

## GEOCHEMICAL MONITORING OF ANTARCTIC LAKES AND THEIR ECOSYSTEMS

Genki I. MATSUMOTO

*Department of Environmental Information Science, School of Social Information Studies, Otsuma Women's University, 7-1, Karakida 2-chome, Tama-shi, Tokyo 206*

**Abstract:** The monitoring of climatic changes, water quality, human activity, biomass, biological composition and biological activity in Antarctic lakes and their ecosystems is discussed from a geochemical viewpoint. The changes in lake water levels, ice thickness and the periods of total melting and freezing of lake ice probably reflect climatic changes at the lake sites. Temperature, electric conductivity, pH, dissolved oxygen and redox potential in lake waters could be monitored continuously. Total organic carbon and petroleum-derived hydrocarbons (such as gasoline, diesel fuels and lubricating oils) could be reflecting human activity in Antarctic lakes near research stations. Chlorophyll-*a* and/or fatty acid concentrations in lake waters may be useful as markers of biomass. Direct microbial observation by naked eye and/or microscope, culture of organisms, and measurement of biomarkers such as hydrocarbons, fatty acids and sterols are important to monitor biological composition in the lake. Also, 16S rRNA profile may be a useful marker of biological composition. Uptake of  $^{14}\text{C}$  labeled compounds and/or DNA synthesis probably reflect biological activity. Normal alkenoic acid/*n*-alkanoic acid ratios may reflect the degree of degradation of organic matter in the lake. *Trans/cis*- $\text{C}_{16:1}$  alkenoic acid ratios could be used as a starvation or stress lipid index in natural environments.

### 1. Introduction

Although Antarctica is the coldest continent in the world, and covered with a thick ice-sheet, ice-free areas, so-called "oases", are distributed in the coastal regions and inland mountains of Antarctica. SIMONOV (1971) reported 16 oases in Antarctica (Fig. 1). Many lakes and ponds, with various salt contents ranging from near pure meltwater to 13 times greater than seawater are scattered in the oases (*e.g.*, TORII and YAMAGATA, 1981; MATSUMOTO *et al.*, 1992).

Antarctic lakes may serve as sensitive indicators of environmental changes, especially climatic changes, because summer temperatures of Antarctic lakes are close to the freezing point of water, so small changes in climate are expected to correspond to a large difference in lake water level and ice thickness (CHINN, 1982; MCKAY *et al.*, 1985; WHARTON *et al.*, 1992). Also, the periods of total melting and freezing of lake ice are considered to reflect climatic changes. Climatic changes may have great influence on Antarctic lakes and their ecosystems.

Antarctica is characterized by special daylight conditions, *i.e.* half year day

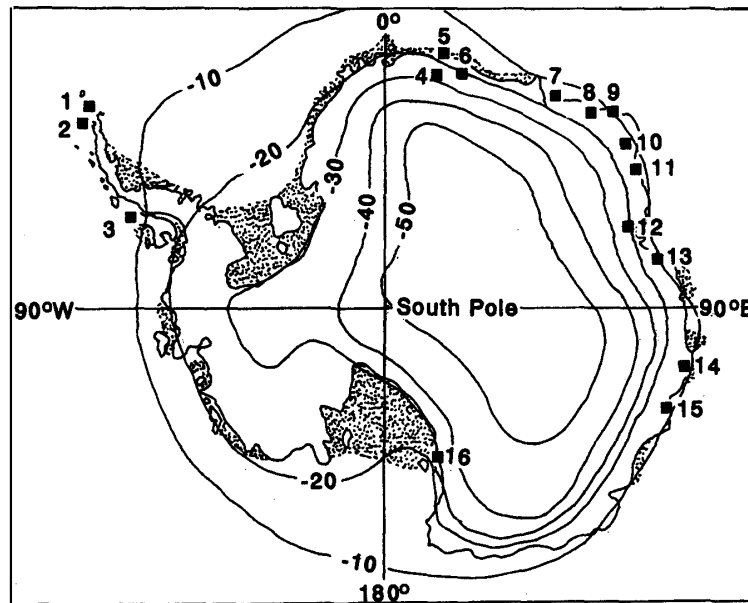


Fig. 1. Oases (SIMONOV, 1971) and mean annual surface air temperatures (NATIONAL WEATHER RECORDS CENTER and WEYANT, 1967) in Antarctica. Oases: 1; Snow Hill. 2; Bellingshausen. 3; Alexander. 4; Zimmermann. 5; Shirmacher. 6; Insel. 7; Syowa. 8; Molodezhnaya. 9; Thule. 10; Øygarden. 11; Stefansson. 12; Amery. 13; Vestfold Hills. 14; Bunger. 15; Greason. 16; McMurdo.

and half year night. Thus, biological activity on the continent is extremely limited. Only cryptogamic organisms are distributed throughout the continent, except in the northern part of the Antarctic Peninsula where vascular plants occur (GREENE *et al.*, 1967). Antarctic lake ecosystems lack higher organisms, and are thought to be simple and labile. These ecosystems can be expected to sensitively reflect environmental changes.

Antarctica lies well beyond the immediate influence of human activity and direct anthropogenic inputs are likely to be negligible. Human activity is also likely to be minimal in this environment. However, the areas around the research stations are thought to be contaminated by human activity.

I will discuss here several geochemical indicators for the monitoring of Antarctic lakes and their ecosystems to estimate climatic changes, water quality, influence of human activity, biomass, biological composition and biological activity.

## 2. Climatic Changes

### 2.1. Lake water level

Generally, Antarctic saline lakes are meromictic and have no outflows (*e.g.*, MATSUMOTO *et al.*, 1992). Thus, lake water level is balanced with the amounts of glacial and snow meltwater supply, and evaporation and/or ablation loss. The increase of lake water level may be largely attributed to the increase of mean annual air temperature, especially in the austral summer, rather than to wet climatic conditions. Because summer temperatures in the oases are around the

freezing point of water, a small increase of temperature ( $>0^{\circ}\text{C}$ ) produces a large quantity of meltwater, whereas a small decrease in temperature ( $<0^{\circ}\text{C}$ ) results in no meltwater (MATSUMOTO, 1993).

Lake Vanda in the Wright Valley of the McMurdo Oasis is a typical meromictic lake, and the bottom layers are strongly density stratified (Fig. 2). WILSON (1964) explained that the lake in the past was almost dried at about 1200 YBP, followed by water supply mainly through the Onyx River, and finally reached the present lake water level. On the other hand, a number of paleolake shorelines are observed in the valley walls of the Lake Vanda basin up to approximately 150 m above the present lake water level (Fig. 3; CHINN, 1993). Carbon-14 dating of dead algae shows that the paleolake shorelines were formed during 1300–2900 years in the past, and reveal that lake water levels fluctuated greatly (YOSHIDA *et al.*, 1975).

Generally, lake water levels in the McMurdo Oasis have been rising due to the increase of the supply of glacial and snow meltwaters, suggesting that there

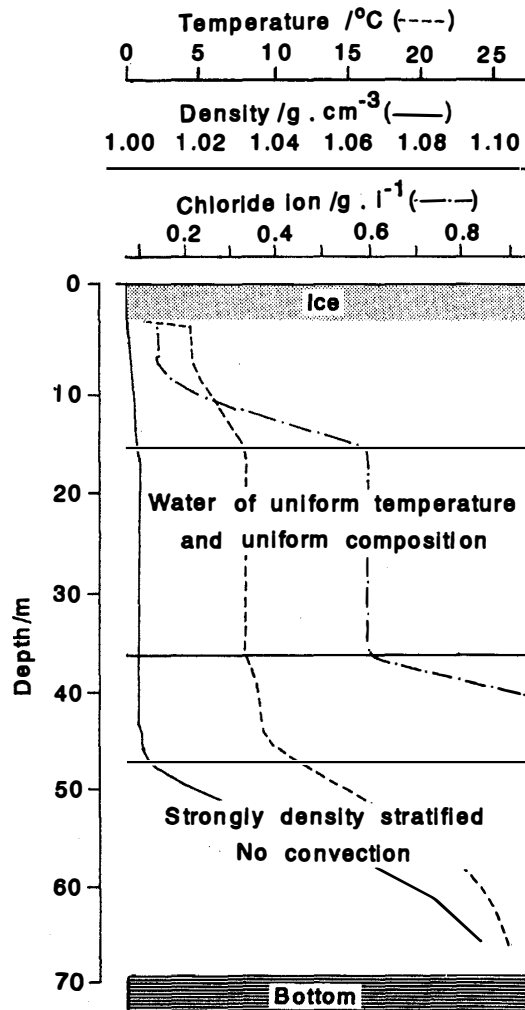


Fig. 2. Stratification of lake waters in Lake Vanda of the Wright Valley, McMurdo Oasis (data from WILSON, 1964).

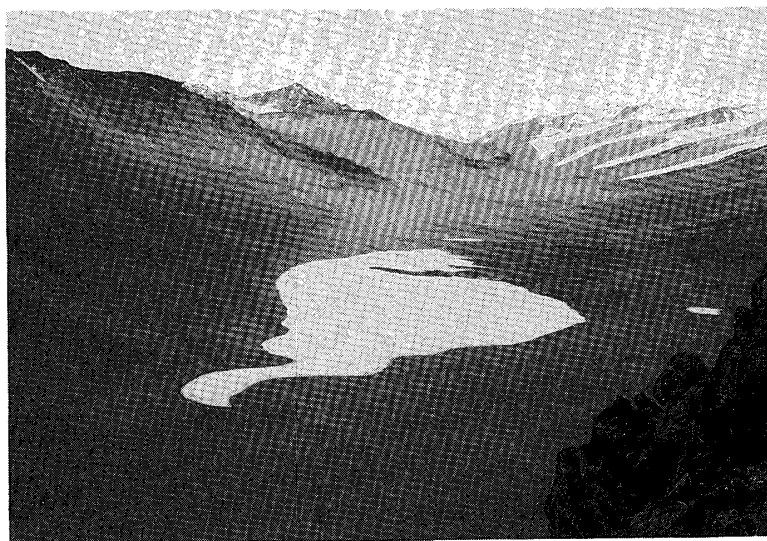


Fig. 3. Paleolake shorelines in the Lake Vanda basin of the Wright Valley.

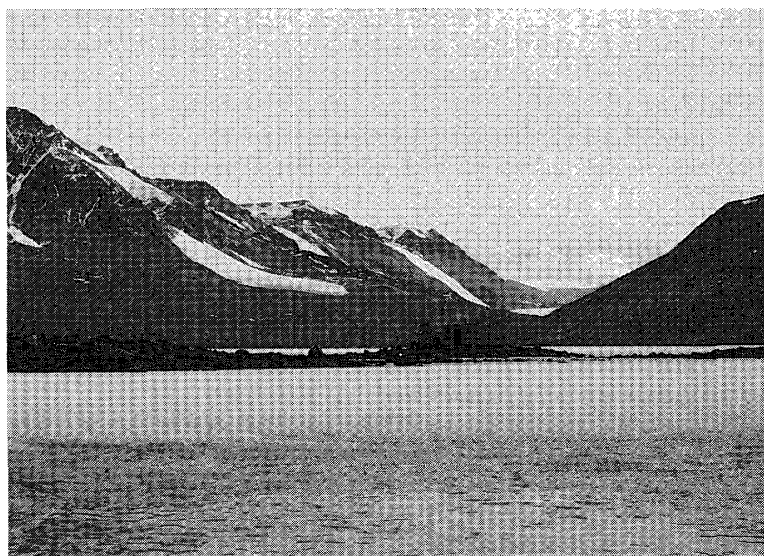


Fig. 4. Bonney Hut (U.S.A.) of Lake Bonney in the Taylor Valley, in December of 1976.

may have been warming in this region over the past two decades (CHINN, 1982). He observed that Lake Hoare in the Taylor Valley of the McMurdo Oasis rose at an average rate of 9 cm/year between January 1972 and January 1980. Also, water levels of Lake Bonney in the Taylor Valley and Lake Vanda in the Wright Valley strikingly increased. Figure 4 shows Bonney Hut (U.S.A.) in the Bonney basin, in December of 1976, but now this site is covered with water due to the rise of lake water level.

Lake and pond water levels have repeatedly varied due to climatic changes: Lake water level decreases in cold periods but increases in warm periods. Also, the fluctuation of lake and pond water level is important in the formation of meromictic lakes (e.g., MATSUMOTO *et al.*, 1992). Hence, the monitoring of lake water level is important to estimate global and/or local climatic changes.

## 2.2. Ice thickness

The occurrence of perennial lake ice depends on mean annual air temperatures at the lake sites. The boundary of the presence and absence of perennial lake ice is considered to correspond to a mean annual air temperature of approximately  $-20^{\circ}\text{C}$ . The  $-20^{\circ}\text{C}$  isotherm lies roughly inside the coast line in Antarctica (Fig. 1; NATIONAL WEATHER RECORDS CENTER and WEYANT, 1967). The mean annual air temperature at Vanda Station of the McMurdo Oasis is about  $-20^{\circ}\text{C}$  (e.g., CLOW *et al.*, 1988). Generally, deep lakes and ponds in the McMurdo Oasis have perennial ice cover. Ice thickness changes considerably in response to air temperature changes. WHARTON *et al.* (1992) reported results of 10 years of ice thickness measurements at perennially ice-covered Lake Hoare (Fig. 5). The ice-cover of the lake had been thinning steadily at a rate exceeding 20 cm/y but seems to have recently stabilized at a thickness of 3.3 m. They suggest that thinning of the ice-cover is due to the increase of summer melting. Thus, monitoring of ice thickness is also important to estimate climatic changes.

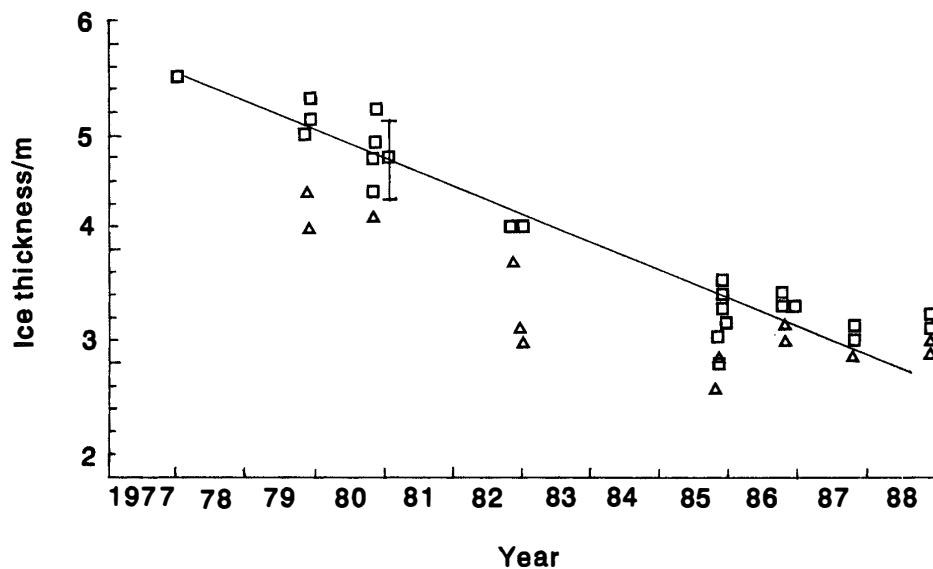


Fig. 5. Changes in the total (squares) and piezometric (triangles) ice thickness of the ice cover in Lake Hoare of the Taylor Valley (data from WHARTON *et al.*, 1992). The solid line is a best fit to the data (1978–1988) and has a slope of 22.5 cm/y.

## 2.3. Periods of melting and freezing of winter-over lake ice

Generally, lakes and ponds in the Syowa Oasis have no perennial ice cover. The mean annual air temperature of this region is  $-10.5^{\circ}\text{C}$ , recorded at Syowa Station, although mean air temperature in January is  $-0.7^{\circ}\text{C}$  (NATIONAL INSTITUTE POLAR RESEARCH, 1985). In this case, the periods of total melting and start of freezing of winter-over lake ice can be used as an important indicator of climatic changes.

### 3. Lake Water Chemistry

Water temperature, electric conductivity, pH, dissolved oxygen (DO) and redox potential in lakes and ponds could be monitored continuously by instrumental methods. Redox potential and dissolved oxygen contents reflect meromictic conditions as well as microbial activity in the lakes. Stable isotopic ratios ( $\delta D$  and  $\delta^{18}O$ ), major ionic components (Na, K, Ca, Mg, Cl and  $SO_4$ ) and trace metals are important indicators of water and salt sources (TORII and YAMAGATA, 1981; MASUDA *et al.*, 1982; TAKAMATSU *et al.*, 1988; MATSUMOTO *et al.*, 1992).

During 1967–1985, pH, DO, major ionic components and nutrients ( $NO_2$ -N,  $NO_3$ -N,  $NH_4$ -N,  $PO_4$ -P and  $SiO_2$ -Si) in Mizukumi Stream (East Ongul Island), Lake Ô-ike (West Ongul Island), Lake Nurume (Langhovde), Lake Hunazoko (Skarvsnes) and/or Lake Skallen Ôike (Skallen) in the Syowa Oasis were monitored by JARE members from the viewpoint of environmental geochemistry (*e.g.*, MURAYAMA *et al.*, 1981, 1984). Although these values varied considerably, no systematic changes in the lake water chemistry were observed, except for Lake Hunazoko in which their changes were relatively small.

### 4. Human Activity

It is well known that an ozone hole due to destruction of the ozone layer by fluorocarbons has been observed in Antarctica since 1982. Organochlorine residues, such as DDT, HCB and PCB (PETERLE, 1969; PEEL, 1975), heavy metals such as lead (MUROZUMI *et al.*, 1969) and mercury (YOSHIDA and MUROZUMI, 1977) are found in the Antarctic ice-sheet. Also, Antarctic ice cores reveal a marked near-surface increase in nitrate concentrations (MAYEWSKI and LEGRAND, 1990). These results indicate that even the remote Antarctic region is sensitive to the global emission of pollutants by industry, biomass burning and/or other human activities. Aside from these global pollutants, research activity in Antarctica uses various kinds of living and life support materials, and discharges several gaseous, liquid (sewage) and solid wastes. Especially, liquid wastes contain organic pollutants, and so the measurements of total organic carbon (TOC) in

Table 1. Features of petroleum derived and recently biologically derived hydrocarbons

	Petroleum	Biological*
Odd/even <i>n</i> -alkane ratio	Close to 1	High
Unresolved complex mixture of hydrocarbons	Abundant	Not common
$\alpha\beta/\beta\beta$ Hopane ratio	High	Low
(22S/22R)- $C_{31}$		
Homohopane ratio	1.0–1.5	Close to 0
(20S/20R)- $C_{29}$ Sterane ratio	0.5–1.2	Close to 0

\*Often  $C_{31}$  homohopanes and/or  $C_{29}$  steranes are absent.

water bodies receiving liquid waste effluents may be useful for the monitoring of water pollution.

Petroleum-derived hydrocarbons (gasoline, diesel fuels and lubricating oils, etc.) are widely used at all Antarctic research stations, and are believed to be suitable markers of human activity. Petroleum-derived hydrocarbons are complex, composed of various acyclic and cyclic isomers, whereas hydrocarbons directly produced by living organisms are generally simple. They are much different from each other. Some geochemical features of petroleum-derived and recently biologically derived hydrocarbons are summarized in Table 1. Usually, the odd/even *n*-alkane ratios in petroleum-derived hydrocarbons are close to unity. In contrast, normal alkanes of biological materials are characterized by a predominance of odd-carbon numbers, and thus the odd/even *n*-alkane ratios are much higher than unity. Unresolved complex mixture of hydrocarbons (hump) is abundant in petroleums, but is not common in biological materials (*e.g.*, MATSUMOTO, 1982). Triterpanes and steranes in petroleum-derived hydrocarbons are thermally mature, and thus the  $\alpha\beta/\beta\beta$ -hopane ratios are very high. Also, the (22S/22R)-C<sub>31</sub> homohopane ratios and (20S/20R)-C<sub>29</sub> sterane ratios are close to equilibrium values of 1.5 and 1.2, respectively (MACKENZIE *et al.*, 1982; PHILP, 1985). In contrast, triterpenes, such as hop-22(29)-ene are often major components of pentacyclic hydrocarbons in Antarctic algal and cyanobacterial mats, and some modern lake sediments. Also, recently biologically derived triterpanes are not mature, thus the  $\alpha\beta/\beta\beta$ -hopane and (22S/22R)-C<sub>31</sub> homohopane ratios, and (20S/20R)-C<sub>29</sub> sterane ratios, are expected to be close to zero, or these compounds are absent (MATSUMOTO *et al.*, 1994). However, in the actual application of these biomarkers, we have to consider the influence of certain sedimentary rocks (*e.g.*, Beacon Supergroup of Gondwanaland sediment), because they contain hydrocarbons similar to those of petroleums (MATSUMOTO *et al.*, 1987a).

## 5. Biomass

The direct observation of organisms by naked eye and/or microscope is the first step to estimate microbial biomass in a lake. Vertical distributions of bacterial population, cell size and cell volume in Lake Vanda have been determined by an acridine orange direct count method with an epifluorescence microscope (TAKII *et al.*, 1986; KONDA *et al.*, 1987). Generally, bacterial population in the bottom anoxic water layer in the lake (60–69 m bottom) is much higher than that in the upper and middle water layers (5–60 m), while cell size in the bottom water layer is small. Also, the bacterial population has been determined by epifluorescence microscopy with regard to different cell size classes and its variability in soils from Wilkes Land, Antarctica (BÖLTER, 1990).

TOC content is a possible biomass marker in the lake. The TOC value in Lake Vanda increases with depth and reaches the maximum value of about 50 mg C/l at the anoxic lake bottom (Fig. 6). However, these extremely high TOC concentrations are due to the occurrence of humic substances in the lake bottom. Generally, Antarctic lakes, especially meromictic lakes, contain large amounts of

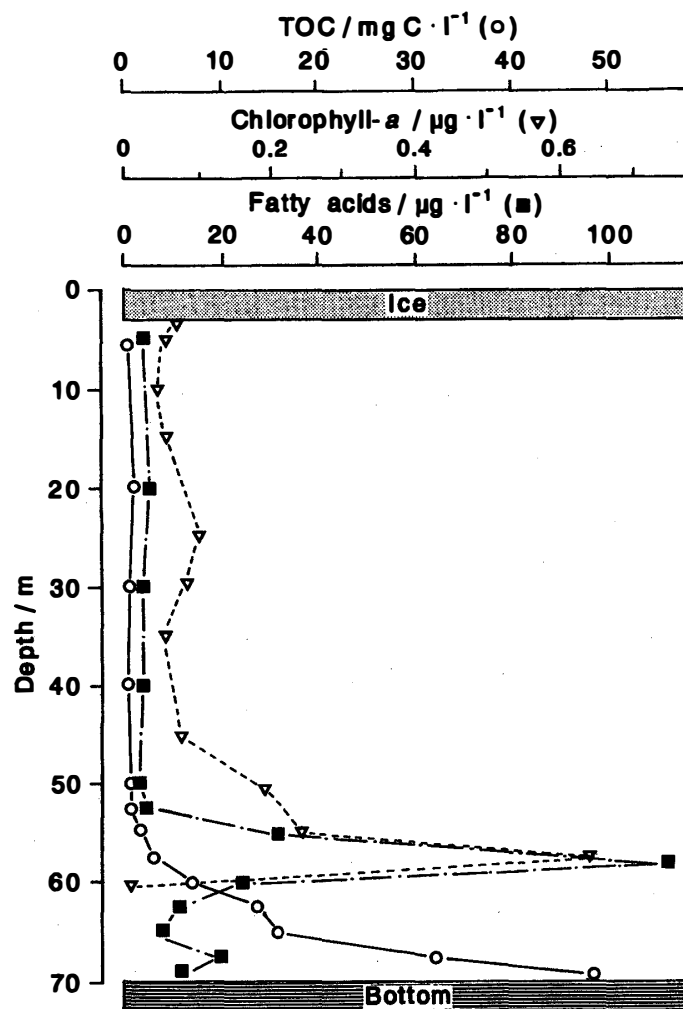


Fig. 6. Vertical distribution of total organic carbon, chlorophyll-a and total fatty acids in Lake Vanda of the Wright Valley (data from VINCENT and VINCENT, 1982; MATSUMOTO *et al.*, 1987b).

humic substances in the stagnant bottom layers, and thus TOC does not reflect biomass in lake waters (MATSUMOTO *et al.*, 1987b, 1989).

Chlorophyll-a concentration is widely used to evaluate phytoplankton biomass in aquatic environments. The concentration of chlorophyll-a in Lake Vanda increases with depth and reaches the highest value at a depth of 57 m just above the anoxic layer (Fig. 6; VINCENT and VINCENT, 1982).

Fatty acids are major lipid components in every organism, except for archaeobacteria. Fatty acids are relatively labile in natural water systems (MATSUMOTO, 1983). The content of fatty acids in lake water is thought to be balanced with the amounts of their biological production and destruction. Thus, fatty acid content may reflect biomass in lake water. The concentration of total fatty acids in Lake Vanda rises with depth, reaching a maximum at a depth of 57 m (MATSUMOTO *et al.*, 1984, 1987b). This is consistent with the chlorophyll-a result in the lake water. Hence, fatty acid content may be a good measure of biomass in Antarctic lake water.



## 6. Biological Composition

The direct observation of organisms by naked eye and microscope is important to estimate microbial composition, as in the case of the study of biomass. Also, culture of bacteria is useful to evaluate the bacterial composition, but some bacteria are difficult to culture. WARD *et al.* (1990) performed a culture-independent analysis of the composition of a natural microbial community, using the cellular component 16S ribosomal RNA. Although no one has applied this method to Antarctic lake ecosystems, in the future it may be a powerful marker of biological composition.

Biomarkers are characteristic organic compounds for each biological group and/or species, such as archaeobacteria, bacteria, microalgae, fungi, mosses and vascular plants. Biomarkers may be important to monitor biological composition. Typical biomarkers in various organisms are summarized in Table 2.

Major lipids of archaeobacteria, such as methanogenic bacteria, halophilic bacteria and thermo-acidphilic bacteria are composed of ether compounds. Also, archaeobacteria produce various acyclic isoprenoid alkanes and alkenes ranging from C<sub>15</sub> to C<sub>40</sub>, including squalane (LANGWORTHY, 1985). These compounds may be useful markers of archaeobacteria. Squalane is found in some lake sediments from Syowa Oasis, indicating the presence of archaeobacteria in the lakes (MATSUMOTO *et al.*, 1994).

*Iso*- and *anteiso*-alkanoic and alkenoic acids are produced only by bacteria (*e.g.*, KANEDA, 1967; O'LEARY, 1982). Also, *iso*- and *anteiso*-3-hydroxy acids are probably synthesized only by bacteria (MATSUMOTO *et al.*, 1989). Generally, bacteria cannot synthesize polyenoic acids. The degradation products (C<sub>27</sub>-C<sub>35</sub>-hopanes) of bacteriohopanetetrol (C<sub>35</sub>) are well known biomarkers in environmental and geochemical studies (*e.g.*, PHILP, 1985). Also, hop-22(29)-ene and various C<sub>30:1</sub> (carbon atoms per molecule: number of unsaturation) hopenes are produced by bacteria (ROHMER *et al.*, 1984; VENKATESAN, 1988). These compounds may be useful to determine bacterial contribution in the lake.

Cyanobacteria are the only organisms known to produce mid-chain branched mono- and di-methyl alkanes in the C<sub>15</sub>-C<sub>20</sub> range (SHIEA *et al.*, 1990). Also, cyanobacteria produce hop-22(29)-ene (GELPI *et al.*, 1970). An Antarctic cyano-

Table 2. Biomarkers of several organisms

Organisms	Biomarkers
Archaeobacteria	Squalane, ether compounds
Bacteria	<i>Iso</i> - and <i>anteiso</i> -alkanoic acids, bacteriohopanetetrol, hop-22(29)-ene, mono-enoic alkenoic acids
Cyanobacteria	Mid-chain branched alkanes and alkenes, hop-22(29)-ene
Microalgae	Short-chain <i>n</i> -alkanes and alkanes
Fungi	Long-chain <i>n</i> -alkanes ?
Moss	C <sub>28</sub> and C <sub>29</sub> sterols
Vascular plants	Long-chain <i>n</i> -alkanes and <i>n</i> -alkanoic acids, C <sub>29</sub> sterol, lignin phenolic acids and aldehydes

bacterial mat sample from the McMurdo Oasis, however, reveals that mid-chain branched alkenes, such as 3-, 4- and 5-methylalkenes and hop-22(29)-ene, are the major hydrocarbons. This may be due to the effect of low temperatures in the habitat of Antarctica (MATSUMOTO *et al.*, 1993).

Short-chain *n*-alkanes and alkenes, such as C<sub>17</sub> and C<sub>17:1</sub>, are often major hydrocarbons in microalgae. These hydrocarbons are believed to be useful markers of microalgae. Cyanobacteria and microalgae produce short-chain *n*-alkanoic and *n*-alkenoic acids (*e.g.*, WEETE, 1976).

The hydrocarbon composition of fungi is often similar to that of the waxes of vascular plants discussed below. However, the close similarity of hydrocarbon composition between fungi and the waxes of vascular plants raises the question as to whether the spore alkanes are actually fungal products. Definitive studies of hydrocarbons in pure cultured fungi are needed (WEETE, 1976). Fatty acids of fungi are generally similar to those of other biological systems. The major fatty acids are C<sub>16</sub> and C<sub>18</sub> (WEETE, 1976).

C<sub>28</sub> and C<sub>29</sub> sterols are predominant components in Antarctic mosses, such as *Pottia heimii*, *Sarconeurum glaciale* and *Bryum pseudotriquetrum* (MATSUMOTO and KANDA, 1985). So, the predominance of these sterols may be useful markers of the contribution of mosses.

The distribution of vascular plants is restricted to only the northern part of the Antarctic Peninsula (GREENE *et al.*, 1967). The composition of vascular plants is characterized by long-chain *n*-alkanes (>C<sub>19</sub>) with a predominance of odd-carbon numbers, long-chain *n*-alkanoic acids with a predominance of even-carbon numbers, and C<sub>29</sub> sterols (*e.g.*, KOLATTUKUDY, 1970; HUANG and MEINSCHEN, 1979). However, these compounds are often predominant components in Antarctic lake sediments and algal mats (MATSUMOTO *et al.*, 1979, 1981, 1982; VOLKMAN, 1986; VOLKMAN *et al.*, 1988). Hence, the application of these compounds as markers of vascular plants is difficult for Antarctic samples.

A series of phenolic acids (syringic, *p*-coumaric and ferulic acids) related to lignin are important markers of vascular plants (MATSUMOTO and HANYA, 1980). These phenolic acids are absent in any samples from the McMurdo and Syowa Oases, while *p*-hydroxy benzoic acid of microbial origin is present there (MATSUMOTO *et al.*, 1979, 1981). Thus, the *p*-coumaric acid/*p*-hydroxybenzoic acid (PCA/PHA) ratios in lake water and sediment samples from Antarctica are all zero, while these ratios in river and pond water and sediment samples from Japan show a wide range of variation (Fig. 7; MATSUMOTO, 1993). The PCA/PHA ratio could be, therefore, useful for a measure of the contribution of vascular plants in environmental studies.

## 7. Biological Activity

Carbon uptake measurements using <sup>14</sup>C labeled compounds, such as carbonate (<sup>14</sup>C-HCO<sub>3</sub>), are widely used to estimate light and dark assimilation of carbon. The maximum photosynthesis result is obtained at a depth of 57 m in Lake Vanda (Fig. 8; VINCENT *et al.*, 1981). This is consistent again with the

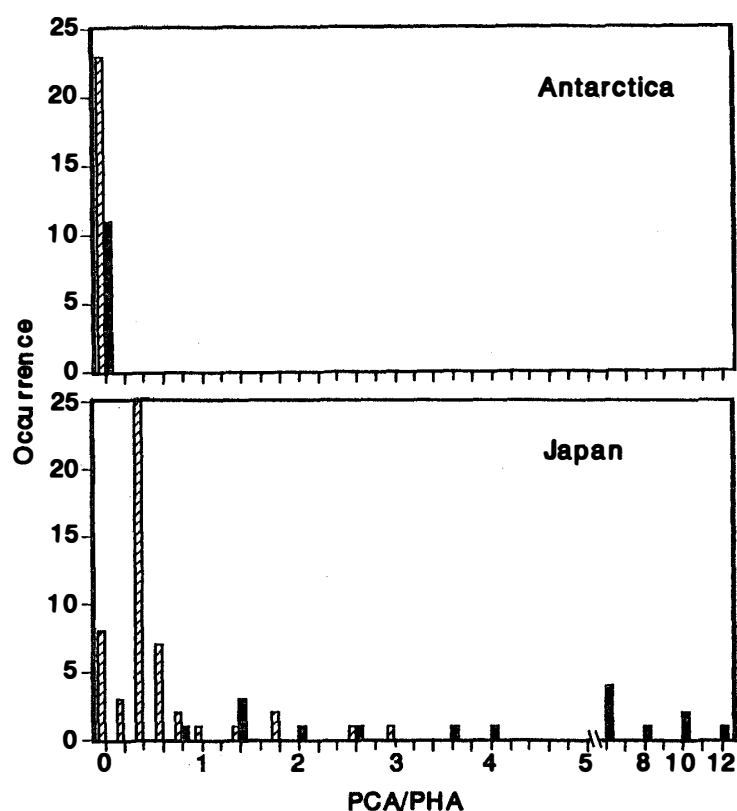


Fig. 7. *p*-Coumaric acid (PCA)/*p*-hydroxybenzoic acid (PHA) ratios for water and sediment samples from Antarctica and Japan (data from MATSUMOTO, 1993).

chlorophyll-*a* data discussed above (Fig. 6).

DNA synthesis is a marker of biosynthesis of organisms. VINCENT *et al.* (1981) reported total microbial activity in Lake Vanda, as estimated by <sup>3</sup>H-thymidine incorporation into DNA (Fig. 8). The maximum DNA synthesis result is obtained at the same depth of 57 m with that of photosynthesis.

In Lake Vanda, the maximum nitrifier activity is observed at depths about 53–55 m just above the NO<sub>3</sub>-N and DNA synthesis peaks (VINCENT *et al.*, 1981). The maximum NO<sub>3</sub>-N peak may be regulated by the supply of NH<sub>4</sub>-N from the anoxic lake bottom.

Normal alkenoic acids are more labile than those of *n*-alkanoic acids in natural environments. Thus the *n*-alkenoic acid/*n*-alkanoic acid ratios may reflect the degree of the degradation of organic matter in natural environments.

GUCKERT *et al.* (1986) reported that nutrient deprivation of *Vibrio cholerae* increases in the *trans/cis* *n*-C<sub>16:1</sub> alkenoic acid ratios (0.02 to 1.56) during 30 days. They show that the *trans/cis* *n*-alkenoic acid ratios may be used as a starvation or stress lipid index in natural aquatic environments.

## 8. Future Problems

I discussed here possible geochemical monitoring methods of Antarctic lakes and their ecosystems. However, a number of technical, instrumental and chemical

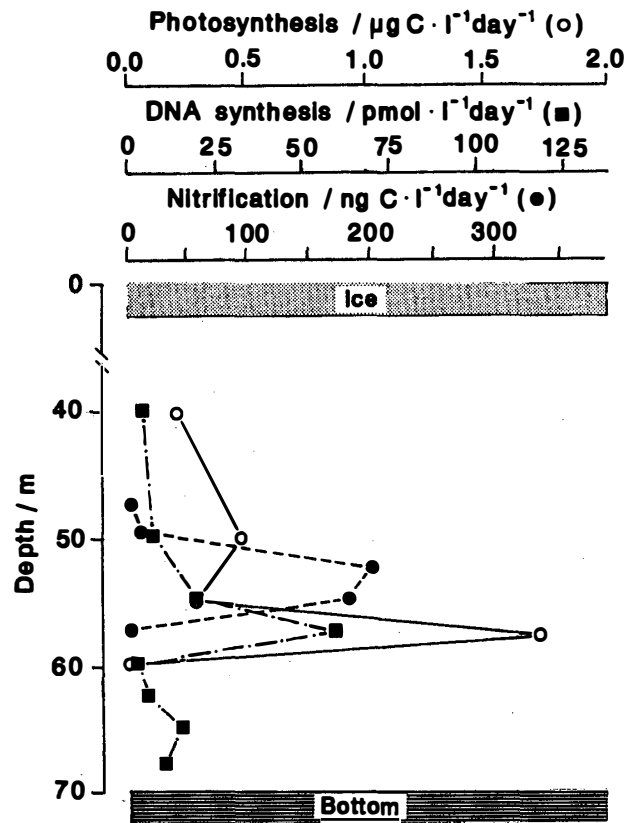


Fig. 8. Vertical distribution of photosynthesis ( $\text{CO}_2$  fixation), DNA synthesis ( $^3\text{H}$ -thymidine incorporation) and nitrification (nitrifier  $\text{CO}_2$  fixation) in Lake Vanda of the Wright Valley (data from VINCENT *et al.*, 1981).

problems remain to be solved before actual application. Although quantitative estimation of microbial composition is difficult by biomarker study alone, changes of microbial composition can be evaluated by this method.

A little is known about the biomarkers of Antarctic organisms; thus, the relationships between organisms and biomarkers are often not clear. Especially, long-chain *n*-alkanes and *n*-alkanoic acids as well as  $\text{C}_{29}$  sterols are generally believed to be biomarkers of vascular plants. However, as stated above, often these compounds are predominant components in Antarctic samples.  $\text{C}_{29}$  sterols may be derived from certain cyanobacteria and/or green algae. Also, the long-chain compounds are considered to be attributed to certain diatoms. However, key species of source organisms are not yet clear (MATSUMOTO, 1989). Therefore, biogeochemical studies of pure cultured Antarctic microorganisms, including microalgae and cyanobacteria, will provide fruitful information.

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