

Organic Acids and Aldehydes in the Ice Samples from Site-J, Greenland

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Abstract

Polar organic compounds, including low molecular weight dicarboxylic acids, oxoacids, and aldehydes, were determined in ice and snow samples collected from Site-J, Greenland by the methods of capillary gas chromatography and mass spectrometry.

Melted waters were dried and reacted with 14% boron trifluoride in n-butanol : carboxylic acids and aldehydes were converted to dibutyl esters and dibutoxy derivatives, respectively. Major organic species detected in the samples were oxalic, succinic, pyruvic, and azelaic acids. Total concentration range was 7–49 ng/g-ice. These compounds were most likely produced in the atmosphere by photochemical oxidation of biogenic and anthropogenic organic molecules and sedimented in the ice field.

1. Introduction

Snow in the high latitude areas scavenges both gaseous and particulate chemical species from the atmosphere and trap them in the ice layers without significant transport and transformation. Thus, chemical analyses of ice core samples provide important informations of past atmospheric environments (e.g., Delmas *et al.*, 1980 ; Craig and Chou, 1982 ; Neftel *et al.*, 1985 ; Barnola *et al.*, 1987). However, previous studies of ice cores have been limited to gases and inorganic species, and organic compounds have rarely been analyzed.

On the other hand, various organic compounds have been extensively studied in the continental and remote marine atmosphere. They have been successfully used as molecular tracers of atmospheric long-range transport and transformations (photochemical reactions) of organic matter (e.g., Gagosian *et al.*, 1981 ; Kawamura and Kaplan, 1986 ; Kawamura and Gagosian, 1987). Organic compounds emitted from biogenic and anthropogenic sources and also derived from photochemically induced reactions in the atmosphere should remain in an Arctic ice sheet after snow falls and dry deposition. Thus, studies of organic matter in ice cores would provide useful informations to understand the geochemical and biogeochemical cycles and processes of natural and anthropogenic

materials in the Arctic atmosphere as well as in circumpolar lands and oceans.

We have started to analyze ice core samples collected from Site-J, Greenland for a variety of organic molecules. Here, we present a preliminary results of low molecular weight dicarboxylic acids, oxoacids and dialdehydes. These polar organic compounds have been detected in the urban atmosphere as major aerosol constituents and considered to be produced mostly in the atmosphere by photochemically induced reactions (Kawamura and Ikushima, 1991, in preparation).

2. Samples and methods

A 206 m long ice core was collected at Site-J, Greenland (latitude : 66°51.9'N ; longitude: 46°15.9'W ; altitude : 2030 m) in May and June, 1989 (Watanabe and Fujii, 1990). Five samples were taken from the depths of 32, 61, 91, 117 and 152 m for the purpose of organic analyses (Table 1). The length of each section was 1.2–1.5 m, which corresponds to 3–4 years. A fresh snow sample (0–5 cm in depth) was also collected from the same location. Sample surfaces were cut off to remove potential contaminations. The remaining samples were cut in pieces and were melted in a pre-cleaned brown gallon bottle cap at the

Table 1. Description of snow and ice core samples collected from the Site-J, Greenland, in 1989.

Depth	Type	Top (M)	Bottom (M)	Approximate age
0	snow	0	0.05	June 22, 1989
32	ice	31.20	32.50	1941
61	ice	90.64	62.07	1881
91	ice	90.36	91.79	1810
117	ice	116.52	118.06	1749
152	ice	151.03	152.38	1667

Age was tentatively determined based on the comparison of the electron conductivity data and records of volcanic events (e.g., volcanic eruption of Laki in 1783 is identified in the depth of 102.8m ; Shoji *et al.*, 1991).

sampling site. The bottle was tightly sealed with a teflon-lined cap. The melt water samples (2.4–2.8 L) were poisoned with mercuric chloride and were air-parceled to Tokyo through Copenhagen.

A 150 ml sample was taken in a 200 ml round bottom flask and concentrated down to 2 ml by using a rotary evaporator under a vacuum. The sample was transferred to a 10 ml test tube with a grounded glass cap, dried by rotary evaporation and nitrogen blow down, and then reacted with 14 % borontrifluoride in n-butanol at 100 °C for 30 min. During the reaction, the carboxyl group was converted to butyl ester and aldehyde group to dibutoxy acetal. The ester and acetal derivatives were washed with pure water (3 ml × 3) in the presence of acetonitrile (0.2 ml) and n-hexane (5 ml) and then concentrated down to 50 microliters.

The esters and acetals in n-hexane solution were determined by a Hewlett Packard 5890 capillary gas chromatograph (GC) installed with a fused silica DB-5 column and an FID detector and by a Finnigan-MAT INCOS 50 or Finnigan-MAT ITS-40 GC-mass spectrometer. Peak identification was performed by a comparison with retention times and mass spectra of authentic standards (Kawamura *et al.*, 1985). Procedural blanks showed contamination for oxalic and some other acids, however, their concentration levels were less than 10 % of the sample results. The data presented here are corrected for the blanks.

3. Results and discussion

Figure 1 shows a capillary gas chromatogram of the carboxylic acid and aldehyde derivatives isolated from the ice core sample (32 m) from Site-J, Greenland. The gas chromatographic peaks were identified as organic acids and aldehydes which contain in

most cases an additional carboxyl or keto functional group. They include C₂–C₁₀ aliphatic dicarboxylic acids, aromatic diacid (phthalic acid), C₂–C₁₀ ω-oxocarboxylic acids, α-ketoacid (pyruvic acid), dicarbonyls (glyoxal and methylglyoxal), tri-carboxylic acid (citric acid). Saturated and unsaturated fatty acids (C₁₄–C₁₈) were also detected in the ice/snow samples. Table 2 gives the concentrations of relatively abundant organic acids and aldehydes detected in the samples from Site-J, Greenland.

Volatile organic acid and aldehydes (formic and acetic acids, formaldehyde, acetaldehyde) were not detected in the samples by the method used in this study. Volatile compounds may have been lost from the samples during the procedure of sample evaporation.

Total concentration of the organic acids and aldehydes ranged from 7 ng/g to 50 ng/g (Table 2). The concentration levels of the Greenland ice/snow samples are much lower than the urban Los Angeles rainwaters (e.g., oxalic acid concentrations of Los Angeles rain were 100–2500 ng/g ; Kawamura and Kaplan, 1987). Major species detected in the Greenland samples were oxalic (C₂), succinic (C₄), pyruvic acid (C₃) and azelaic (C₉) acids. The dicarboxylic acids and some ketoacids listed in Table 2 have been reported in urban and rural aerosols and rainwaters (Norton *et al.*, 1983 ; Kawamura and Kaplan, 1987 ; Kawamura *et al.*, 1985 ; Steinberg *et al.*, 1985). These difunctional organic compounds have been considered to originate from primary sources such as incomplete combustion of fossil fuels as well as secondary photochemical oxidations of organic compounds in the atmosphere.

Distributions of the dicarboxylic acids studied in the ice/snow samples are different from those detected in the urban aerosols (Kawamura and Kaplan,

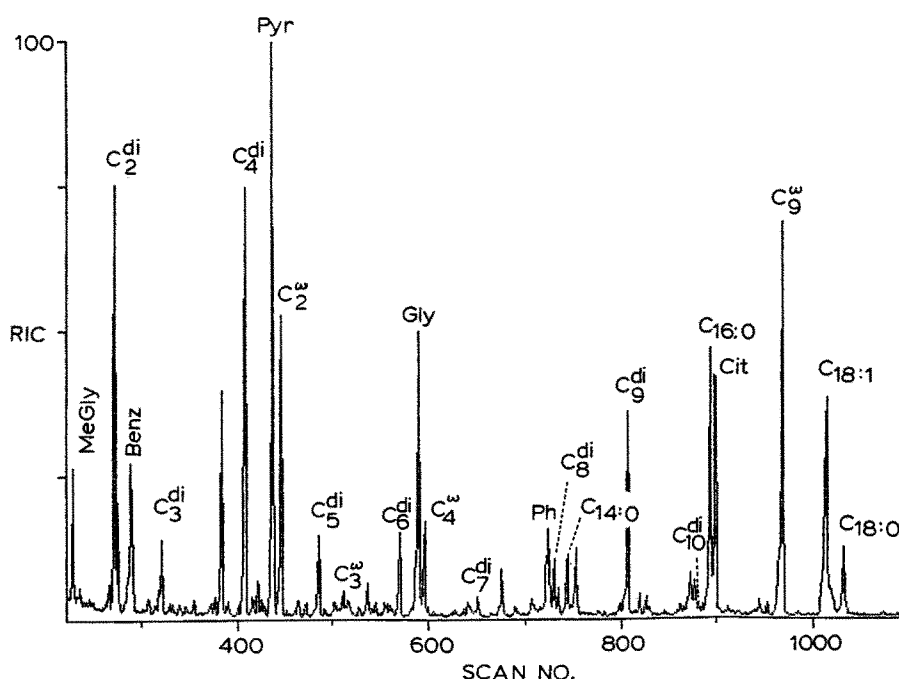


Fig. 1. Reconstructed ion chromatogram of polar organic compounds isolated from the ice core sample (32 m in depth) from Greenland, Site-J.

Abbreviation ; MeGly : Methylglyoxal, Benz : Benzoic acid, Pyr : Pyruvic acid, Gly : Glyoxal, Ph : Phthalic acid, Cit : Citric acid; C_n^{di} : α,ω -Dicarboxylic acids with n carbon numbers, C_n^w : ω -Oxocarboxylic acids with n carbon numbers, $C_{n,m}$: Fatty acids with n carbon numbers and m double bonds. For full name of the compounds, see Table 2.

Gas chromatographic conditions; column : fused silica DB-5 capillary column (30m \times 0.32mm), column oven temperature : programmed from 60 $^{\circ}$ C (1 min.) to 120 $^{\circ}$ C (30 $^{\circ}$ C/min.) then to 300 $^{\circ}$ C (6 $^{\circ}$ C/min.), injection : splitless injector. Mass spectrum (m/z 40–500) was scanned every one second.

1985 ; Kawamura and Ikushima, 1991, in preparation). For example, although oxalic acid is one of the dominant diacids in the ice samples, its relative abundance (19–32 %) in the total diacids is less than that of the urban aerosols (41–73 %) from Tokyo (Kawamura and Ikushima, 1991, in preparation). In accordance with this, azelaic acid (C_9) is relatively abundant in the ice samples : the third or fourth most abundant diacid, and is greater than phthalic acid in the Greenland ice core. The C_9 diacid has been considered as a photo-oxidation product of unsaturated fatty acids which contain a double bond generally at the C-9 position (Kawamura and Gagosian, 1987). These results indicate that Greenland ice samples have trapped the dicarboxylic acids whose distributions were influenced by photo-oxidation of biogenic organic compounds probably of marine origin.

Previous aerosol and rainwater studies have

shown that maleic acid (*cis* configuration) is generally twice or more abundant than fumaric acid (*trans*) although they are minor species (Kawamura *et al.*, 1985 ; Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1991, in preparation). The predominance of *cis* configuration have been explained by preferential production of maleic acid over fumaric acid through oxidative degradation of benzene structures (Kawamura *et al.*, 1985). The fresh snow sample showed the maleic/fumaric acid ratio of 2.3 (Table 2), being consistent with aerosol results (Kawamura and Kaplan, 1987). However, the ratios in the ice core samples are less than unity. The discrepancy between the snow and ice samples suggests that maleic acid was degraded more rapidly than fumaric acid or that maleic acid was transformed to fumaric acid. The results obtained in deeper ice sections suggests that *cis/trans* isomerization of maleic acid to fumaric

Table 2. Concentrations (ng/g) of polar organic compounds in the snow and ice core samples collected from Site-J, Greenland in 1989.

Compounds	Carbon No	Depth of ice samples (M)					
		0 (snow)	32	61	91	117	152
<u>Dicarboxylic acids</u>							
Oxalic acid	C 2	7.60	5.67	3.97	2.55	4.28	1.92
Malonic acid	C 3	0.93	1.37	0.30	0.17	0.17	0.31
Methylmalonic acid	C 4	0.44	0.28	0.16	0.15	0.15	0.15
Maleic acid	C 4	0.32	0.42	0.17	nd	nd	nd
Succinic acid	C 4	11.02	8.14	6.01	3.54	4.19	3.32
Methylsuccinic acid	C 5	0.54	0.60	0.32	nd	2.21	nd
Fumaric acid	C 4	0.14	0.49	0.18	nd	nd	nd
Citraconic acid	C 5	0.27	nd	nd	nd	nd	nd
Malic acid	C 4	0.18	0.25	0.08	bb	0.04	bb
Glutaric acid	C 5	2.25	1.49	0.75	0.35	0.76	0.35
Adipic acid	C 6	0.60	1.72	0.54	0.28	0.32	0.17
Pimelic acid	C 7	0.24	0.61	0.18	nd	nd	nd
Suberic acid	C 8	nd	1.54	0.21	nd	nd	nd
Phthalic acid	C 8	0.56	1.67	0.57	0.06	bb	bb
Azelaic acid	C 9	0.97	5.97	0.95	0.96	1.26	0.47
<u>ω-Oxocarboxylic acids</u>							
Glyoxylic acid	C 2	0.23	0.79	0.74	nd	nd	nd
Malonic semialdehyde	C 3	0.97	0.48	0.18	0.20	0.21	0.13
Succinic semialdehyde	C 4	1.72	1.25	0.28	bb	0.01	bb
<u>Aldehydes</u>							
Methylglyoxal	C 3	0.80	0.66	0.17	0.01	bb	bb
Glyoxal	C 2	0.54	7.74	1.50	0.25	0.13	0.03
<u>Others</u>							
Pyruvic acid	C 3	2.14	11.64	1.58	0.66	0.81	0.61
Total		32.46	49.78	18.84	9.18	14.54	7.46

nd : not detected, bb : below blank

acid occurs when the sun light penetrates snow and ice layers.

Limited numbers of the ice samples have shown a large fluctuation in the concentrations of polar organic compounds in the ice core (Table 2). The highest concentration was obtained in the 32 m sample, which corresponds to ca. 1940 A.D. On the other hand, the lowest concentration was observed in the 152 m sample, corresponding to 1660 A.D. (Table 1). These vertical changes may be related with past changes in the atmospheric environments over Greenland. More analysis of the ice sections would provide informations on the recent changes in biogenic and anthropogenic emission in the northern hemisphere, atmospheric transport of these organic compounds from oceans and continents over Greenland, and secondary production of oxygenated organic compounds by photo-oxidation reactions.

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