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Environmental changes in Syowa Station area of Antarctica during the last 2300 years inferred from organic components in lake sediment cores

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Abstract: Organic components in sediment cores from Namazu Ike (lake) (length 40 cm) and Ô-ike (lake) (length 32 cm) from Syowa Station area, Antarctica were studied to clarify their features in relation to paleoenvironmental changes, together with carbon-14 dating by Tandetron accelerator mass spectrometry. Namazu Ike sediment core was mainly composed of algal (mainly cyanobacteria) and aquatic moss debris, whereas Ô-ike sediment core was comprised of coarse and fine sands with the influence of algal (mainly cyanobacteria) debris. The ages of core bottoms of Namazu Ike and Ô-ike were estimated to be 1550 and 2330 years before present (yBP), respectively. The sedimentation rates of Namazu Ike and Ô-ike were calculated to be 30 and 59 years/cm, respectively. Very high total organic carbon (TOC) contents (average 24.5%) of Namazu Ike revealed that the sediment core was mainly composed of organic matter. Dramatic increase of TOC/total nitrogen ratios at a depth of 25 cm in Namazu Ike strongly suggests that aquatic moss increased from 1100 yBP to the core top. Changes in *n*-alkanes, *n*-alkanoic and *n*-alkenoic acids, and sterol compositions in the Ô-ike sediment core, suggest that microbial composition changed considerably, but their source organisms are not clear and further studies are required.

key words: Antarctic lake, environmental change, sediment core, aquatic moss, organic components, carbon-14 AMS dating

Introduction

Studies of paleoenvironmental changes are important to estimate the influence of future global warming induced by human activity. The influence of climatic changes will be amplified in polar regions (*e.g.*, Short *et al.*, 1991). Information on paleoenvironmental changes has been obtained by the analyses of marine and lake sediment cores, and ice cores (*e.g.*, Shackleton *et al.*, 1990; Raymo and Ruddiman, 1992; Kawamuro *et* *al*., 2000; Kashiwaya *et al*., 2001; Matsumoto *et al*., 2000, 2003). A large number of lakes and ponds with various salt concentrations are distributed in Syowa Station area, Antarctica (*e.g*., Murayama, 1977; Imura *et al*., 2003). These lakes and ponds probably record paleoenvironmental changes in Syowa Station area. Recently, paleoenvironmental changes in the postglacial period have been studied by Japanese Antarctic Research Expedition (JARE) members and changes in marine to lacustrine environments have been found to be due to the regression of glaciers (Miura *et al*., 2002; Seto *et al*., 2002).

Organic components in lake sediments are supplied by living and dead organisms, and are biomarkers of biological production, source organisms, and environmental changes in the drainage basin (*e.g*., Matsumoto *et al*., 2000, 2003). Here we report on organic components in sediment cores from Namazu Ike and Ô-ike (lakes) in Syowa Station area to clarify environmental changes in the past 2300 years, along with carbon-14 dating by Tandetron accelerator mass spectrometry (AMS).

Materials and method

Sampling sites and samples

The lake and pond surfaces in Syowa Station area are usually covered with thick ice (less than 2 m) except for austral summer (*e.g*., Murayama, 1977; Imura *et al*., 2003). Namazu Ike (535×270 m) with the maximum depth of 20 m is a freshwater lake located at Skarvsnes (Murayama, 1977, Fig. 1, Table 1). A sediment core (length 40 cm) was taken at the deepest point (20 m) of the lake on January 17, 2001 by a Satake-type corer (Rigosha, *ca.* 50 mm in diameter).

Ô-ike (370×215 m), with the maximum depth of 11.2 m, is a freshwater lake located on West Ongul Island (Murayama, 1977, Fig. 1, Table 1). A sediment core (length 32 cm) was taken at the center of the lake on December 4, 1987 (Fig. 1). Surface sediments containing aquatic mosses were taken from Namagi Ike (tentative name, *Leptobryum* sp., Skarvsnes), Akebi Ike (*Leptobryum* sp., Langhovde), Gokuh Ike (tentative name, *Bryum* sp., Langhovde) and Yukidori Ike (*Bryum* sp., Langhovde) in Syowa Station area (Fig. 1, Table 2). These mosses were identified by *in situ* observation of the samples. A directory and maps of each lake are shown on the web page (http://www.isc.nipr.ac.jp/~penguin/Terrestrial/regal/DataBase/index.htm).

The Namazu Ike sediment core was transported and kept cool in a refrigerator. The Ô-ike sediment core and surface sediments containing aquatic mosses were kept frozen at -20°C in a freezer until chemical analyses.

Analytical methods

Ages of sediment cores (conventional age) were determined by carbon-14 AMS dating after calibration with δ^{13}C data (Geo-Science Laboratory Co. Ltd.). Total organic carbon (TOC) and total nitrogen (TN) contents were determined at 2 cm intervals by a Fisons NCS 2500 automatic elemental analyzer after treatment with hydrochloric acid to remove carbonate-carbon. Total sulfur (TS) contents were determined by the same analyzer without hydrochloric acid treatment. The analytical uncertainty of TOC, TN and TS was within $\pm 5\%$.

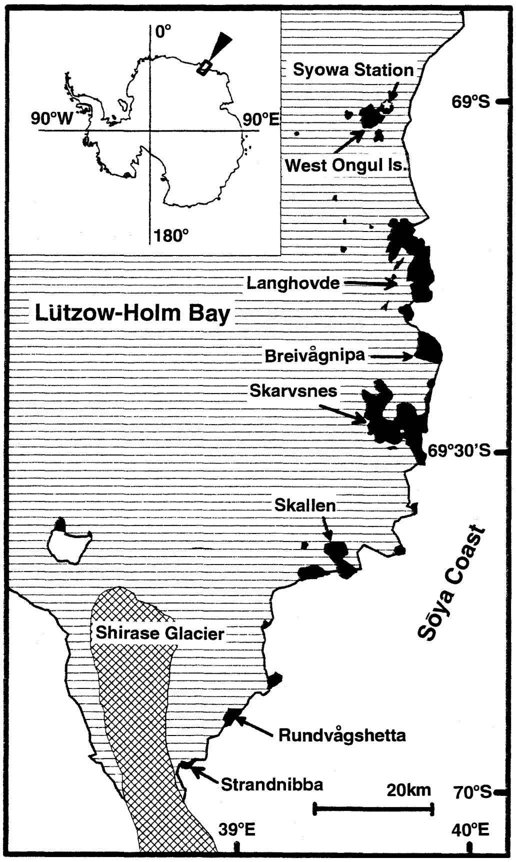

Fig. 1. Sampling sites in Syowa Station area, Antarctica (after Imura *et al.*, 2003).

Table 1. General features of studied lakes in Syowa Station area, Antarctica.

Lake	Akebi Ike	Yukidori Ike	Gokuh Ike*	Namagi Ike*	Namazu Ike	Ô-ike
Locality	Langhovde	Langhovde	Langhovde	Skarvsnes	Skarvsnes	West Ongul Island
Altitude (m)	-4#	125#	185$	110$	95#	13#
Length (m)	420#	275#	225$	350$	535#	370#
Width (m)	125#	225#	25$	325$	270#	215#
Area (m^2)	43750$	41000$	31200$	65000$	91500$	51500#
Maximum depth (m)	5.7$	8.2$	ND	8.2$	20.0#	11.2#
Chloride ion (mg/l)	7700#	10.4#	ND	ND	36#	125#

*Tentative name.

#Murayama (1977).

$Polar Terrestrial Biology Group (2005, http://www.isc.nipr.ac.jp/penguin/Terrestrial/regal/DataBase/index.htm).

ND: no datum.

Table 2. Aquatic mosses, and TOC and TN contents in surface sediments of studied lakes in Syowa Station area, Antarctica.

Lake	Akebi Ike	Yukidori Ike	Gokuh Ike*	Namagi Ike*	Namazu Ike	Ô-ike
Sampling date	Feb. 9, 2001	Feb. 7, 2001	Jan. 4, 2001	Jan. 18, 2001	Feb. 9, 2001	Feb. 9, 2001
Depth (m)	3.0	3.0	2.0	5.0	20.0	11.0
Aquatic moss	*Leptobrium* sp.	*Bryum* sp.	*Bryum* sp.	*Bryum sp.*, *Leptobrium sp.*	*Bryum sp.*, *Leptobrium sp.*	Absent
TOC (%)	9.55	25.2	33.5	15.5	29.3	5.46
TN (%)	0.260	2.15	2.09	1.10	2.21	0.514
TOC/TN	36.7	11.8	16.1	14.0	13.3	10.6

*Tentative name.

Hydrocarbons, fatty acids and sterols in the Ô-ike sediment core were analyzed at 2 cm intervals by the methods of Matsumoto *et al.* (1979, 1982, 2003) and Matsumoto and Watanuki (1992). Briefly, organic components in the samples were extracted with ethyl acetate after saponification with 0.5 mol/*l* potassium hydroxide/methanol (80°C, 2 h). The ethyl acetate extracts were chromatographed on a silica gel column (160 mm ×6 mm i.d., 100 mesh, 5% water). Hydrocarbon and fatty acid-sterol fractions were obtained by elution with hexane and ethyl acetate, respectively. Half of the fatty acid-sterol fraction was methylated with diazomethane. The another half of the fatty acid-sterol fraction was trimethylsilylated (TMS) with 25% *N,O*-bis(trimethylsilyl acetamide) acetonitrile solution, and sterol TMS derivatives obtained. Hydrocarbons, fatty acid methyl esters and sterol-TMS derivatives were analyzed by a JEOL JMS Automass 150 gas chromatograph-mass spectrometer equipped with a fused silica capillary column (DB5, 30 m×0.25 mm i.d., film thickness 0.1 μm, and/or DB225, 30 m ×0.25 mm i.d., film thickness 0.25 μm). The analytical uncertainty was within ±10%.

Results and discussion

General features and ages of sediment cores

Namazu Ike: Algal mat (mainly cyanobacteria) and some aquatic moss communities (*Bryum pseudotriquetrum* and *Leptobrium* sp.) are now distributed in the lake bottom (*e.g.*, Imura *et al.*, 2003). The sediment core of Namazu Ike was grayish olive, and was composed mainly of algal debris with some aquatic mosses. Living algae were not found in the core sample. The structure of the algae in the core was decomposed and identification of the species was impossible.

The carbon-14 AMS dating of depths 0–2, 22–24 and 36–38 cm in the sediment core from Namazu Ike showed 410±40, 1030±40 and 1470±40 years before present (yBP), respectively (Fig. 2). The depth-age relationship showed a good correlation (r^2=0.999). No remarkable change in sedimentation rate was found in the core, and the sedimentation rate was calculated to be 30 years/cm (y/cm). The ages of the core top and bottom (40 cm) were estimated to be 370 and 1550 yBP, respectively. For the age of the core top there are two possibilities: 1) the core top was lost in the coring, 2) old carbon having low carbon-14 concentration was supplied from the drainage basin, since glacial melt-

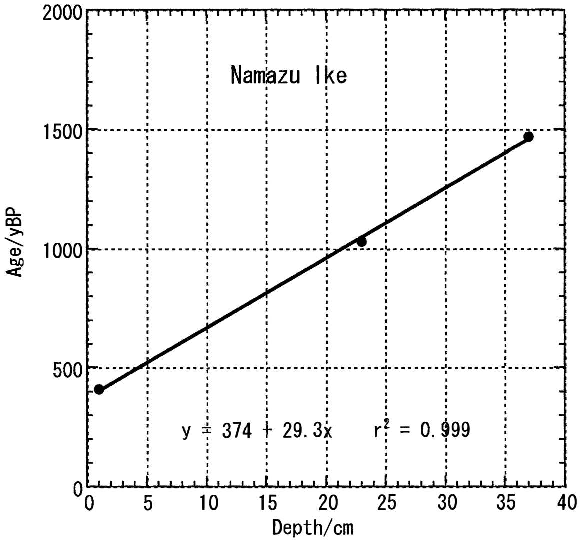

Fig. 2. Relationship between depth and age (conventional age) of sediment core of Namazu Ike (lake) at Skarvsnes in Syowa Station area.

water contains old carbons (*e.g.*, Doran *et al.*, 1999; Takahashi *et al.*, 1999). It is reported, however, that no glacial meltwater has been supplied from the drainage basin (Murayama, 1977). Thus, the core top must be lost in sampling. Additional evidence is the lack of living cyanobacteria in the core top.

Ô-ike: The sediment core of Ô-ike was olive black or black, and was composed of coarse and fine sands with some algal debris. Oguni and Takahashi (1989) found 5 species of Cyanophyceae (cyanobacteria), 1 species of Bacilariophyceae and 2 of species Chlorophyceae in algal (mainly cyanobacteria) mat samples. *Lyngbya limnetica* (cyanobacteria) is abundant in the mat samples. The species of algae could not, however, be identified in the sediment core because the cell structure was destroyed, as in the case of Namazu Ike.

The carbon-14 AMS dating of depths 4–6, 14–16 and 30–32 cm of the sediment core from Ô-ike revealed 530±40, 1450±40 and 2200±40 yBP, respectively (Fig. 3). The depth-age relationship showed a good correlation (r^2=0.964). No remarkable change in sedimentation rate was found in the core, and the sedimentation rate was calculated to be 59 y/cm. The ages of the core top and bottom (32 cm) were estimated to be 330 and 2330 yBP, respectively. No glacial meltwater containing old carbon is flowing into the lake (Murayama, 1977). However, the ages of surface sediments of common lakes composed of sand and silt deposits are usually older than several hundred years (*e.g.*, Nakamura and Oda, 1998). Thus the lost core top in Ô-ike may be small.

TOC, TN and TS

Namazu Ike: TOC, TN and TS contents in the sediment core of Namazu Ike ranged from 11.2 to 31.3% with an average of 24.5±5.1% (standard deviation), 0.588 to 2.95% with an average of 1.85±0.61% and from 0 to 1.96% with an average of 0.77±0.74%, respectively (Fig. 4). TS contents were low and some samples were less than detection limits. Very high TOC contents showed that the sediment layer was mostly composed of algal and moss debris. The TOC and TN contents tend to decrease from

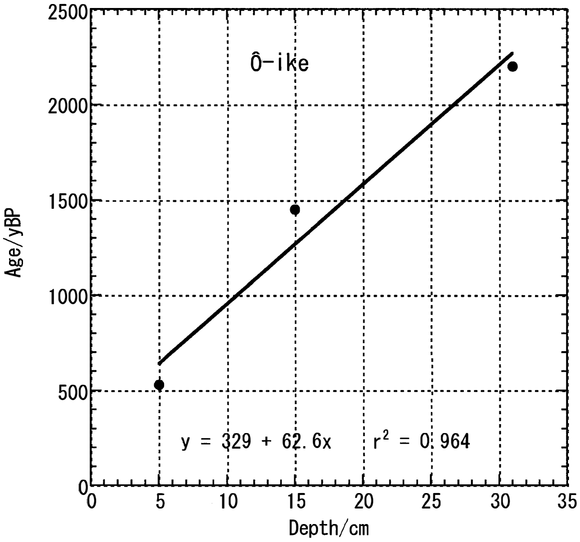

Fig. 3. Relationship between depth and age (conventional age) of sediment core in Ô-ike (lake) of West Ongul Island in Syowa Station area.

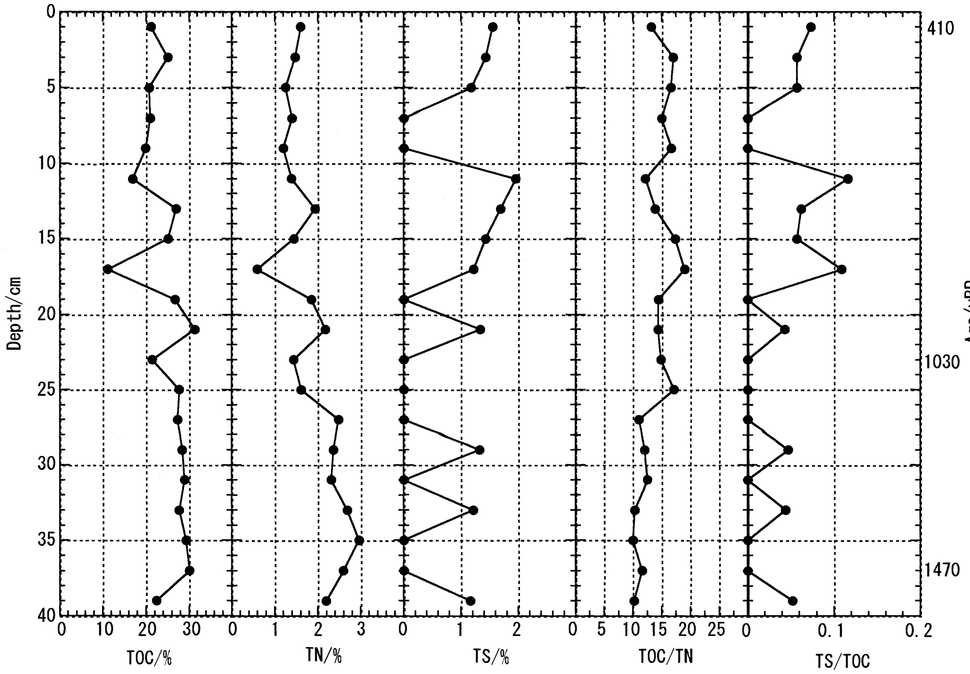

Fig. 4. Depth profile of TOC, TN and TS results in Namazu Ike sediment core.

depths of approximately 35 cm (1400 yBP) to the core top, suggesting increase of the supply of coarse and fine sands. The lake has no inflow streams. Lake water is supplied from snow meltwater in the drainage basin (Murayama, 1977). These sandy materials are probably supplied through eolian dusts. It is likely that the regression of glaciers in the Holocene (*e.g.*, Miura *et al.*, 2002) expanded the ice-free areas around the lake.

TOC/TN ratios are marker of sources of organic matter. They were approximately 10 for depths 40–27 cm in Namazu Ike, increasing to over 12 (12–18) for depths 25–0 cm. The TOC/TN ratios of surface sediments containing aquatic mosses ranged from 11.8 to 36.7 (Table 2). Thus, the dramatic increase of TOC/TN ratios at a depth of 25 cm in the lake strongly suggests that the contribution of aquatic mosses increased from 1110 yBP to the core top.

Ô-ike: TOC, TN and TS contents in the sediment core of Ô-ike ranged from 2.2 to 11.8% with an average of 8.1±3.2%, 0.18 to 1.26% with an average of 0.79±0.34% and 0 to 4.07% with an average of 1.43±1.12%, respectively (Fig. 5). TOC and TN contents in the sediment core of Ô-ike were much lower than those of Namazu Ike, although TOC and TN contents varied largely with depth (Fig. 4). No major meltwater streams are in the lake. The lake water is supplied from snow meltwater (Murayama, 1977). Algal mats mainly composed of cyanobacteria are developed in the lake bottom (Oguni and Takahashi, 1989). The fluctuations of TOC and TN contents in the lake could, therefore, be explained by the relative contributions of the development of algal mats and sandy materials of eolian dusts. Namely, low TOC and TN contents at depths of 29, 23, 11 and 5 cm may be largely due to the contribution of eolian dusts.

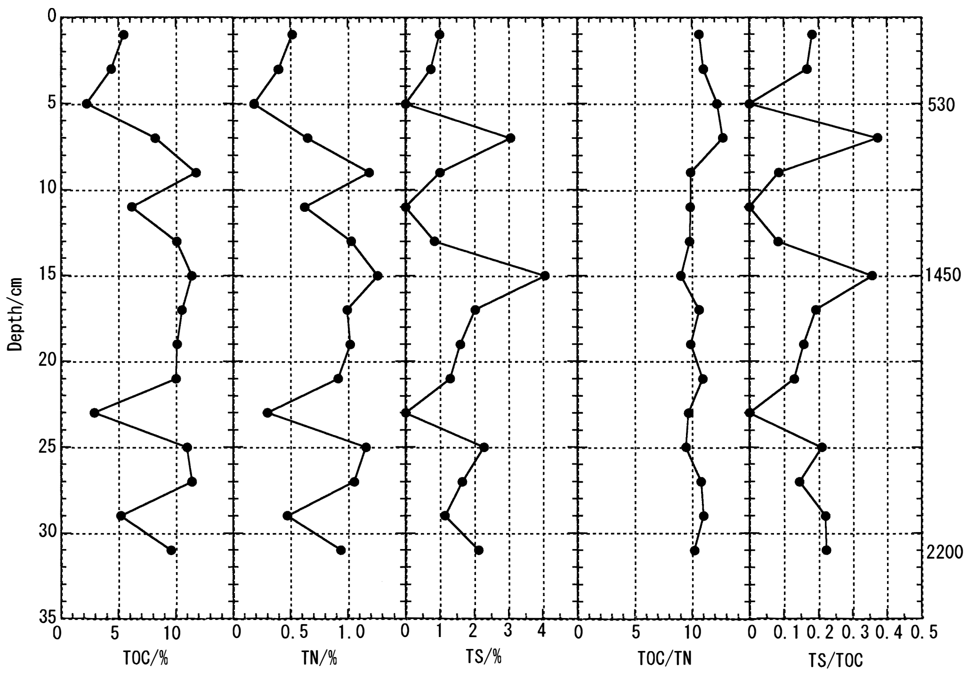

Fig. 5. Depth profile of TOC, TN and TS results in Ô-ike sediment core.

TOC/TN ratios of the surface sediment layer of Ô-ike were near 10, which is consistent with the fact that presently aquatic mosses are absent in the lake (Oguni and Takahashi,1989; Imura *et al.*, 2003). TOC/TN ratios of approximately 10 in the lake sediment core strongly suggest that aquatic mosses were absent in the past 2300 years except in the 7 and 5 cm depth samples. Further studies are required for these depths.

TS/TOC ratios are marker of redox conditions in the lake (*e.g.*, Berner, 1982; Watanabe *et al.*, 2003). TS/TOC ratios of the sediment core of Ô-ike varied from 0 (no sulfur) to 0.37 (Fig. 5). The pattern of TS concentrations was, however, similar to those of TOC and TN contents. Thus, the changes in TS/TOC ratios probably reflect the supply of sulfate rather than redox conditions in the lake.

Molecular markers in Ô-ike

A suite of *n*-alkanes ranging in carbon chain length from *n*-C_{15} to *n*-C_{36} were found in Ô-ike sediment core with bimodal distributions maximizing at *n*-C_{17} and *n*-C_{23}, together with isoprenoid-alkanes (i-C_{18}, i-C_{19}, i-C_{20} and squalane). Major hydrocarbons in the sediment core of the lake were *n*-C_{17}, *n*-C_{21}, *n*-C_{23}, and/or *n*-C_{25} alkanes (Fig. 6). Long-chain *n*-alkanes (*n*-C_{20}–*n*-C_{35}) were relatively abundant in the sediment core, as in the case of other sediment samples from Antarctica in spite of the absence of vascular plants (*e.g.*, Matsumoto, 1993). Thus the *n*-long/*n*-short (*n*-C_{15}–*n*-C_{19}) alkane ratios

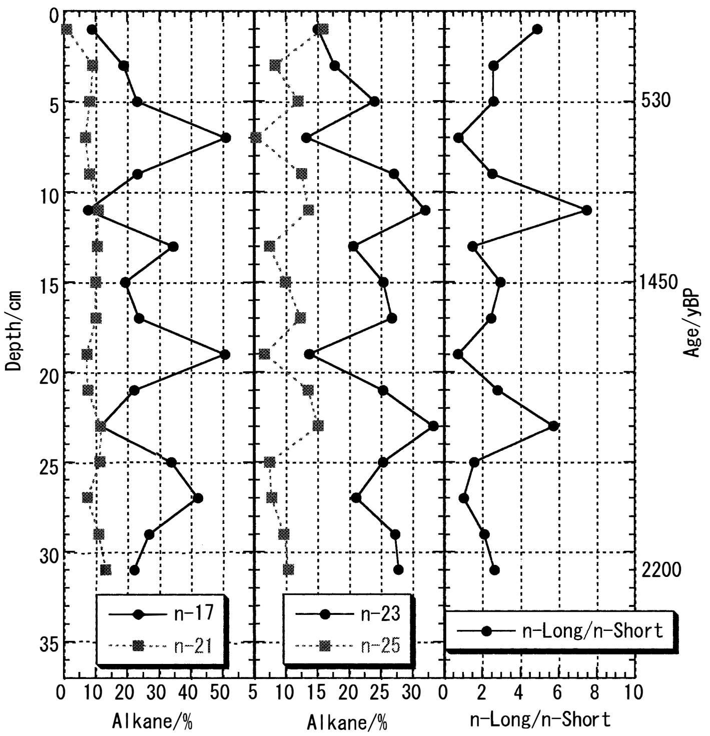

Fig. 6. Depth profile of hydrocarbons in Ô-ike sediment core.
n-Long: *n*-C_{20}–*n*-C_{35}. *n*-Short: *n*-C_{15}–*n*-C_{19}.

were greater than unity in the sediment core.

A series of n-alkanoic acids ranging from n-C_{12} to n-C_{22}, maximizing at n-C_{16}, were detected in the sediment core samples, together with n-alkenoic and branched (*iso* and *anteiso*) acids. The major fatty acids were n-$C_{16:0}$ (carbon chain length: number of unsaturation), n-$C_{16:1}$, and/or n-$C_{18:1}$ acids in the sediment core (Fig. 7). Branched acids are the marker of bacteria (*e.g.*, Albro, 1976; Matsumoto *et al.*, 2004), and were found in all the samples, but changes in their percentages were small. The pattern of n-long (n-C_{20}–n-C_{22})/n-short (n-C_{12}–n-C_{18}) alkanoic acid ratios was similar to that of n-long/n-short alkane ratios, suggesting again the contribution of similar source organisms. The absence of systematic changes in n-alkenoic/n-alkanoic acid ratios suggest again the difference of source organisms in the sediment core rather than the degradation of fatty acids (Fig. 7).

Stenols (cholesterol, brassicasterol, 24-methylcholesterol, stigmasterol and 24-ethylcholesterol) and stanols (cholestanol, 24-methylcholestanol and 24-ethylcholestanol) were found in the Ô-ike sediment core. The major sterols were brassicasterol, stigmasterol, 24-ethylcholesterol and 24-ethylcholestanol.

Stenols and stanols are widely distributed in lacustrine and marine environments. Although 24-ethylcholesterol (C_{29}) is the most predominant sterol of vascular plants,

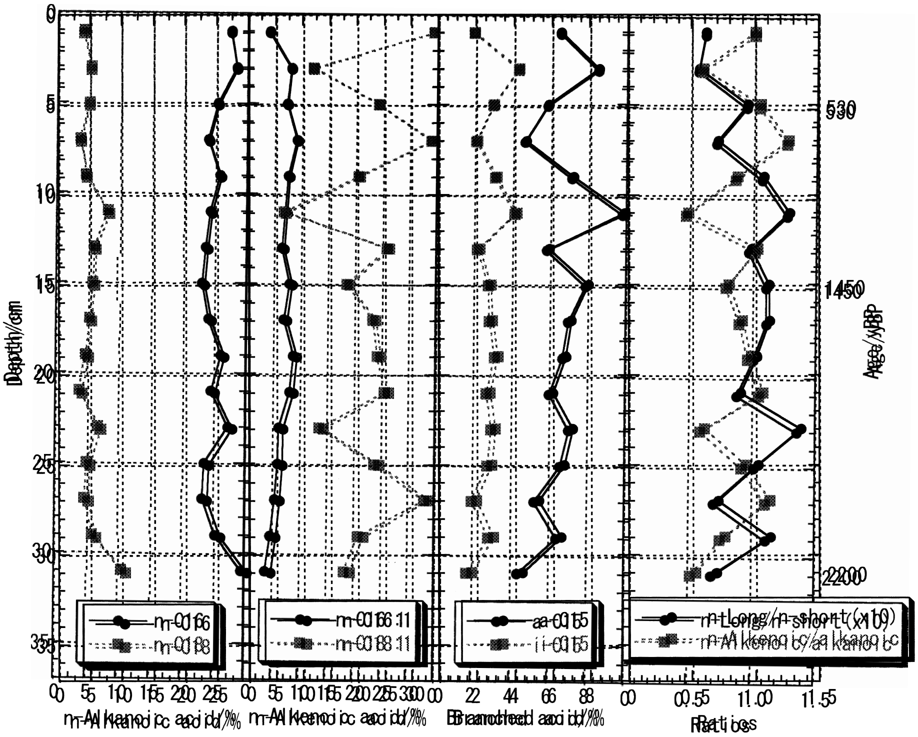

Fig. 7. Depth profile of fatty acids in Ô-ike sediment core.
n-Long: n-C_{20}–n-C_{22}. n-Short: n-C_{12}–n-C_{18}. n-Alkanoic: n-C_{12}–n-C_{22}.
n-Alkenoic: n-$C_{16:1}$ and n-$C_{18:1}$–n-$C_{18:3}$.

cholesterol (C_{27}) is a major sterol of microalgae (*e.g.*, Matsumoto *et al.*, 1982; Volkman *et al.*, 1998). It is known, however, that many kinds of microalgae synthesize C_{29} sterols, including 24-ethylcholesterol (*e.g.*, Matsumoto *et al.*, 1982: Volkman *et al.*, 1998). Stanols are often found in microalgae, such as dinoflagellates, diatoms and raphidophyte (e.g. Volkman *et al.*, 1998).

$C_{29}/(C_{27}–C_{29})$ stenol, $C_{29}/(C_{27}–C_{29})$ stanol and $C_{29}/(C_{27}–C_{29})$ sterol ratios ranged from 50 to 78%, and thus C_{29} sterols are abundant in the Ô-ike sediment core in spite of the absence of vascular plants in the studied areas (Fig. 8). These C_{29} sterols are probably originated from microalgae in the lake (*e.g.*, Matsumoto *et al.*, 1982; Volkman *et al.*, 1998).

Stanol/sterol ratios depend on the microalgal sources, relative stability of stanols and stenols, and reduction of stenols into stanols. The rate of the microbial degradation of stenols is greater than that of stanols, and thus the stanol/sterol ratios increase with the degradation of organic matter (Nishimura, 1977; Pearce *et al.*, 1998). Also, stanols are formed by the reduction of stenols (Volkman *et al.*, 1998). The stanol/sterol ratios are a possible marker of redox conditions of the sedimentary environment of the lake (Matsumoto *et al.*, 2003).

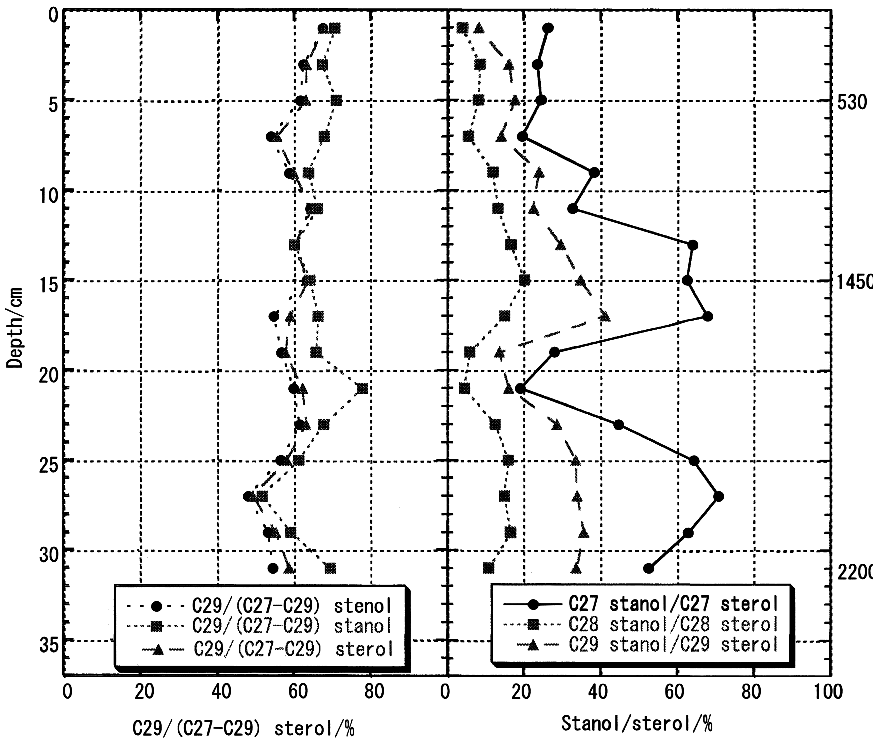

Fig. 8. Depth profile of sterols in Ô-ike sediment core.
C_{27} stenol: Cholesterol. C_{27} stanol: Cholestanol. C_{28} stenol: Brassicasterol and 24-methylcholesterol. C_{28} stanol: 24-Methylcholestanol. C_{29} stenol: Stigmasterol and 24-ethylcholesterol. C_{29} stanol: 24-Ethylcholestanol.

C_{27}, C_{28} and C_{29} stanol/sterol ratios of the Ô-ike sediment core showed a wide range of fluctuation, but their patterns are similar to each other (Fig. 8). The high stanol/sterol ratios were found at depths of 13–17 cm and 25–29 cm. There are three possibilities, 1) difference of source organisms, 2) changes in redox conditions, 3) preferential degradation of stenols. No marked changes in TOC contents, hydrocarbon and fatty acid compositions were found at these depths. It is possible that these sediment layers are relatively anoxic as compared with other layers. Further studies are required for the confirmation of this hypothesis together with source organisms of stanols in the lake.

Conclusions

TOC, TN, hydrocarbons, fatty acids and sterols in sediment cores from Namazu Ike (length 40 cm) and Ô-ike (length 32 cm) from Syowa Station area, Antarctica were studied to clarify their features in relation to environmental changes, together with carbon-14 AMS dating.

1) The Namazu Ike sediment core was mainly composed of algal and aquatic moss debris, while the Ô-ike sediment core was composed of coarse and fine sands with some influence of algal debris.

2) The ages of core bottoms for Namazu Ike and Ô-ike are estimated to be 1550 yBP with a sedimentation rate of 30 y/cm, and 2330 yBP with a sedimentation rate of 59 y/cm, respectively.

3) The dramatic increase of TOC/TN ratios at a depth of 25 cm in Namazu Ike strongly suggests that aquatic moss vegetation increased from 1110 yBP to the core top.

4) Large varieties of *n*-alkanes, *n*-alkanoic and *n*-alkenoic acids, and sterol compositions in the Ô-ike sediment core, suggest that microbial composition changed considerably, but their source organisms are not clear and further studies are required.

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