concentration in the 1980s. These ice core records of fatty acids suggest that atmospheric transport of organic materials over the Greenland ice sheet stayed relatively low in the 1500s to mid 1800s, but significantly increased in the 1920s–1940s and 1980s. Surprisingly, the amplitude of the fatty acid fluctuations in the 20th century is a factor of three. Such a significant fluctuation cannot be explained by the estimated changes (within 20%) in snow accumulation rate, based on the variation of the rates (20% at most) at Dye 3 (near Site-J) (REEH *et al.*, 1978). Thus, the fluctuations of fatty acids are most likely caused by significant changes of their air-to-snow flux, which should be controlled by climatological conditions such as the atmospheric circulation.

Figures 2b–2d present ice core records of normal saturated FAs, branched chain FAs and unsaturated FAs, respectively. Normal saturated FAs showed fluctuation similar to that of total FAs with higher concentrations at around 1800, 1900–1940, and 1980 AD (Fig. 2b). Their concentrations (*ca.* 20 μg/kg-ice) in the 1940s and 1980s are *ca.* 10 times higher than that of the background level (*ca.* 2 μg/kg-ice) before 1900 AD, suggesting that the biological contribution was significantly enhanced in these periods. Similar trends are recognized for the historical trend of branched chain FAs (see Fig. 2c). Because branched chain FAs are characteristic of bacterial cell walls (KANEDA, 1967), their variation suggests that the contribution of microbial lipids to the Greenland ice sheet was enhanced during the 1900s–1940s and 1980s. As seen in Figs. 2b and 2c, unsaturated fatty acids are generally much more abundant than saturated fatty acids. These unsaturated FAs showed concentration changes similar to n-saturated and branched chain fatty acids, suggesting increased transport of marine-derived materials in the 1920s to 1940s and 1980s.

Interestingly, concentration changes of fatty acids in the ice core were found to be apparently consistent with the reconstructed arctic temperature departures based on tree ring data (JACOBY and D'ARRIGO, 1989; D'ARRIGO and JACOBY, 1993). They showed warmer climate in the 1700s to 1800s with a maximum at around 1780 AD, cooler climate in the 1810s to 1910s with a minimum at around 1830 AD, warmer climate in the 1920s to 1960s with a maximum at around 1950 AD, cooler climate in the 1970s, and warmer climate in the 1980s. The historical trend of fatty acid concentrations (Fig. 2) is similar to the reconstructed arctic temperature trends. Further, warmer climate was also recorded in the sea surface temperatures of the Northern Hemisphere during the 1920s–1940s (FOLLAND and PARKER, 1990). Although we have no logical evidence at present to link the two parameters, *i.e.*, concentrations of ice core fatty acids and the arctic temperature, it is likely that sea-to-air emission of marine organic matter is enhanced during a warmer period. Alternatively, changes in the atmospheric circulation patterns may have caused changes of the intensity of atmospheric transport of marine-

derived organic matter over Greenland.

3.3. Enhanced atmospheric transport of marine and terrestrial organic matter over the past 450 years

Although palmitic acid (C_{16}) is the most abundant n-saturated FA throughout the ice core sections, HFAs were abundantly detected in some ice sections. As shown in Fig. 3, the relative abundance of HFAs in the total n-saturated fatty acids (C_{12}-C_{32}) stayed rather low at around 10% in the mid 1500s to 1600s. However, it started to increase in 1700 AD, peaked in the 1750s (ca. 30%), and decreased toward the 1940s (ca. 5%). In the 1940s to 1980s, the relative abundance of HFAs significantly fluctuated in the range of 4–12%, but seems to have increased in the 1980s. Higher molecular weight fatty acids are characteristic of terrestrial higher plants (KOLATTUKUDY, 1976) and not found as major species in marine organisms, whose fatty acid composition is dominated by C_{14}, C_{16} and C_{18} (HITCHCOCK and NICHOLS, 1971). Hence, the ice core record of fatty acids suggests that atmospheric transport of continent-derived organic matter over Greenland was enhanced in 1700–1850 AD in comparison to marine derived organic matter. It is important to note that, in the same periods, the concentrations of HFAs normalized by total organic carbon in the ice core also increased by a factor of ca. 5 compared to those in the late 1600s, but those of LFAs divided by TOC stayed rather constant or showed slightly higher values (data not presented here).

In contrast, the relative abundance of HFAs revealed a minimum in the 1950s, suggesting that atmospheric transport of marine-derived organic materials over Greenland overwhelmed that of continental materials. Although a significant fluctuation was observed in the 1980s, the averaged relative abundance of HFAs is low (ca. 6%), suggesting that atmospheric transport of marine-derived organic matter over the Greenland ice sheet relative to continental materials was enhanced in the 20th century. At
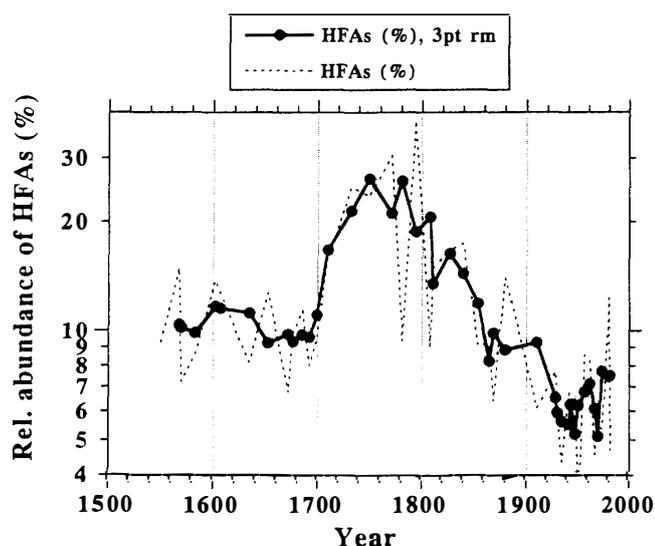
Fig. 3. Historical records of relative abundance of higher molecular weight fatty acids (HFAs: C_{20}-C_{32}) in the concentrations of total n-saturated fatty acids (C_{12}-C_{32}) in the Greenland ice core.

present, we have no conclusive explanation for the fluctuations of marine/terrestrial source strength; however, we consider that they should be linked to the past atmospheric circulation and climate in the Northern Hemisphere. The enhanced transport of continentally derived organic matter in 1700–1850 AD may be related to climate change, the so-called "Little Ice Age" which may have begun in the early 16th century and ended in the 19th century (BRADLEY and JONES, 1992). During the "Little Ice Age", either expansion of the arid area over continents or enhanced wind speeds may have occurred.

3.4. Bacterial contribution to the Greenland ice sheet

Figure 4 shows historical records for ratios of the amounts of branched chain fatty acids ($C_{15} + C_{17}$) to those of normal saturated ones. The ratios seem to be rather constant in the mid 1500s to 1700s. The branched/normal ratios started to increase in the 1820 s and showed a peak at around 1860 AD. After the peak, they decreased toward the 1930s and then started to increase again. The gradual increase continued until the 1980 s. Because the branched chain FAs are characteristic of bacteria as stated above, the increased ratios in the 1840s to 1860s and 1930s to 1980s suggest that the bacterial contribution to the Greenland ice sheet has increased in those periods. At present, we have no direct evidence to explain the enhanced bacterial lipid contribution, but these signals could be associated with changes in the past climate such as temperature. During warmer periods, bacterial activity may have increased in the partially melted snow layer on the surface ice sheet, which has been recorded in the Greenland ice core (KAMEDA et al., 1992).
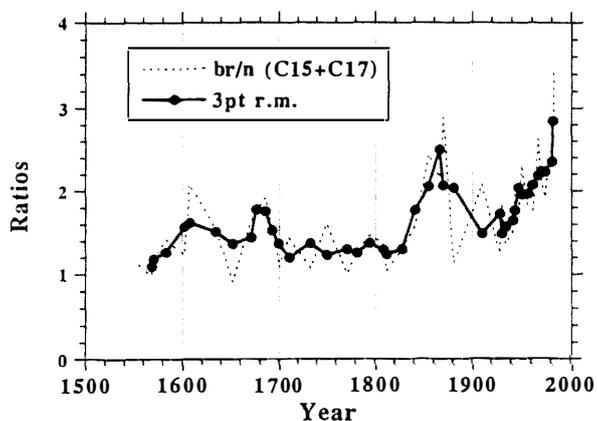
Fig. 4. Historical records of ratios of the amounts of branched chain fatty acids ($C_{15} + C_{17}$) to those of corresponding normal saturated fatty acids in the Greenland ice core.

5. Concluding Remarks

The molecular distributions of ice core fatty acids indicate that organic materials of both marine and terrestrial origin are transported over Greenland through the atmosphere and supplied to the ice sheet by wet and dry deposition processes. Using chain length distributions of these biomarker compounds, three major chronological events

were postulated to occur over the past Greenland ice sheet; (1) enhanced atmospheric transport of terrestrial materials occurred in 1700–1850 AD, whereas atmospheric transport of marine derived materials stayed rather constant; (2) significantly enhanced transport of marine derived organic matter over Greenland occurred in 1920 AD to 1950 AD while the terrestrial contribution also increased in the same period; (3) atmospheric transport of both marine and terrestrial materials was significantly enhanced from the 1970s to the 1980s. The postulated events may be linked to the changes in the atmospheric circulation, temperature, and other climate parameters. Further study to interpret the apparent consistency which exists between fatty acid distributions and climate changes may provide an advantage of fatty acids as a proxy of past climate changes.

Acknowledgments

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