Bulletin of Glacier Research 9 (1991) *65 – 70*

Lipid Class Compounds in the Greenland Ice Core Samples : a Preliminary Result

Kimitaka KAWAMURA and Ikuko SUZUKI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1–1 Minami-Ohsawa, Hachioji, Tokyo 192–03, Japan

(Received January 17, 1991 ; Revised manuscript received February 21, 1991)

Abstract

Ice core samples (32 m and 61 m in depth) collected from Site-J, Greenland were studied to find lipid class compounds such as hydrocarbons and carboxylic acids by using a capillary gas chromatography (GC) and GC-mass spectrometry. Normal alkanes ($C_{24}-C_{31}$) showed a predominance of odd-carbon numbers with odd/even ratios of 1.34–1.48, indicating the transport of land-derived plant waxes and fossil fuel-derived pollutants in the late 19th and 20 centuries. Fatty acids (C_8-C_{26}) showed an even-carbon predominance with a maximum at C_{16} followed by C_{14}, C_{12}, and C_{18}, suggesting a significant contribution of marine-derived organic matter. ω-Oxocarboxylic acids and β-hydroxyacids, which showed a signature of photochemical origin, were also found in the ice samples.

1. Introduction

Lipid class compounds such as hydrocarbons and fatty acids in the continental and marine atmosphere have been studied to understand the origin of aerosol particles (Simoneit and Mazurek, 1982 ; Kawamura and Kaplan, 1986), transformations of organic matter in the atmosphere (Kawamura and Gagosian, 1987) and long-range transport processes of continent-originated materials over open oceans (Gagosian *et al.*, 1981). These studies have proved that lipid compounds are useful tracers to evaluate biogenic and/or anthropogenic input of organic materials to the atmosphere and to understand their geochemical cycles in the earth surface.

On the other hand, ice core analyses for inorganic chemical species provided an excellent approach to understand the past atmospheric environments (*e.g.*, Neftel *et al.*, 1985 ; Barnola *et al.*, 1987). However, lipid class compounds in ice have rarely been studied despite their potential usefulness in the applications to paleo-atmospheric studies. We started to search lipid class compounds in the ice core samples collected from Greenland. Here, we present preliminary results of analyses of n-alkanes, fatty acids, oxocarboxylic acids, and hydroxyacids.

2. Samples and analytical procedures

An ice core (206 m long) was taken from Site-J, Greenland (latitude : 66°51.9'N ; longitude : 46°15.9'W ; altitude : 2030 m) during the Japanese Arctic Glaciological Expedition in 1989 (JAGE'89) (Watanabe and Fujii, 1990). Five ice samples were cut off from the core and melted at the site in a pre-cleaned Gallon bottle with a Teflon-lined cap. The samples (2.4–2.8 L) were poisoned with mercuric chloride and transported to Tokyo. Two samples taken from 32 m and 61 m in depth were used in this study. The age of the samples was determined as 1941 and 1881 A.D., respectively, based on the analyses of the electric conductivity profile of the core and volcanic event records such as Laki (Shoji *et al.*, 1991).

An aliquot (0.35–1.8 L) of the samples was acidified to pH=2 with a 6 M HCl solution (2–8 ml), which was pre-cleaned by extraction with methylene chloride and hexane to remove organic contaminants, and was extracted with methylene chloride/ethyl acetate (2:1) mixture (70+40+40 ml). The extracts were concentrated down to 2 ml by using a rotary evaporator. A 0.1 M KOH solution (15 ml) was added to the concentrates and the neutral components were extracted with methylene chloride (15 ml). The neutral fraction was run on a silica gel column to isolate aliphatic hydrocarbons.

The remaining alkaline solution was acidified with 6 M HCl (1.5 ml) and carboxylic acids were separated by extraction with methylene chloride (10 ml×3). The acids were then esterified with 14 % BF_3 in methanol and the esters were further divided into three subfractions on a silica gel column : A−1, monocarboxylic acid methyl esters ; A−2, dicarboxylic acid dimethyl esters ; A−3, hydroxyacid methyl esters and ω,ω-dimethoxy (acetal) methyl esters (derivatives of ω-oxoacids).

Aliphatic hydrocarbon, A−1 and A−3 subfractions were concentrated and analyzed with a Hewlett-Packard 5890 gas chromatograph (GC) installed with a split/splitless injector, fused silica DB−5 capillary column (0.32 mm i.d. ×30 m) and an FID detector. The column temperature was programmed from 60 ℃ (1 min.) to 120 ℃ at 30 ℃/min., then to 310 ℃ at 6 ℃/min. The compounds were further determined by a Finnigan-MAT ITS 40 mass spectrometer interfaced with a Varian 3400 capillary GC. Mass spectra (m/z 50−650) were obtained continuously with a scan speed of one scan/sec. Identification of the compounds was confirmed by mass spectral comparison with authentic standards.

Procedural blanks were run along with the sample. The blank levels for the compounds reported here were less than 10 % of the peak levels of the samples. The data presented here were corrected for the blanks.

3. Results and discussion

3.1. Hydrocarbons

Fig. 1 shows mass chromatograms at m/z 71 (n-alkanes), m/z 191 (triterpenoid hydrocarbons), and total ion chromatogram (TOT) of aliphatic hydrocarbon fraction isolated from the ice core sample (61 m in depth). Similar results were obtained for the 32-m depth sample. Normal $C_{14}-C_{35}$ alkanes were detected in the samples studied. The concentrations of total n-alkanes were 240−510 ng/kg-ice. Their distribution shows no odd/even carbon-number predominance in the range of $C_{14}-C_{20}$, however, it shows a

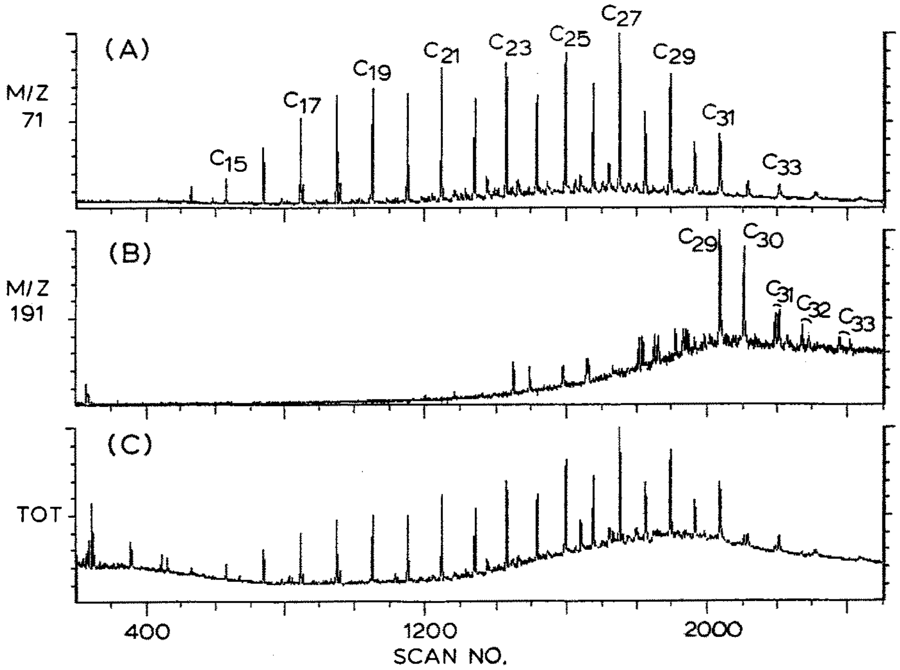

Fig. 1. (A) Mass chromatogram of n-alkanes (m/z 71), (B) mass chromatogram of triterpenoid hydrocarbons (m/z 191), and (C) total ion chromatogram (TOT) of aliphatic hydrocarbon fraction isolated from the ice core sample (61 m in depth) collected from Greenland.

Cn : Carbon numbers of hydrocarbons.

weak odd carbon-number predominance in the range of $C_{20}-C_{33}$ (Fig. 1A). The $C_{14}-C_{20}$ alkanes are derived from fossil fuel combustion whereas the $C_{21}-C_{33}$ alkanes are from both fossil fuel combustion and higher plant waxes. This is due to the knowledge that the ratios of the amounts of odd carbon-numbered n-alkanes to those of even carbon-numbers in fossil fuel (petroleum and coal) combustion are close to unity (Tissot and Welte, 1984) whereas those of plant wax hydrocarbons are 5−10 (Gagosian et al., 1981 ; Kawamura and Kaplan, 1986).

The odd/even ratios in the 32 and 61 m ice samples were 1.21 and 1.38, respectively. The values are fairly low compared to those of urban rainwaters from Los Angeles (1.9−3.0 ; Kawamura and Kaplan, 1986) and those of tropical north Pacific aerosols (2.2−4.0, Gagosian *et al.*, 1981). These results suggest that, in late 19 and early 20 centuries, pollutants derived from incompletely combusted fossil fuels in Europe, North America and Asia were significantly emitted to the atmosphere and were long-range transported over Greenland. Although plant wax hydrocarbons are present in the ice samples, their contribution is less significant than fossil fuel hydrocarbons. This is probably due to an absence of local vegetation around the sampling site in Greenland and due to winter snow coverage of northern lands when strong winds blow from mid-latitudes to the Arctic.

A long-range transport of fossil fuel combustion products over Greenland is supported by the distribution pattern of triterpenoids such as norhopane (C_{29}) and hopane (C_{30}) hydrocarbons (see Fig. 1B). Hopanoid hydrocarbons have been reported in oils, automobile exhaust and urban aerosols and used as molecular markers of vehicular exhaust (Simoneit, 1985). The mass chromatogram of Fig. 1B (m/z 191) is similar to those reported for petroleum and urban aerosol samples by Simoneit and Mazurek (1989). A combustion product transport is also supported by the presence of unresolved hydrocarbon mixture (UCM) appeared as a hump on the total ion chromatogram (Fig. 1C), which is a signature of internal engine combustion of oils (Boyer and Laitinen, 1975).

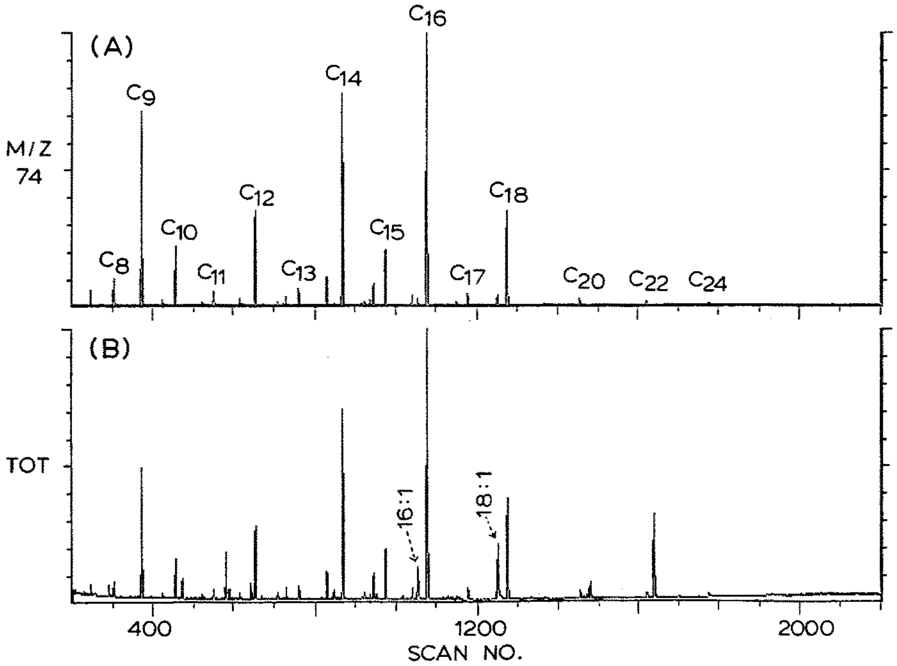

Fig. 2. (A) Mass chromatogram (m/z 74) and (B) total ion chromatogram (TOT) of fatty acid methyl ester fraction isolated from the ice core sample (61 m in depth) collected from Greenland.
Figures on the peaks of (B) denote (carbon chain length) : (double bond numbers).

3.2. Fatty acids

Saturated and unsaturated monocarboxylic acids with carbon numbers of C_7-C_{26} were detected in the ice samples. As shown in Fig.2, their distribution shows the predominance of even carbon-numbers with a maximum at C_{16} (palmitic acid) and a relatively large peak of C_9 (nonanoic acid). Palmitic acid and other fatty acids ($C_{10}-C_{18}$) are abundant in phytoplankton whereas higher molecular weight acids ($C_{20}-C_{32}$) are characteristic of terrestrial higher plants. Figure 2A suggests that fatty acids in the ice originated mostly from marine planktonic algae and the contribution from continental plants was relatively insignificant. Marine-derived lipids in the Greenland ice core are emitted from the seawater to the atmosphere by sea-spray and bubble bursting mechanisms and reached Greenland. Lipid components and bacteria are known to be enriched in the skin layer of the sea. Concentrations of total n-saturated fatty acids in the 32 and 61-m ice samples were 4.9 and 1.6 μg/kg, respectively.

Branched (*iso*- and *anteiso*-) chain C_{13}, C_{15} and C_{17} fatty acids were detected as minor monocarboxylic acids (Fig. 2A). The branched chain acids exist in bacteria as the major fatty acids (Kaneda, 1967, Cranwell, 1982). The present study suggests that bacterial lipids also consist of the organic matter in the ice samples. The marine-derived organic matter is transported in the atmosphere and deposited over the Greenland ice fields.

Unsaturated fatty acids are another minor acid group detected in the ice: $C_{16:1}$, $C_{18:1}$, $C_{18:2}$ fatty acids ($C_{n:m}$: n is carbon numbers, m is numbers of double bonds). They probably originate from marine phytoplankton which contain these acids as dominant species. However, unsaturated acids are minor species in the ice samples, suggesting that the double bonds of unsaturated fatty acids are oxidized in the atmosphere during the transport. This is consistent with the abundant presence of azelaic acid (C_9 diacid) in the ice (the result is not given here). The C_9 diacid is an ozone oxidation product of unsaturated fatty acids containing a double bond at the C−9 position, and has been detected in the remote marine atmosphere from the North Pacific (Kawamura and Gagosian, 1987).

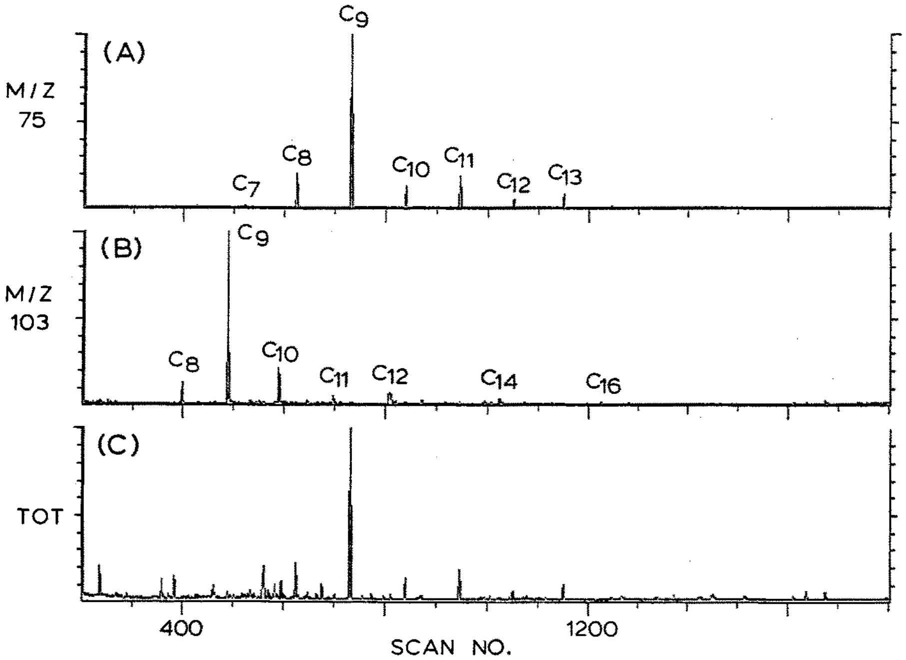

Fig. 3. (A) Mass chromatogram (m/z 75) of acetal methyl esters (derivatives of ω-oxoacids), (B) mass chromatogram (m/z 103) of β-hydroxyacid methyl esters, and (C) total ion chromatogram (TOT) of A−3 fraction (acetal and hydroxyacid methyl esters) isolated from the ice core sample (61 m in depth) collected from Greenland.

3.3. ω-Oxocarboxylic acids and β-hydroxyacids

ω-Oxocarboxylic acids with C_9 as a dominant species have been identified in the marine aerosols from the North Pacific and interpreted as photochemically-induced oxidation products of unsaturated fatty acids which contain a double bond predominantly at the C−9 position (Kawamura and Gagosian, 1987). The present study showed that ω-oxoacids (C_6-C_{14}) are also present in the ice from Greenland (Fig. 3A). The predominance of C_9 oxoacid in the ice sample (Fig. 3A) is same with the result reported in the marine atmosphere (Kawamura and Gagosian, 1987), suggesting that marine-derived unsaturated fatty acids are oxidized during atmospheric transport to Greenland. Photochemical degradation of unsaturated fatty acids in the atmosphere is consistent with the relatively poor abundance of these acids in the ice (Fig. 2B).

β-Hydroxy fatty acids (C_8-C_{16}) were detected in the ice core as minor species (Fig. 3). Because β-hydroxyacids are present in the cell walls of gram-negative bacteria (Shaw, 1974) and their distributions are characterized by the predominance of C_{16} and other even-carbon numbered species (Kawamura and Ishiwatari, 1981 ; Cranwell, 1982), the C_{12}, C_{14} and C_{16} hydroxyacids suggest a bacterial contribution to the ice, although their contribution is insignificant compared to other organic matter. The distribution of β-hydroxyacids in the ice demonstrates the predominance of C_9 species. It is unlikely that the C_9 acid is of bacterial origin. This acid may, rather, be produced in the atmosphere probably by the oxidation (β-hydroxylation) of C_9 monocarboxylic acid, which is a counterpart of atmospheric oxidation of oleic acid and was detected abundantly in the marine atmosphere (Kawamura and Gagosian, 1987). This consideration is consistent with the abundant presence of C_9 monoacid in the ice (Fig. 2).

4. Conclusions

This preliminary study showed that lipid class compounds exist in the ice core samples from Greenland, including n-alkanes, triterpenoid hydrocarbons, fatty acids, ω-oxocarboxylic acids, and β-hydroxyacids. The lipid class compounds are primarily emitted to the atmosphere from the continental (anthropogenic and higher plants) and marine (phytoplankton and bacteria) sources. Some compounds are secondarily produced in the atmosphere by photochemically-induced oxidations of biogenic organic compounds. They are transported over Greenland and sedimented in the ice sheet by snow fall and dry deposition. This study suggested that detailed analyses of ice cores for organic molecules and dry deposition would provide useful informations on the past changes of biogeochemical cycles of as well as anthropogenic inputs to the atmosphere the oceans and lands.

Acknowledgments

We thank the members of JAGE'89 (Leader : Prof. O. Watanabe, National Institute of Polar Research) for the collaboration in collecting ice samples. This study was partly supported by the Japanese Ministry of Education, Science and Culture through a Grant-in-Aid No. 01140041 and a Grant-in-Aid for Overseas Scientific Research.

References

1. Barnola, J. M., Raynaud, D., Korotkevich, Y. S. and Lorius, C. (1987) : Vostok ice core provides a 160,000-year record of atmospheric CO_2. Nature, **329**, 408−414.
2. Boyer, K. K. and Laitinen, H. A. (1975) : Automobile exhaust particulates. Environ. Sci. Technol. **9**, 457−459.
3. Cranwell, P. A. (1982) : Lipids of aquatic sediments and sedimentary particulates. Proc. Lipid Res. **21**, 271−308.
4. Gagosian, R. B., Peltzer, E. T., and Zafiriou, O. C. (1981) : Atmospheric transport of continentally derived lipids to the tropical North Pacific. Nature **291**, 312−314.
5. Kaneda, T. (1967) : Fatty acids in the genus *Bacillus* I. Iso- and anteiso-fatty acids as characteristic constituents of lipids in 10 species. J. Bacteriol. **93**, 894−903.
6. Kawamura, K. and Ishiwatari, R. (1981) : Tightly bound β-hydroxy acids in a recent sediment. Nature, **297**, 144−145.
7. Kawamura, K. and Kaplan, I. R. (1986) : Biogenic and anthropogenic organic compounds in rain and snow samples collected in southern California. Atmos. Environ., **20**, 115−122.
8. Kawamura, K. and Gagosian, R. B. (1987) : Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. Nature, **325**, 330−332.
9. Neftel, A., Moor, E. ; Oeschger, H. and Stauffer, B. (1985) : Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. Nature, **315**, 45−47.
10. Shaw, N. (1974) : Lipid composition as a guide to the classification of bacteria. Adv. Appl. Microbiol. **17**, 63−108.
11. Shoji, H. ; Clausen, H. B., and Kameda, T. (1991) : Accumulation rate at Site-J and Dye-2. Bull. Glacier Res. **9**, 85−88.
12. Simoneit, B. R. T. (1985) : Application of molecular marker analysis to vehicular exhaust for source reconciliations. Intern. J. Environ. Anal. Chem. **22**, 203−233.

13. Simoneit, B. R. T. and Mazurek, M. A. (1982) : Organic matter on the troposphere. II. Natural background of biogenic lipid matter in aerosols over the rural western United States. Atmos. Environ. **16**, 2139–2159.
14. Simoneit, B. R. T. and Mazurek, M. A. (1989) : Organic tracers in ambient aerosols and rain. Aerosol Sci. and Technol. **10**, 267–291.
15. Tissot, B. T. and Welte, D. H. (1984) : *Petroleum Formation and Occurrence*, 2nd ed., Berlin, Springer-Verlag, 699p.
16. Watanabe, O. and Fujii, Y. (1990) : Outline of the Japanese Arctic Glaciological Expedition in 1989 (JAGE). Bull. Glacier Res., **8**, 103–106.