# A REVIEW OF ORGANIC GEOCHEMISTRY IN ANTARCTICA

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***Abstract:*** Organic constituents of the McMurdo, Syowa and Vestfold Oases have been reviewed with the viewpoint of organic geochemistry. The concentrations of total organic carbon (TOC), extractable organic carbon with ethyl acetate, total nitrogen (TN), hydrocarbons, fatty acids, sterols, hydroxy acids and phenolic acids in lake and pond waters and sediments show a wide range of variation depending on the sampling depths and locations, reflecting probably the difference of the distribution and activity of organisms there, although the contents of the organic compounds studied are generally low. Normal, branched and unsaturated hydrocarbons and fatty acids are found in the water and sediment samples, but their compositions differ considerably among the lakes and ponds. Six $\Delta^5$-stenols and three $5\alpha$-stanols are identified in the water and/or sediment samples. Surprisingly, 24-ethylcholesterol is the most dominant sterol, which must come from blue-green algae and green algae in the lakes and ponds. The $C_{29}/C_{27}$ sterol ratios are considerably high ($>1$), and are not good geochemical markers for the Antarctic environment as usual meaning. The dominance of *p*-hydroxybenzoic acid among the phenolic acids found along with the absence of syringic, *p*-coumaric and ferulic acids in water and sediment samples reflect the absence of vascular plants in the areas studied, and are believed to be an important indicator for the absence of vascular plants.

The concentrations of TOC, TN, hydrocarbons and fatty acids in soils in the dry valley areas of the McMurdo Oasis are extremely low, reflecting that organic carbon sources are highly restricted there. However, very long-chain *n*-alkanoic acids extending to $C_{40}$ are found, having a small even-carbon predominance, and comprising a large proportion of the fatty acids in soils. They apparently originate in the Beacon sandstone.

## 1. Introduction

Antarctica is the unique continent, in which vascular plants are absent except in the northern part of the Antarctic Peninsula. Numerous kinds of endemic species of microorganisms have been found throughout Antarctica. Thus the organic constituents in the Antarctic environment can be expected to differ considerably from those in the mid and lower latitudes. Furthermore, Antarctica is situated in farthest from industrialized areas, and so its environment is considered to be the least polluted in the world.

There are a number of ice-free areas, so-called "oasis" throughout Antarctica, where numerous lakes and ponds including saline lakes are distributed. The oasis is the most important as a clue to the recognition of Antarctica, because the greater

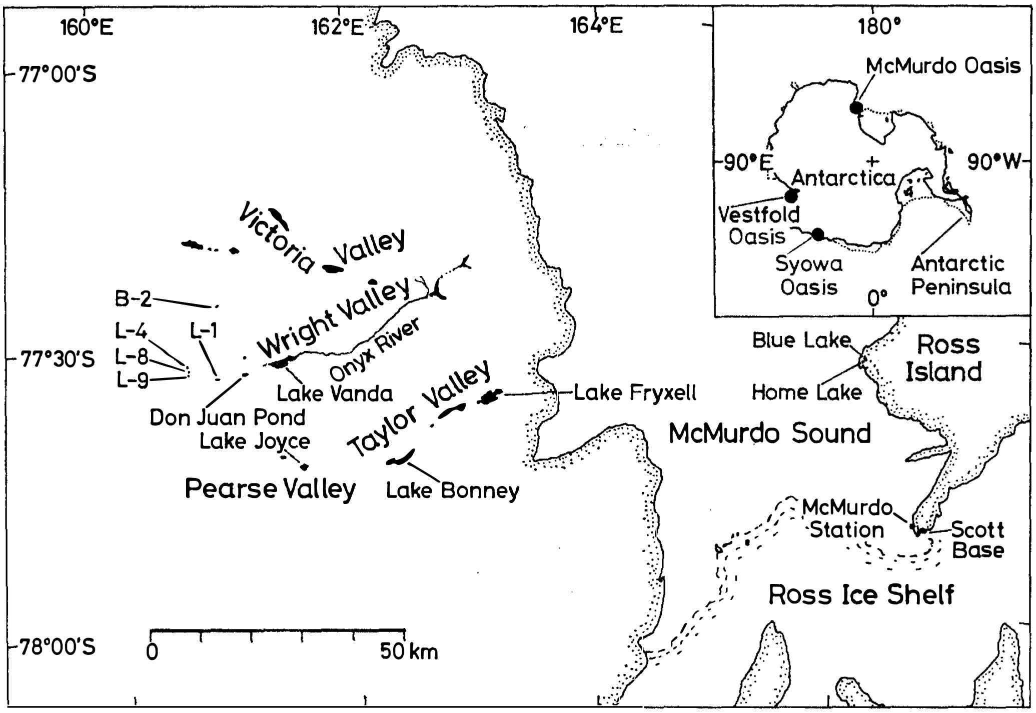


*Fig. 1. Sampling locations in Ross Island and in the dry valley areas of the McMurdo Oasis, Antarctica. B-2, L-1, L-4, L-8 and L-9 are unnamed ponds.*

part of the continent is covered with thick ice. Although a large number of geochemical studies on inorganic constituents have been carried out for Antarctica, little attention has been paid to organic constituents. Organic carbons of fresh and saline lakes including meromictic lakes have been investigated for Ross Island and the dry valleys of the McMurdo Oasis, Fig. 1 (PARKER *et al.*, 1974; MATSUMOTO and HANYA, 1977; MATSUMOTO *et al.*, 1978, 1979), Syowa Oasis, Fig. 2 (TOMINAGA and FUKUI, 1981), and for the Vestfold Oasis (BARKER, 1980; BURTON, 1980, 1981). Recently MATSUMOTO and his co-workers have studied organic constituents, hydrocarbons, fatty acids, phytol, sterols, hydroxy acids and phenolic acids in several environmental samples from these oases (MATSUMOTO and HANYA, 1977; MATSUMOTO *et al.*, 1978, 1979, 1981a, b, 1982a, b, 1983a, b, c, 1984). We reviewed here the organic geochemical results of the McMurdo, Syowa and Vestfold Oases in Antarctica.

## 2. Organic Constituents in Lake and Pond Waters

Very little is known on the organic constituents other than organic carbon in lake and pond waters in Antarctica except in Ross Island and in the dry valley areas of the McMurdo Oasis. In most Antarctic lakes organic materials are largely autochthonous, since terrestrial vegetation is virtually non-existent in the lake catchments (BURTON, 1981). PARKER *et al.* (1974) have reported the higher concentrations and seasonal variations of total organic carbon (TOC) in Lake Bonney in the Taylor Valley of the dry valley areas. Higher concentrations of TOC have also been found in the bottom waters of Lakes Vanda and Fryxell in the dry valley areas and Home

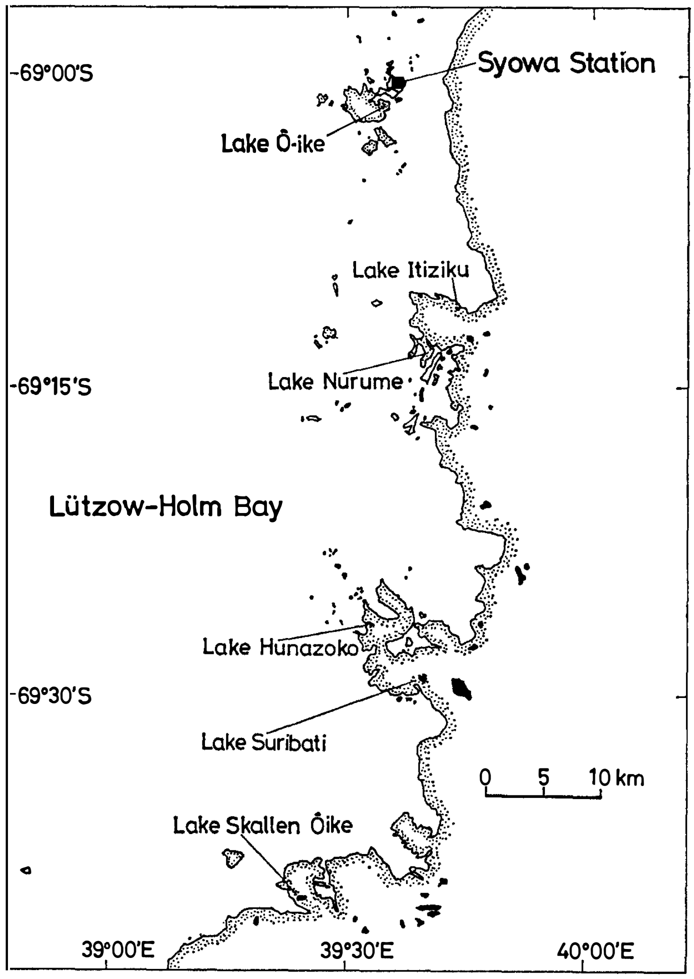


*Fig. 2. Sampling locations in the Syowa Oasis in East Antarctica.*

Lake of Ross Island as well as Lake Bonney (15–110 mgC/$l$), while the TOC values of Lake Joyce in the Pearse Valley are considerably low (0.31–3.4 mgC/$l$), Table 1 (MATSUMOTO and HANYA, 1977; MATSUMOTO *et al.*, 1978, 1979, 1984). For the higher TOC values of the bottom water of Lake Vanda, MATSUMOTO *et al.* (1984) have discussed based on the features of organic constituents that the sinking of dead plankton may be prevented by the high density (1.1) of the warm bottom water, because the salinity of the bottom water is much higher than that of the overlying waters. The degradation of organic materials should occur and thus refractory organic materials are concentrated there. An extremely higher value of TOC has been found in Home Lake (110 mgC/$l$), in which the water is strongly influenced by the excretions of Adélie penguin and skua around the lake (MATSUMOTO *et al.*, 1978, 1979).

Higher values of dissolved organic carbon (DOC) have been found in Lake Hunazoko (103–186 mgC/$l$), Lake Nurume (2–30 mgC/$l$) and Lake Suribati ($10^1$–$10^2$ mgC/$l$) of the Syowa Oasis, whereas those of 35 fresh lakes in the same area are low (1–2 mgC/$l$), Table 1 (TOMINAGA and FUKUI, 1981). They reported a significant correlation between DOC and chlorinity, although there is a considerable difference in the concentration with depths and lakes. On the other hand, the higher TOC

*Table 1. Total organic carbon (TOC) and extractable organic carbon with ethyl acetate (EOC) values for lake, pond and stream waters from the McMurdo, Syowa and Vestfold Oases.*

| Locality (depth) | TOC (mgC/*l*) | EOC (mgC/*l*) | EOC/TOC (%) |
|---|---|---|---|
| McMurdo Oasis*[1] | | | |
| Blue Lake (surface) | 0.43 | 0.08 | 19 |
| Home Lake (surface) | 110 | 8.5 | 7.7 |
| Onyx River (surface) | 0.72 | 0.10 | 14 |
| Lake Vanda (5.4–66 m) | 0.31–63.8 | 0.05–5.1 | 6.0–30 |
| L-1 pond (surface)*[2] | 3.0 | 0.48 | 16 |
| Lake Bonney, east lobe (5.4–33.5 m) | 0.52–28.0 | 0.10–4.7 | 14–19 |
| Lake Bonney, west lobe (5.4–30.4 m) | 0.44–18.6 | 0.11–3.8 | 3.4–25 |
| Lake Fryxell (18 m) | 29.1 | 9.1 | 31 |
| Lake Joyce (5.4–30.4 m) | 0.31–3.4 | 0.51*[3] | 15*[3] |
| Syowa Oasis*[4] | | | |
| Lake Nurume (0–15 m) | 2–30 | ND | — |
| Lake Hunazoko (0–7 m) | 103–186 | ND | — |
| Lake Suribati (0–29 m) | $10^1$–$10^2$ | ND | — |
| Thirty five fresh lakes | 1–2 | ND | — |
| Vestfold Oasis | | | |
| Ace Lake*[5] | >60 | ND | — |
| Deep Lake*[6] | 50 | ND | — |

*[1]: MATSUMOTO and HANYA (1977); MATSUMOTO *et al.* (1979, 1984).
*[2]: Unnamed pond.
*[3]: 30.4 m.
*[4]: TOMINAGA and FUKUI (1981); dissolved organic carbon.
*[5]: BURTON (1980).
*[6]: BARKER (1980).
ND: No datum.

values of 50 mgC/*l* in Deep Lake and up to 60 mgC/*l* in Ace Lake of the Vestfold Oasis have been reported by BARKER (1980) and BURTON (1980), respectively. BARKER (1980) considers that the TOC derived from both melt streams and lake itself, has accumulated due to the absence of significant microbial decomposition.

The EOC values are also remarkably different according to the sampling depths and locations (Table 1). The highest value is found in Home Lake as in the case of the TOC value. The percentages of the EOC to TOC values for water samples range from 3.4 to 30%, which are similar to those of the Tokyo area and the Ogasawara Islands (MATSUMOTO, 1980; MATSUMOTO and HANYA, 1981).

In general the concentrations of hydrocarbons are extremely low. Hydrocarbons are found in the bottom layers (60.4 and 65.9 m) of Lake Vanda and the surface waters of an unnamed pond (L-1) in the Labyrinth and Home Lake, Table 2 (MATSUMOTO *et al.*, 1978, 1979, 1984). Of special interest is the occurrence of 2,6-dimethylhexadecane and 2,6,10-trimethylhexadecane (tentatively identified) in the bottom water of Lake Vanda. Surprisingly, 2,6-dimethylhexadecane constituted 75% of the total hydrocarbons. Although their presence has not yet been reported for living organisms, they may arise from some microorganisms, though their hydrocarbon composition is not yet known, in the bottom water and surface sediment of the lake.

Normal, branched (iso and anteiso), and unsaturated fatty acids between carbon chain lengths $C_8$–$C_{32}$ have been found in Blue and Home Lakes of Ross Island, in the Onyx River, and in Lakes Vanda, Bonney, Fryxell and Joyce, together with the dominance of even-carbon numbers except for branched acids (MATSUMOTO and HANYA, 1977; MATSUMOTO *et al.*, 1978, 1979, 1984). The major fatty acids are $nC_{12}$, $nC_{14}$, $nC_{16}$, $nC_{18}$, and unsaturated-$C_{16}$ and -$C_{18}$. The total concentrations of the acids in the lakes of the dry valley areas range from 2.5 to 61 $\mu g/l$, which are considerably low, while the content of the acids in Home Lake is extremely high (1600 $\mu g/l$) as in the case of the TOC and EOC contents (Table 2).

Table 2. *Organic constituents found in lake, pond and stream waters from the McMurdo Oasis* ($\mu g/l$)*[1].

| Locality | Hydro-carbons*[2] | Fatty acids*[3] | Sterols*[4] | Phenolic acids*[5] |
|---|---|---|---|---|
| Blue Lake (surface) | LD | 5.9 | ND | 0.06 |
| Home Lake (surface) | 4.8 | 1600 | ND | 4.0 |
| Onyx River (surface) | LD | 4.6 | 0.1 | 0.05 |
| Lake Vanda (5.4–66 m) | 0.0–6.5 | 4.0–6.1 | 0.1–1.4 | LD–0.6 |
| L-1 pond (surface) | 0.22 | 7.1 | ND | LD |
| Lake Bonney, east lobe (5.4–33.5 m) | LD | 2.8–14 | ND | 0.07–7.6 |
| Lake Bonney, west lobe (5.4–30.4 m) | LD | 2.5–7.8 | ND | 0.06–12 |
| Lake Fryxell (18 m) | LD | 19 | ND | ND |
| Lake Joyce (30.4 m) | LD | 5.9 | ND | 0.1 |

*[1]: MATSUMOTO and HANYA (1977); MATSUMOTO *et al.* (1979, 1984).
*[2]: Normal, branched and unsaturated ($C_{15}$–$C_{34}$).
*[3]: Normal, branched and unsaturated ($C_8$–$C_{32}$).
*[4]: Cholesterol, 24-methylcholesta-5,22-dien-3$\beta$-ol, 24-methylcholesterol, 24-ethylcholesta-5,22-dien-3$\beta$-ol and 24-ethylcholesterol.
*[5]: *o*-, *m*- and *p*-Hydroxybenzoic, and vanillic acids.
LD: Less than detection limits.
ND: No datum.

Stenols, cholest-5-en-3$\beta$-ol (cholesterol, $C_{27}$), 24-methylcholesta-5,22-dien-3$\beta$-ol ($C_{28}$), 24-methylcholest-5-en-3$\beta$-ol (24-methylcholesterol, $C_{28}$), 24-ethylcholesta-5,22-dien-3$\beta$-ol ($C_{29}$) and 24-ethylcholest-5-en-3$\beta$-ol (24-ethylcholesterol, $C_{29}$) have been identified in water samples from Lake Vanda and the Onyx River, Table 2 (MATSUMOTO *et al.*, 1984). The total contents of stenols are considerably low ranging from 0.1 to 1.4 $\mu g/l$. The highest concentration is obtained in the lake bottom. Surprisingly the most dominant stenol is 24-ethylcholesterol, since it is usually not abundant in microorganisms and algae. Analytical results of epibenthic algae (mostly blue-green algae such as *Phormidium* spp.) from the dry valley areas have shown, however, that they are important sources of 24-ethylcholesterol (MATSUMOTO *et al.*, 1982a, 1983a, 1984).

$C_{29}$ sterols are abundant in vascular plants, whereas $C_{27}$ sterols are often dominant in planktons. Thus the $C_{29}/C_{27}$ sterol ratio has been believed to be indicator of both allochthonous and autochthonous contributions of organic materials for lakes and of terrigenous sources of organic materials in marine environments (HUANG and

MEINSCHEIN, 1976, 1979; NISHIMURA, 1977, 1978; ISHIWATARI *et al.*, 1980; CRANWELL and VOLKMAN, 1981). In the water of Lake Vanda, the $C_{29}/C_{27}$ sterol ratio is considerably high (1.1–5.3), comparable with that of lake sediments in the temperate zone (0.48–8.5, GASKELL and EGLINTON, 1976; NISHIMURA, 1977, 1978; HUANG and MEINSCHEIN, 1979; ISHIWATARI *et al.*, 1980), and that of lake and pond sediments in the dry valley areas (1.4–7.2, MATSUMOTO *et al.*, 1982a). These results indicate that the $C_{29}/C_{27}$ sterol ratio can not applied to the water of Lake Vanda as usual meaning.

*p*-Hydroxybenzoic, and/or *o*- and *p*-hydroxyphenylacetic acids have been identified, and *o*- and *m*-hydroxybenzoic, and vanillic acids are suggested to be present in water samples from Home Lake, and Lakes Vanda, Bonney and/or Joyce (MATSUMOTO *et al.*, 1978, 1979, 1984). Although their concentrations are generally low, the contents of *p*-hydroxybenzoic acid in the bottom waters of the east and west lobes of Lake Bonney are considerably high, 6.1 and 12 $\mu$g/*l*, respectively (MATSUMOTO *et al.*, 1979). The composition of the phenolic acids found in the water samples from the McMurdo Oasis is quite different from those of river and pond waters from the Tokyo area and the Ogasawara Islands in Japan (MATSUMOTO *et al.*, 1977; MATSUMOTO, 1980, 1982), in which a series of phenolic acids (*p*-hydroxybenzoic, vanillic, syringic, *p*-coumaric and ferulic acids) are found, but *o*- and *p*-hydroxyphenylacetic acids are not detected in both areas. The lack of syringic, *p*-coumaric and ferulic acids in the McMurdo Oasis must be attributable to the absence of vascular plants, since the wide occurrence of a series of phenolic acids in living organisms except for vascular plants is not known. Therefore, the dominance of *p*-hydroxybenzoic acid and the absence of syringic, *p*-coumaric and ferulic acids are, *vice versa*, believed to be an useful indicator for the absence of vascular plants in the environment (MATSUMOTO *et al.*, 1979, 1984).

## 3. Organic Constituents of Lake and Pond Sediments

Organic constituents of lake and pond sediments have been studied for the McMurdo, Syowa and Vestfold Oases. The concentrations of TOC, EOC and total nitrogen (TN) vary remarkably among the lakes and ponds, ranging from 0.18 to 190 mgC/g of dry sediment, 0.0015 to 11 mgC/g and from 0.021 to 21 mgN/g, respectively, reflecting presumably the differences of the distribution and activity of organisms in the lakes and ponds, Table 3 (MATSUMOTO *et al.*, 1978, 1979, 1981a, 1983a, b, 1984). Generally these concentrations are considerably lower than those in the Tokyo area and the Ogasawara Islands (MATSUMOTO, 1980, 1983). Extremely higher values are, however, found in the sediment sample from Lake Skallen Ôike of the Syowa Oasis. This sample is comprised mostly of algal materials. The EOC/TOC and TOC/TN values of the sediments from the McMurdo Oasis change considerably among the lake and ponds, but are similar to those of the Syowa and Vestfold Oases (Table 3).

Alkanes, alkenes and branched hydrocarbons in carbon chain lengths $C_{12}$–$C_{37}$ have been found in sediment samples from the oases, Table 4 (MATSUMOTO *et al.*, 1978, 1979, 1981a, 1983a, 1984). The major constituents of hydrocarbons are remarkably different among the lakes and ponds, reflecting probably the difference of

*Table 3. TOC, EOC and total nitrogen (TN) values for lake and pond sediments from the McMurdo, Syowa and Vestfold Oases.*

| Locality | TOC (mgC/g) | EOC (mgC/g) | TN (mgN/g) | EOC/TOC (%) | TOC/TN |
|---|---|---|---|---|---|
| McMurdo Oasis*[1] | | | | | |
| Home Lake | 41 | 4.2 | 11 | 10 | 3.7 |
| B-2 pond*[2] | 5.7 | ND | 0.62*[3] | ND | 9.2 |
| Lake Vanda | 1.9 | 0.077*[3] | 0.23*[3] | 4.1*[3] | 8.3*[3] |
| Don Juan Pond | 0.18 | 0.0015*[3] | 0.021*[3] | 0.83*[3] | 8.6*[3] |
| L-1 pond*[2] | 0.59 | 0.074 | 0.11 | 13 | 5.4 |
| L-4 pond*[2] | 0.94 | 0.044*[3] | 0.13*[3] | 4.7*[3] | 7.2*[3] |
| L-8 pond*[2] | 2.3 | ND | 0.25*[3] | ND | 9.2*[3] |
| L-9 pond*[2] | 1.7 | 0.065*[3] | 0.24*[3] | 3.8*[3] | 7.1*[3] |
| Lake Bonney, west lobe | 1.8 | 0.51 | 0.31 | 28 | 5.8 |
| Lake Fryxell | 17 | 0.83*[3] | 1.7*[3] | 4.9*[3] | 10*[3] |
| Lake Joyce | 4.1 | 0.46 | 0.63 | 11 | 6.5 |
| Syowa Oasis*[4] | | | | | |
| Lake Ô-ike | 24 | 2.5 | 2.7 | 10 | 8.9 |
| Lake Itiziku | 2.8 | 0.43 | 0.48 | 16 | 5.8 |
| Lake Nurume | 14 | 1.6 | 2.3 | 12 | 6.1 |
| Lake Hunazoko | 3.8 | 1.1 | 0.75 | 29 | 5.1 |
| Lake Skallen Ôike | 190 | 11 | 21 | 5.9 | 9.0 |
| Vestfold Oasis*[4] | | | | | |
| Deep Lake | 4.6 | 0.47 | 0.99 | 10 | 4.6 |

*[1]: MATSUMOTO *et al.* (1979, 1983b, 1984).
*[2]: Unnamed ponds
*[3]: MATSUMOTO *et al.* (unpublished results).
*[4]: MATSUMOTO (1980); MATSUMOTO *et al.* (1981a, 1983a).
ND: No datum.

dominant lake and pond organisms. Isoprenoid alkanes ($C_{18}$, $C_{19}$ and $C_{20}$) are the major constituents in Lakes Itiziku and Hunazoko in the Syowa Oasis and Deep Lake in the Vestfold Oasis (MATSUMOTO *et al.*, 1981a, 1983a). 2,6-Dimethylhexadecane and 2,6,10-trimethylhexadecane (tentatively identified) are also found in the sediment sample from Lake Vanda as in the case of the bottom water sample (MATSUMOTO *et al.*, 1979, 1984). The total concentrations of hydrocarbons range from 0.0015 to 32 $\mu$g/g, which are generally fairly lower than those of polluted areas in the mid and lower latitudes (MATSUMOTO *et al.*, 1979; MATSUMOTO, 1980, 1983).

Saturated, unsaturated and branched (iso and anteiso) fatty acids in carbon chain lengths $C_8$–$C_{34}$ have been detected in the sediment samples from the oases, along with the abundance of even-carbon numbered short-chain acids ($<C_{20}$) as in the case of the water samples from the McMurdo Oasis, Table 4 (MATSUMOTO *et al.*, 1978, 1979, 1981a, 1984). Of special interest is the occurrence of long-chain *n*-alkanoic acids ($nC_{24}$ and $nC_{26}$) as the major constituents from Lakes Ô-ike, Itiziku and Skallen Ôike of the Syowa Oasis, although their source materials are not clear (MATSUMOTO *et al.*, 1981a). The total concentrations of the acids differ remarkably among the sediment samples, ranging from 0.071 to 2000 $\mu$g/g. The lowest value is found in the Don Juan Pond, while the higher values are detected in Home Lake and Lake

*Table 4. Concentrations of organic constituents found in lake and pond sediments from the McMurdo, Syowa and Vestfold Oases (μg/g).*

| Locality | Hydro-carbons*[1] | Fatty acids*[2] | Sterols | | β-Hydroxy acids*[5] | Phenolic acids*[6] |
|---|---|---|---|---|---|---|
| | | | Stenols*[3] | Stanols*[4] | | |
| McMurdo Oasis | | | | | | |
| Home Lake | 40 | 2000 | ND | ND | ND | 2.3 |
| Lake Vanda | 7.4 | 15 | 4.1 | 0.0 | 2.0 | LD |
| Don Juan Pond | 0.0015*[7] | 0.071*[7] | 0.11 | 0.016 | ND | LD*[7] |
| L-1 pond | 1.1 | 64 | ND | ND | ND | 0.054 |
| L-4 pond | 0.016*[7] | 4.0*[7] | 1.7 | 0.47 | ND | 0.028*[7] |
| L-8 pond | 0.0020*[7] | 5.3*[7] | 1.5 | 0.42 | ND | 0.094*[7] |
| Lake Bonney, west lobe | 5.2 | 140 | 8.2 | 0.075 | 6.2 | 0.18 |
| Lake Fryxell | 1.3*[7] | 350*[7] | 19 | 7.0 | 53 | ND |
| Lake Joyce | 0.51 | 94 | 16 | 0.73 | 9.8 | 0.26 |
| Syowa Oasis | | | | | | |
| Lake Ô-ike | 13 | 240 | 0.67 | ND | ND | 1.8 |
| Lake Itiziku | 2.9 | 27 | 0.079 | ND | ND | 2.7 |
| Lake Nurume | 0.72 | 300 | 3.8 | ND | ND | 1.5 |
| Lake Hunazoko | 0.38 | 120 | 1.0 | ND | ND | 0.76 |
| Lake Skallen Ôike | 32 | 1900 | 9.0 | ND | ND | 7.6 |
| Vestfold Oasis | | | | | | |
| Deep Lake | 1.5 | 120 | 3.6 | ND | ND | 0.01 |

*[1]: Normal, branched and unsaturated ($C_{12}$–$C_{37}$); MATSUMOTO *et al.* (1978, 1979, 1981a, 1984).
*[2]: Normal, branched and unsaturated ($C_8$–$C_{34}$); MATSUMOTO *et al.* (1978, 1979, 1981a, 1984).
*[3]: Cholesta-5,22-dien-3β-ol, cholesterol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesterol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholesterol. MATSUMOTO *et al.* (1982a, 1983a, 1984).
*[4]: 5α-cholestan-3β-ol, 24-methyl-5α-cholestan-3β-ol and 24-ethyl-5α-cholestan-3β-ol. MATSUMOTO *et al.* (1982a, 1983a, 1984).
*[5]: Normal, branched and unsaturated ($C_8$–$C_{26}$). MATSUMOTO *et al.* (1982b, 1983c).
*[6]: *o*-, *m*- and *p*-Hydroxybenzoic, *p*-hydroxyphenylacetic and vanillic acids. MATSUMOTO (1980), MATSUMOTO *et al.* (1978, 1979, 1981a, 1984).
*[7]: MATSUMOTO *et al.* (unpublished results).
ND: No datum.
LD: Less than detection limits.

Skallen Ôike, Table 4 (MATSUMOTO *et al.*, 1979, 1981a, 1984).

Stenols, cholesta-5,22-dien-3β-ol ($C_{27}$), cholesterol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesterol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholesterol and stanols, 5α-cholestan-3β-ol ($C_{27}$), 24-methyl-5α-cholestan-3β-ol ($C_{28}$) and 24-ethyl-5α-cholestan-3β-ol ($C_{29}$) have been identified in sediment samples from the McMurdo Oasis, Table 4 (MATSUMOTO *et al.*, 1982a, 1984). These stenols are also found in sediment samples from the Syowa and Vestfold Oases (MATSUMOTO *et al.*, 1983a). The total concentrations of stenols and stanols found in the sediment samples from the McMurdo Oasis range from 0.11 to 19 and 0.0 to 7.0 μg/g, respectively, Table 4 (MATSUMOTO *et al.*, 1982a). The amounts of sterols in the sediment samples from the Don Juan Pond of the McMurdo Oasis and Lake Itiziku from the Syowa

Oasis are extremely low, while those of Lakes Fryxell and Joyce are considerably higher. The ratios of sterol carbon to the TOC contents of the McMurdo Oasis differ considerably, ranging from 0.26 to $3.9\times10^{-3}$, comparable with those of contemporary lake sediments in the temperate zone, $0.27\text{–}5.2\times10^{-3}$ (NISHIMURA, 1977, 1978; ISHIWATARI *et al.*, 1980), but appreciably higher than those of the Syowa and Vestfold Oases, $0.023\text{–}0.66\times10^{-3}$ (MATSUMOTO *et al.*, 1983a). This is presumably attributed to differences of source materials as suggested by the organic composition.

Unusually the most dominant sterol in the McMurdo Oasis is 24-ethylcholesterol as in the case of water samples from Lake Vanda noted before. It is also found in the sediment samples from Lakes Ô-ike, Itiziku and Skallen Ôike (MATSUMOTO *et al.*, 1983a). Thus the $C_{29}/C_{27}$ sterol ratio for these sediment samples is considerably high (1.2–7.2), and comparable with that of lake sediments in the temperate zone (0.48–8.5) as discussed before. These results indicate that the $C_{29}/C_{27}$ ratio is not a good ecological marker for Antarctic lake sediments as usual meaning as in the case of waters from Lake Vanda, although they are used as an indicator of the relative contribution of vascular plants and planktons in lake and marine environments in mid and lower latitudes (MATSUMOTO *et al.*, 1983a).

$\alpha$-, $\beta$- and $\omega$-1-Hydroxy acids in carbon chain lengths $C_8$–$C_{28}$ have been detected in the sediment samples and epibenthic algae (mostly blue-green algae) from the dry valley areas of the McMurdo Oasis (MATSUMOTO *et al.*, 1982b, 1983c). The major constituents are generally short- ($<C_{20}$) and long- ($\geqq C_{20}$) chain normal and branched (iso and anteiso) $\alpha$-hydroxy acids, short-chain normal and branched $\beta$-hydroxy acids (except for Lake Vanda), and long-chain ($C_{24}$, $C_{26}$ and $C_{28}$) $\omega$-1-hydroxy acids. The total concentrations of $\beta$-hydroxy acids ranging from 0.66 to 53 $\mu$g/g are reported for the lakes of the McMurdo Oasis, Table 4 (MATSUMOTO *et al.*, 1983c).

*m*- and *p*-Hydroxybenzoic, *o*- and *p*-hydroxyphenylacetic acids have been identified and *o*-hydroxybenzoic and vanillic acids are indicated to be present in the sediment samples from the McMurdo Oasis (MATSUMOTO *et al.*, 1978, 1979). *o*-, *m*- and *p*-Hydroxybenzoic and vanillic acids are also detected in the sediment samples from the Syowa and Vestfold Oases (MATSUMOTO, 1980; MATSUMOTO *et al.*, 1981a). Although a little is known on the occurrence of these phenolic acids in organisms and their metabolites other than vascular plants, microorganisms including fungi and bacteria, and algae, which are widely distributed in the areas studied, are believed to be the important sources of these phenolic acids (MATSUMOTO *et al.*, 1979, 1981a).

The features of the phenolic acids in the sediment samples from the oases are quite different from those of sediments from the Tokyo area and the Ogasawara Islands (MATSUMOTO, 1980; MATSUMOTO and HANYA, 1980) as in the case of water samples described before, reflecting the absence of vascular plants in the areas studied. Again it indicates, *vice versa*, that the presence of a series of phenolic acids is an important indicator of the contribution of vascular plants in natural environment.

## 4. Organic Constituents in Soil

Little is known on the organic constituents in the Antarctic soil. The concentrations of TOC and TN in soils of the dry valley areas of the McMurdo Oasis are

*Table 5. TOC and TN values for soils from the dry valley areas of the McMurdo Oasis.*

| | TOC*1 (mgC/g) | TN*2 (mgN/g) | TOC/TN*3 |
|---|---|---|---|
| Range | 0.037–3.2 | 0.00–0.34 | 0.093–24 |
| Average±90% confidence limits | 0.64±0.35 | 0.13±0.071 | 7.0±2.5 |

*1: MATSUMOTO *et al.* (1979, 1983b). $n=18$.
*2: MATSUMOTO *et al.* (unpublished results). $n=18$.
*3: MATSUMOTO *et al.* (unpublished results). $n=17$.

generally extremely low ranging from 0.037 to 3.2 mgC/g of dry soil with an average of 0.64±0.35 mgC/g at 90% confidence limits and from 0.00 to 0.34 mgN/g with an average of 0.13±0.071 mgN/g, respectively, Table 5 (MATSUMOTO *et al.*, 1979, 1983b). They reflect that organic carbon sources are highly restricted there. The TOC/TN ratio also differs remarkably among the samples. This may be due to the contribution of inorganic nitrogen, since higher concentrations of inorganic nitrogen have been found in the dry valley areas (TORII *et al.*, 1975).

Normal alkanes ($nC_{15}$–$nC_{35}$) with the dominance of $nC_{23}$, $nC_{25}$, $nC_{27}$ and $nC_{29}$ are found in two soil samples from the dry valley areas, although their concentrations are extremely low, 0.046 and 0.014 μg/g (MATSUMOTO *et al.*, 1979).

The total fatty acid contents in soils are fairly low, ranging from 0.16 to 3.7 μg/g, reflecting presumably low organic carbon contents, Table 6 (MATSUMOTO *et al.*, 1981b). Normal alkanoic acids ranging from $C_8$–$C_{40}$ are found with a bimodal distribution maximized at $C_{16}$ and $C_{28}$, together with branched (iso and anteiso) and unsaturated acids (Fig. 3). As far as we know, this is the first report of the occurrence of such long-chain *n*-alkanoic acids ($>C_{38}$) in soils and modern and ancient sediments. Surprisingly, long-chain *n*-alkanoic acids constituted most of the fatty acids, ranging from 30.2 to 81.9% with an average of 53.8±18.7% at 90% confidence limits, with a small even-carbon predominance (Table 6). Thus the ratios of long- to short-chain *n*-alkanoic acids are very high (2.7±1.7) and comparable to the value estimated for a forest soil (2.3) (MATSUDA and KOYAMA, 1977). The carbon preference indices, $CPI_{AL}$, $CPI_{AH}$ and $CPI_{AT}$, calculated over the ranges $C_{13}$–$C_{19}$, $C_{19}$–$C_{33}$ and $C_{13}$–$C_{33}$ according to KVENVOLDEN (1966), range from 4.5 to 13, 1.4 to 3.6 and 1.7 to 5.7, respectively. In general, these values are lower than those in common biological materials. In particular, $CPI_{AH}$ values of the three Bonney samples are extremely low, and are thought to be the smallest values ever reported for soils, although $CPI_A$ values close to unity have been found in some sedimentary rocks and shales (KVENVOLDEN, 1966, 1967, 1970). However, long-chain *n*-alkanoic acids with small $CPI_A$ values, which make up a high proportion of the fatty acids are not found in lake waters, sediments and epibenthic algae (mostly *Oscillatoria* spp., *Phormidium* spp. and *Calothrix* spp.) from the dry valley areas (MATSUMOTO and HANYA, 1977; MATSUMOTO *et al.*, 1978, 1979, unpublished results). Glacial erosion of sedimentary rocks containing organic materials may have contributed to long-chain *n*-alkanoic acids, since it is well known that the Beacon sandstone of Jurassic to Silurian (?) age, composed of sandstone, siltstone, conglomerate and carbonaceous beds, and including various fossils such as coal and silicified wood, is widely distributed in the dry valley

*Table 6. Fatty acids found in soils collected from the dry valley areas of Victoria Land in Antarctica*[*1].*

| Locality | Range | Max. at carbon number[*2] | Conc. (μg/g) | Composition (%) | | | | Long[*4] / Short[*3] | $CPI^{*7}_{AL}$ | $CPI^{*7}_{AH}$ | $CPI^{*7}_{AT}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Short[*3] | Long[*4] | Branched[*5] | Unsaturated[*6] | | | | |
| Wright Valley | | | | | | | | | | | |
| Vanda-1 | $C_{10}$–$C_{32}$ | $\underline{C_{16}}$, $C_{24}$ | 3.7 | 31.1 | 31.6 | 5.4 | 31.9 | 1.0 | 13 | 3.6 | 5.7 |
| Vanda-2 | $C_8$–$C_{34}$ | $\underline{C_{16}}$, $C_{28}$ | 2.4 | 30.4 | 46.7 | 9.4 | 13.5 | 1.5 | 7.8 | 3.2 | 4.3 |
| Taylor Valley | | | | | | | | | | | |
| Bonney, east lobe | $C_8$–$C_{40}$ | $C_{16}$, $\underline{C_{28}}$ | 0.94 | 17.1 | 52.2 | 5.8 | 24.9 | 3.1 | 6.1 | 1.7 | 2.2 |
| Bonney, west lobe-1 | $C_8$–$C_{40}$ | $C_{16}$, $\underline{C_{28}}$ | 0.43 | 16.7 | 80.2 | 1.3 | 1.8 | 4.8 | 4.8 | 1.4 | 1.7 |
| Bonney, west lobe-2 | $C_8$–$C_{37}$ | $C_{16}$, $\underline{C_{28}}$ | 0.91 | 15.5 | 81.9 | 1.4 | 1.2 | 5.3 | 4.5 | 1.5 | 1.8 |
| Pearse Valley | | | | | | | | | | | |
| Joyce | $C_8$–$C_{35}$ | $\underline{C_{16}}$, $C_{28}$ | 0.16 | 56.1 | 30.2 | 9.0 | 4.7 | 0.54 | 5.3 | 1.5 | 3.1 |
| Average, 90% confidence limits | | | 1.4 ±1.1 | 27.8 ±12.8 | 53.8 ±18.7 | 5.4 ±2.9 | 13.0 ±10.6 | 2.7 ±1.7 | 6.9 ±2.6 | 2.2 ±0.81 | 3.1 ±1.3 |

*1: MATSUMOTO *et al.* (1981b).
*2: The major distribution maximum is underlined.
*3: Short-chain *n*-alkanoic acids ($C_{13}$–$C_{19}$).
*4: Long-chain *n*-alkanoic acids ($\geq C_{20}$).
*5: Branched acids (iso and anteiso-$C_{13}$–$C_{17}$).
*6: Unsaturated acids ($C_{16}$ and $C_{18}$).
*7: Carbon preference indices; $CPI_{AL}$, $CPI_{AH}$ and $CPI_{AT}$ values were calculated from the carbon chain lengths $C_{13}$–$C_{19}$, $C_{19}$–$C_{33}$, and $C_{13}$–$C_{33}$, respectively.

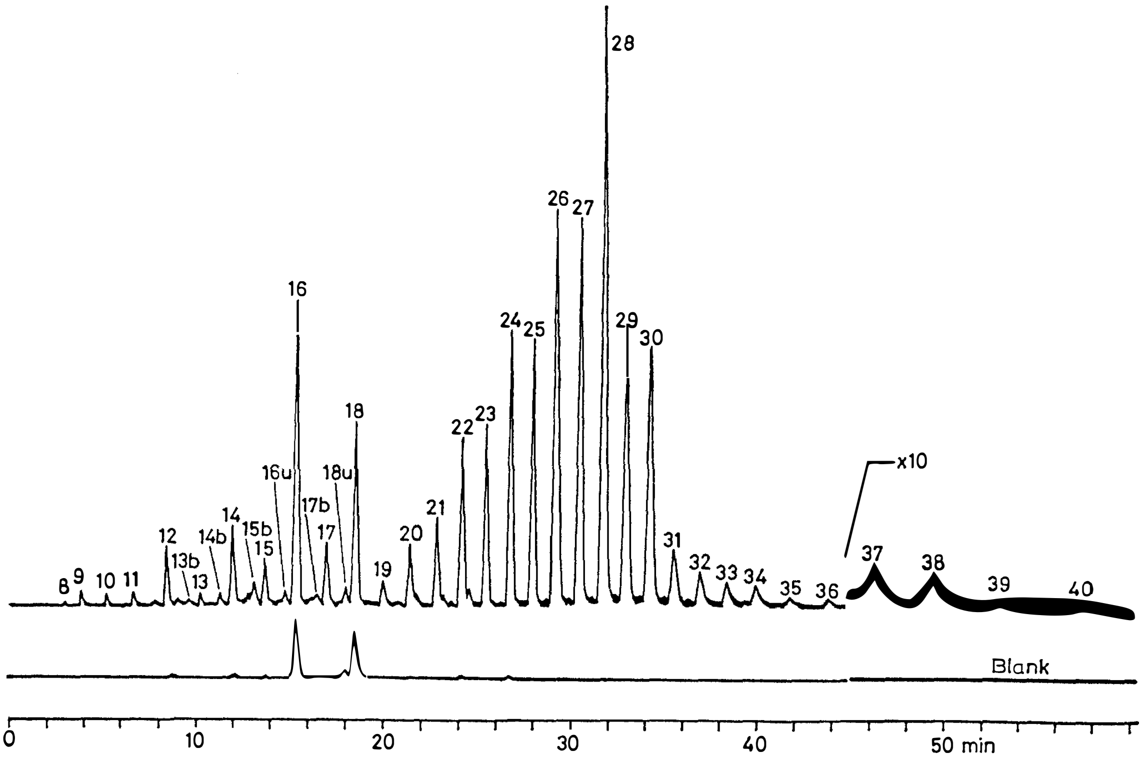


*Fig. 3. Mass fragmentogram (m/z 74) of the fatty acid fraction obtained from soil sample collected from the dry valley areas of the McMurdo Oasis (Bonney, west lobe-1). MATSUMOTO et al. (1981a). Arabic figures at the peaks indicate the carbon chain length of fatty acids. 13b, 14b, 15b and 17b are branched (iso and anteiso) $C_{13}$, $C_{14}$, $C_{15}$ and $C_{17}$ acids, respectively. 16u and 18u are unsaturated-$C_{16}$ and -$C_{18}$ acids, respectively.*

areas (WARREN and GUNN, 1961), as long-chain *n*-alkanoic acids having small $CPI_A$ values, and high long/short chain ratios have been found in sedimentary rocks and shales of Palaeozoic to Cenozoic age from the United States (KVENVOLDEN, 1966, 1967, 1970). Much of the sedimentary organic carbon in the Ross Sea is reported to be derived from the rocks being eroded by glaciers on the Antarctic continent (SACKETT *et al.*, 1974). It is therefore likely that the long-chain *n*-alkanoic acids found in the Antarctic soils come from the Beacon sandstone (MATSUMOTO *et al.*, 1981b). Further studies on the distribution of fatty acids in the Beacon sandstone should be fruitful.

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