Organic Carbons and Fatty Acids in Antarctic Saline Lakes

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南極塩湖水中の有機炭素および脂肪酸の測定

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要旨：南極ドライバレーのバンダ湖，ボニー湖およびフリクセル湖の底層水中の全有機炭素（TOC），酢酸エチル抽出有機炭素（EOC）および脂肪酸の測定を行った．その結果，高濃度の TOC（18.6–63.8 mg/*l*）および EOC（3.8–9.1 mg/*l*）が測定された．脂肪酸は不飽和の $C_{16:1}$（炭素数：不飽和数）と $C_{18:1}$ を含む $C_{8:0}$ から $C_{32:0}$ の範囲のものが同定された．それらの全濃度は 2.8–19 μg/*l* である．また，ボニー湖からはフェニル酢酸が同定された．これらの有機化合物は主として湖水中の藻類，バクテリアおよび菌類などの微生物に由来するものと思われる．

Abstract: Total organic carbon (TOC), extractable organic carbon (EOC), and fatty acids were determined in bottom waters of Lakes, Vanda, Bonney, and Fryxell in the Dry Valleys of Victoria Land, Antarctica. The high concentrations of TOC and EOC were found, ranging from 18.6 to 63.8 mg/*l* and from 3.8 to 9.1 mg/*l*, respectively. Fatty acids ranging from $C_{8:0}$ (carbon numbers: numbers of unsaturation) to $C_{32:0}$ including $C_{16:1}$ and $C_{18:1}$ were determined by using a combined gas chromatograph—mass spectrometer (GC–MS), and their total concentrations were 2.8–19 μg/*l*. Furthermore, phenylacetic acid was identified in the bottom waters of Lake Bonney. The sources of those organic compounds may be due to the lake organisms, such as algae, bacteria, and fungi.

1. Introduction

In Antarctica, no vascular plants were present except in the Antarctic Peninsula (MATSUDA, 1973). The chemistry of inorganic components in the Antarctic lakes has been reported by YAMAGATA *et al.* (1967), TORII *et al.* (1975), and others. The presence of organic compounds in the Antarctic lakes was preliminarily reported by TORII and WAGURI (1975). However, the most part of their environmental organic geochemistry is not known.

This paper gives the results of determination of total organic carbon (TOC), extractable organic carbon (EOC) with ethyl acetate, and fatty acids ranging from $C_{8:0}$ (carbon numbers : numbers of unsaturation) to $C_{32:0}$ including $C_{16:1}$

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and $C_{18:1}$ in the bottom waters of saline Lakes, Vanda, Bonney, and Fryxell in the Dry Valleys of Victoria Land, Antarctica.

2. Experimental

2.1. Water samples

The water samples were collected by a Kitahara-type water sampler, and then were transferred into 2 *l* brown glass bottles with tefron caps and acidified with concentrated hydrochloric acid (3 m*l*/2 *l*) to prevent biological activity. Those samples were stored at the temperature below 5°C until the analyses. Table 1 shows the sampling location, date, depth, and water temperature.

Table 1. Sampling location.

Sampling location	Sampling date	Water temp. (°C)	Depth (m)	Bottom (m)
Taylor Valley				
Lake Bonney, east lobe No. 2 hole	Dec. 18, 1974	−1.4	33	34.5
Lake Bonney, east lobe No. 3 hole	Dec. 21, 1974	−2.8	33.5	34.5
Lake Bonney, west lobe No .3 hole	Dec. 22, 1974	−3.9	28	28.5
Lake Fryxell, west side	Dec. 25, 1974	1.6	18	18.8
Wright Valley				
Lake Vanda, point R	Dec. 30, 1974	17.9	55	68.6
Lake Vanda, point R	Dec. 30, 1974	24.2	66	68.6

2.2. Analyses of water samples

TOC and EOC: TOC of the water samples were determined by the method of MENZEL and VACCARO (1964). The water samples (0.9–1.5 *l*) were extracted 3 times with ethyl acetate (300 m*l*, 150 m*l*×2) under acidic conditions (pH<2) in a 2 *l* separating funnel, then the organic extracts were combined and concentrated to 5.0 m*l* under reduced pressure at the temperature below 30°C. To determine EOC, the duplicate 50 μl concentrates were taken with syringe and transferred to 10 m*l* glass ampoules. The ethyl acetate was removed under the same conditions for 6 hours. Five m*l* redistilled water was added to the ampoules and those TOC were determined.

Fatty acids: To determine fatty acids, the concentrates were evaporated to dryness, redissolved in 50 μl benzene : ethyl acetate (1:1), and chromatographed through silica gel column (18 cm×4 mm i.d., 5% water, 100 mesh). Fatty acids were eluted with 3 column volumes of benzene : ethyl acetate (95:5) after eluting hydrocarbons with 3 column volumes of haxane. The benzene : ethyl acetate (95:5) eluates were concentrated, and methylated with 15% boron

trifluoride methanol solution (2 hours at 80°C). The methyl esters of fatty acids were determined by using a Shimadzu LKB—9000 gas chromatograph—mass spectrometer (GC–MS). The GC–MS conditions were as follows. Coiled glass column (200 cm×3 mm i.d.) was packed 1% OV–1 on 80–100 mesh Chromosorb W. Flow rate of carrier gas (helium) was 30 m*l*/min. Column temperature was programmed from 100 to 280°C at 8°C/min. The molecular separator and ion source were maintained at 300°C and 330°C, respectively. Gas chromatograms were recorded with total ion current monitor (TICM) at 20 eV. Mass spectra were taken at 70 eV with accelerator voltage of 3.5 kV.

The fatty acids were identified by comparison of the retention times and mass spectra with those of authentic compounds.

3. Results and Discussion

3.1. TOC and EOC

Table 2 shows the concentrations of TOC and EOC of the water samples collected from the three saline lakes. The concentrations of TOC and EOC of bottom waters were ranging from 18.6 to 63.8 mg/*l* and from 3.8 to 9.1 mg/*l*, respectively. The ratio of EOC to TOC values was 8.0 to 31%.

Table 2. TOC and EOC.

Sampling location	TOC (mg/*l*)	EOC (mg/*l*)	EOC/TOC×100 (%)
Lake Bonney, east lobe No. 2 hole	28.0	4.7	17
Lake Bonney, east lobe No. 3 hole	27.5	3.9	14
Lake Bonney, west lobe	18.6	3.8	20
Lake Fryxell, west side	29.1	9.1	31
Lake Vanda, point R, 55 m depth	1.9	0.2	11
Lake Vanda, point R, 66 m depth	63.8	5.1	8.0

The concentrations of TOC and EOC of bottom waters were very high compared with those of ordinary fresh water lakes in Japan. For example, those TOC values are much higher than those of a eutrophic lake, Lake Suwa, range from 1.8 to 3.7 mg/*l* (SAKAMOTO *et al.*, 1975). Dissolved organic carbon in the waters of Lake Bonney has been also reported to be very high by PARKER (1974).

On the other hand, the concentration of TOC of the bottom water (66 m depth) is about 30 times higher than that of the 55 m depth water in Lake Vanda. This fact is noteworthy in connection with the stratification of the lake water.

3.2. Fatty acids

Fig. 1 shows a gas chromatogram and mass fragmentogram of fatty acid fraction obtained from the 55 m depth sample of Lake Vanda. The mass

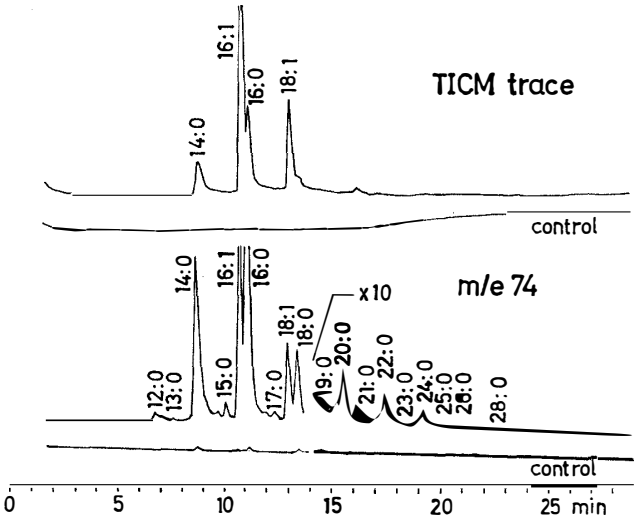

Fig. 1. Gas chromatogram and mass fragmentogram of fatty acid fraction obtained from the 55 m depth sample of Lake Vanda.

fragmentography was run at the base peak [m/e 74, $CH_3OC(OH)CH_2^+$] of the methyl esters of straight chain fatty acids. In the chromatogram, fatty acids were found with dominance of saturated acids of even carbon numbers ranging from $C_{12:0}$ to $C_{28:0}$ and with great predominance of unsaturates ($C_{16:1}$ and $C_{18:1}$). Typical peaks of mass spectra of those saturated acids were found at m/e 74, 87[$CH_3OC(OH)CHCH_2^+$], 101[$CH_3OCO(CH_2)_3^+$], 143[$CH_3OCO(CH_2)_6^+$], 157, 171, 185, etc. [$CH_3OCO(CH_2)_{7,8,9}^+$, etc.], M-43, M-29, and M-31 (M-OCH_3) (McCLOSKY, 1969). In Fig. 2 the mass spectrum of methyl palmitoleic acid of the

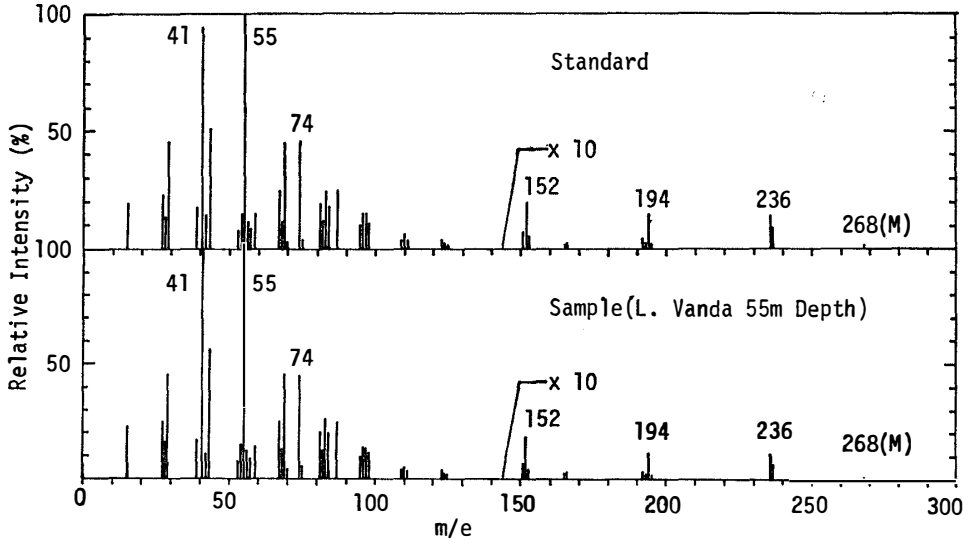

Fig. 2. Mass spectrum of methyl palmitoleate.

sample (Lake Vanda 55 m depth) was compared with that of authentic compound.

Table 3 lists the fatty acids determined in the six water samples. Fatty acids ranging from $C_{8:0}$ to $C_{32:0}$ were found in the waters. The total concentrations of the fatty acids determined by mass fragmentography were ranging from 2.8 to 35 $\mu g/l$. The ratio of carbon in fatty acids to EOC in weight shows a wide range of variation from 0.05 to 13% due to the samples.

Table 3. Fatty acids.

Sampling location	Range of carbon number	Total concentration ($\mu g/l$)
Lake Bonney, east lobe No. 2 hole	8–26	2.8
Lake Bonney, east lobe No. 3 hole	8–24	14
Lake Bonney, west lobe	10–30	7.8
Lake Fryxell, west side	10–28	19
Lake Vanda, point R, 55 m depth	12–28	35
Lake Vanda, point R, 66 m depth	8–32	16

The percentages of unsaturates in C_{16} and C_{18} were very high (about 70%) in the waters from the 55 m depth in Lake Vanda and bottom of Lake Fryxell. However, those values of unsaturates in bottom waters of Lakes, Vanda and Bonney were smaller than 40%. Those saturated and unsaturated acids may have been derived from algae, bacteria, and fungi in the lake (SUGIYAMA *et al.*, 1967; GOLDMAN, 1970; FUKUSHIMA, 1970 etc.) and in the soils around the lakes (BENOIT and HALL, 1970; CAMERON *et al.*, 1970; HOROWITZ *et al.*, 1972 etc.).

3.3. Other compounds identified

Fig. 3 shows a gas chromatogram of fatty acid fraction obtained from the

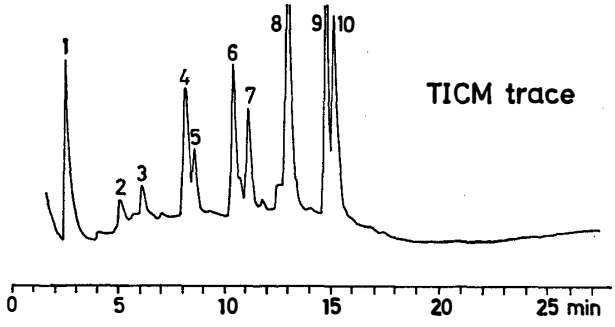

Fig. 3. Gas chromatogram of fatty acid fraction obtained from west lobe sample of Lake Bonney. Peaks: #1, methyl phenylacetate; #2, dimethyl phthalate; #3, $C_{12:0}$; #5, $C_{14:0}$; #7, dibutyl phthalate+$C_{16:0}$; #8, $C_{18:0}$+?; #10, borneol?; #4, #6, and #9, unknown.

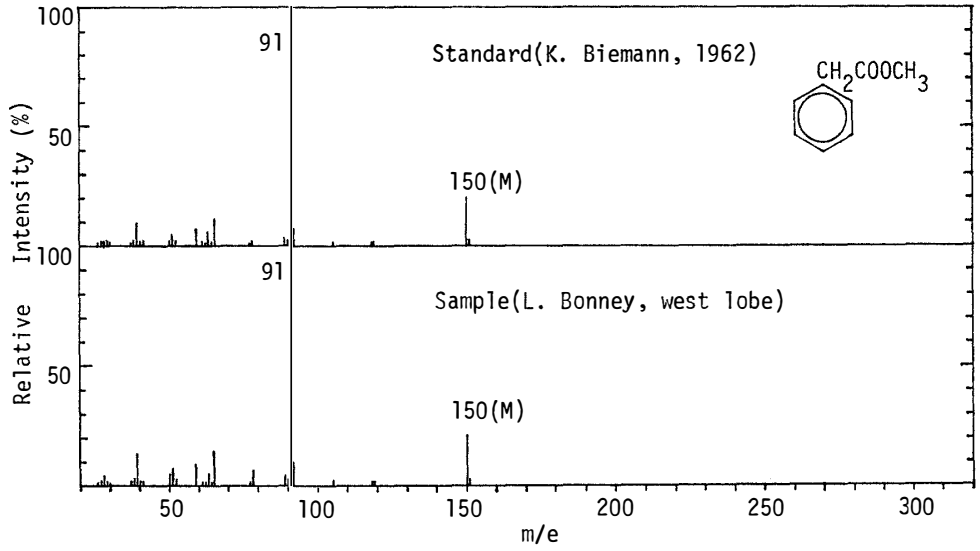

Fig. 4. Mass spectrum of methyl phenylacetate.

east lobe sample of Lake Bonney. Ten major peaks were found in the chromatogram. The peak #1 was identified as methyl phenylacetate. Fig. 4 shows the mass spectrum of methyl phenylacetate with that of reference spectrum (BIEMANN, 1962). This compound was also found in the waters from the east lobe of Lake Bonney. Its concentrations were about 0.3 μg/*l*. Phenylacetic acid is present in the mould metabolites; clinical penicillin (CRAM and TISHLER, 1948). Penicillin spp. were found in the lake waters and in the soils around the lakes in the Dry Valleys (SUGIYAMA *et al.*, 1967). The peaks #2 and #7 were identified as dimethyl phthalate and dibutyl phthalate + $C_{16:0}$, respectively. Dibuthyl phthalate was found in all the bottom waters analyzed so far. But dimethyl phthalate was found only in the west lobe water of Lake Bonney. The concentrations of dibutyl phthalate were ranging from 0.1 to 0.5 μg/*l*. Those phthalate esters might be contaminated during sampling and analyses. The peaks #3, #5, and #8 were $C_{12:0}$, $C_{14:0}$, and $C_{18:0}$ + ?, respectively. The peak #10 was assumed to be borneol. But the peaks #4, #6, and #9 were unknown.

The authors wish to make further studies to identify organic compounds including hydrocarbons, sterols, aromatic acids, and phenolic compounds in lake waters, sediments, soils, and organisms, in Antarctica. The authors' interests are also to elucidate their distribution, chemical forms, alteration, and their connection with stratification of lake water.

4. Conclusion

The high concentrations of TOC and EOC were found in the bottom waters of the three Antarctic saline lakes. Fatty acids ranging from $C_{8:0}$ to $C_{32:0}$ includ-

ing $C_{16:1}$ and $C_{18:1}$ were found in the waters. Phenylacetic acid was found in waters of Lake Bonney. The sources of those organic compounds may be due to the lake organisms, such as algae, bacteria, and fungi.

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