

## HYDROCARBON RECORD OF A MARINE SEDIMENT CORE FROM LÜTZOW-HOLM BAY, ANTARCTICA

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**Abstract:** We have attempted to reconstruct the palaeoenvironment of the coastal region around Syowa Station in Lützow-Holm Bay, Antarctica using organic compounds in a marine sediment core from this region. The vertical variation pattern of organic carbon (OC) in the sediment core was similar to that of total nitrogen (TN). The OC and TN values decreased from 0.3 to 0.02 and 0.046 to 0.004% by weight from the surface to the bottom, respectively. <sup>14</sup>C age showed a smooth pattern of change from about 3000 yBP at the surface to 14000 yBP at the bottom (129 cm), except for an abrupt age gap at a depth of 70 cm in the sediment core. Normal-alkanes ranging from C<sub>15</sub> (carbon chain length) to C<sub>33</sub> were found with a predominance of C<sub>21</sub> in the low hydrocarbon content sections (0.16–0.79 µg/g) at depths of 0–5, 55–60 and 120–125 cm of the core, whereas long-chain *n*-alkanes (C<sub>22</sub>, C<sub>23</sub>, C<sub>24</sub>) were relatively dominant in the high hydrocarbon content sections (11.8–12.2 µg/g) at depths of 45–50 and 90–95 cm. The differences in the δ<sup>13</sup>C values of the *n*-alkanes (C<sub>17</sub>–C<sub>32</sub>) analyzed by a GC-IRMS system for the high and low hydrocarbon content sections of the core (–26.0 to –28.5‰) were not appreciable, suggesting a common source of origin of these compounds. Normal-alkane distribution and the δ<sup>13</sup>C values of each *n*-alkane indicate that the major source of these compounds is probably a mixture of marine organisms and eroded material from older sediments.

### 1. Introduction

Hydrocarbons are integral components of all organisms. Although collectively they are ubiquitous in living organisms, individual compounds that constitute this fraction are characteristic of each organism (BLUMER *et al.*, 1971; GELPI *et al.*, 1970; CORRIGAN *et al.*, 1973; JOHNSON and CALDER, 1973; KVENVOLDEN *et al.*, 1987). Marine phytoplankton for example have preferentially a high proportion of short-chain *n*-alkanes such as C<sub>15</sub> and C<sub>17</sub> with odd-carbon numbers relative to long-chain *n*-alkanes (>C<sub>20</sub>) with even-carbon numbers (BLUMER *et al.*, 1971; GELPI *et al.*, 1970). On the other hand, higher plants have a high proportion of long chain *n*-alkanes with a strong odd-carbon *n*-alkane preference (CORRIGAN *et al.*, 1973; JOHNSON and CALDER, 1973; KVENVOLDEN *et al.*, 1987). This wide

variability in the *n*-alkane composition from different sources makes the study of these compounds a useful tool in geochemical investigations. In previous studies, hydrocarbons in sinking and suspended particles in the water column and in the marine sediment have been utilized as powerful biomarkers for: (1) elucidating sources of organic materials (BLUMER *et al.*, 1971; CORRIGAN *et al.*, 1973; NICHOLS *et al.*, 1988; MATSUMOTO, 1993), (2) biogeochemical processes of alternation or degradation of organic materials which occurred early on the geological time scale, and biogeochemical processes in marine food chain (MATSUEDA, 1986; NACHMAN, 1985), (3) palaeoenvironmental conditions of sedimentation (KVENVOLDEN *et al.*, 1987; MATSUMOTO *et al.*, 1992) and (4) environmental pollution (LIPIATOU and SALIOT, 1991). Since Antarctica is the harshest environment for living organisms and its land mass is isolated from polluted industrialized areas, its oceanic sediment records are of particular geochemical interest relative to the studies listed above. A major objective of the present study is to reconstruct the palaeoenvironment of the coastal region around Syowa Station in Lützow-Holm Bay, Antarctica with the help of hydrocarbon records in conjunction with measurements of organic carbon, total nitrogen,  $^{14}\text{C}$  age and  $\delta^{13}\text{C}$  in a sediment core from this region. In sediment samples,  $\delta^{13}\text{C}$  analysis of individual organic compounds can provide important information on the source of these compounds because  $\delta^{13}\text{C}$  signatures found in various organisms are typical of each organism and are not affected by diagenesis. Therefore, an attempt has also been made to determine the origin of organic materials in this region on the basis of the results obtained.

## 2. Materials and Methods

A 129 cm sediment core sample (Lh-2) was obtained on October 15 during the 33rd Japanese Antarctic Research Expedition (JARE-33) off Langhovde in Lützow-Holm Bay, Antarctica ( $69^{\circ}14'48''\text{S}$ ,  $39^{\circ}11'33''\text{E}$ , water depth 497 m, Fig. 1) when the sea ice sheet was the hardest of all seasons. At first, a hole approx. 30 cm in diameter was drilled through the 1 to 3 m thick sea ice sheet using an ice drill and then a tripod was placed over it. A stainless steel wire with a gravity core sampler (length 200 cm, diameter 6.5 cm) attached to the loose end was passed over the tripod and rolled down to the sea floor. The sediment core sample obtained was carefully cut into 5 cm thick sections and immediately stored at  $-20^{\circ}\text{C}$  until analysis.

Organic carbon and total nitrogen contents in separate portions of sediment samples were measured on a CHN corder (YANACO MT IS) after treatment with 2M HCl solution to remove inorganic carbon. Extraction and separation of *n*-alkanes was carried out by first preparing the samples as per methods outlined in FARRINGTON *et al.* (1988). Aliphatic components from the sediments were extracted by sonication (20 min), first in isopropyl alcohol and then in methanol-chloroform (2:1, 1:1, 1:3 v/v, respectively). After centrifugation (3000 rpm, 10 min), the supernatant solutions were combined and deionized water (MILLI-Q®) was added to separate the chloroform phase which was then concentrated using a

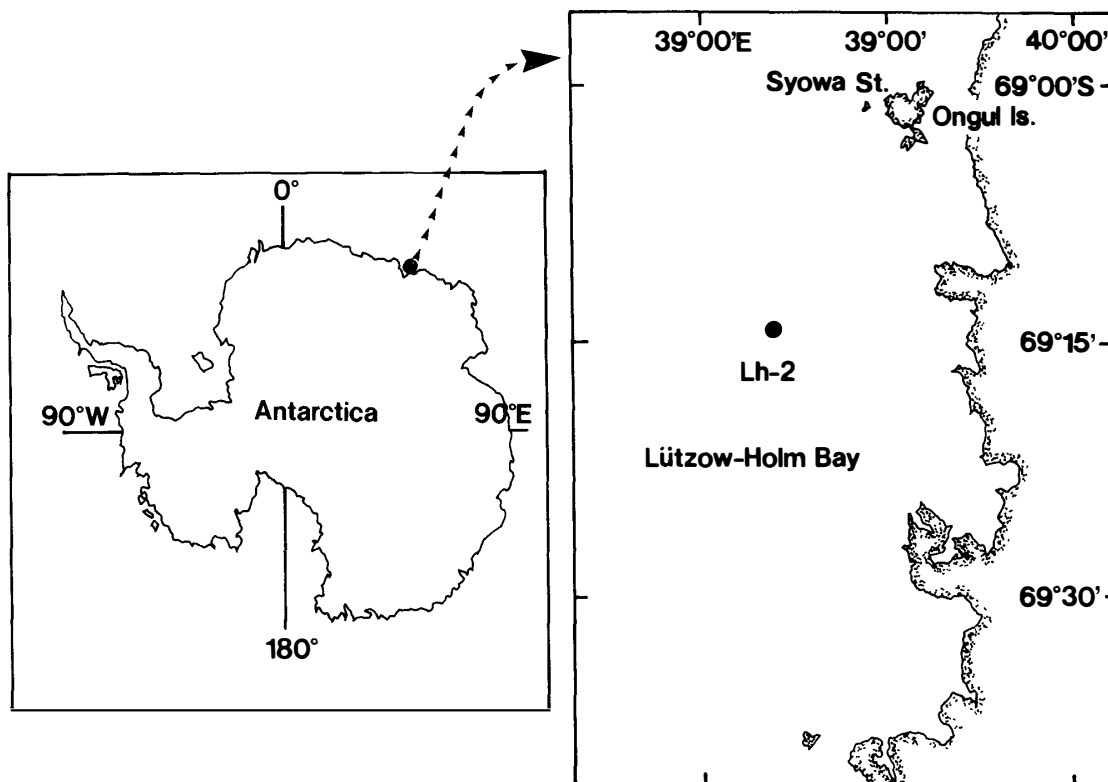


Fig. 1. Sampling location of a sediment core (Lh-2) in Lützow-Holm Bay, Antarctica ( $69^{\circ}14'48''S$ ,  $39^{\circ}11'33''E$ , water depth: 497 m).

rotary evaporator. The chloroform was dried under  $N_2$  gas and the residual matter was redissolved in hexane. Extracts in small quantities of hexane were placed on the top of a silica gel column (Kiesel gel 60, 70–230 mesh, 1 g) in order to separate 8 different fractions by passing organic solvents through the column. Alkanes eluted in this manner were thereafter identified by a Shimadzu GC-9A gas chromatograph equipped with a flame ionizer detector (FID) using a DB-5 (30 m  $\times$  0.32 mm, film thickness 0.25  $\mu$ m) fused-silica column. The GC oven temperatures were programmed as follows: 160°C for 5 min, 160 to 290°C at 3°C/min, at 290°C for 10 min, 290 to 320°C at 4°C/min, and maintained at 320°C for 20 min.

Radiocarbon analysis using separate portions of each sample (13–14 g) was undertaken by the hydrogen reduction method (KITAGAWA *et al.*, 1991; VOGEL *et al.*, 1984, 1987). In this method, it is possible by a direct reaction to obtain graphite from carbon dioxide with Fe powder as a catalyst.  $^{14}C$  age determination using a graphite target was carried out using the Tandemtron accelerator mass spectrometer (AMS; GENERAL IONIC, 1.8 MeV, 25 nA) of the Dating and Materials Research Center, Nagoya University (NAKAMURA and NAKAI, 1988). Five times replicates of radiocarbon analysis were alternately carried on between sample and working standard of new oxalic acid (NBS) to obtain the standard deviation.  $\delta^{13}C$  analysis of bulk organic matter in the sediments was carried out using a Finnigan MAT 251 mass spectrometer. The  $\delta^{13}C$  analysis of individual *n*-alkanes was done using a Finnigan MAT GC-IRMS system using a delta-S mass spectrometer.

### 3. Results and Discussion

#### 3.1. Organic carbon and total nitrogen contents

Figure 2 shows the vertical profiles of organic carbon and total nitrogen contents in the sediment core (Lh-2). Organic carbon content in the sediment core varied from about 0.3% in the surface layer to 0.02% in the bottom layer. These values are quite similar to those reported in a previous study from this area (MATSUMOTO *et al.*, 1992). Generally, organic carbon content decreased with depth of the sediment core except for an unusually high value of 0.26% at 70 cm. The variation pattern of total nitrogen content with depth was remarkably similar to that of organic carbon, decreasing from 0.045% at the surface to 0.004% at the bottom except for a high value at 70 cm.

#### 3.2. $^{14}\text{C}$ age

$^{14}\text{C}$  ages of the sediment core sections as calculated by STUIVER and POLACH (1977) and STUIVER (1983) are shown in Fig. 3. The  $^{14}\text{C}$  age profile showed a smooth pattern of change from 3010 (standard deviation  $\pm 110$ ) yBP at the surface to  $13690 \pm 180$  yBP at the bottom except for an abrupt age gap ( $7400 \pm 170$  yBP) between *ca.* 60 and 90 cm. It is a bit difficult to pinpoint the exact reason for this age

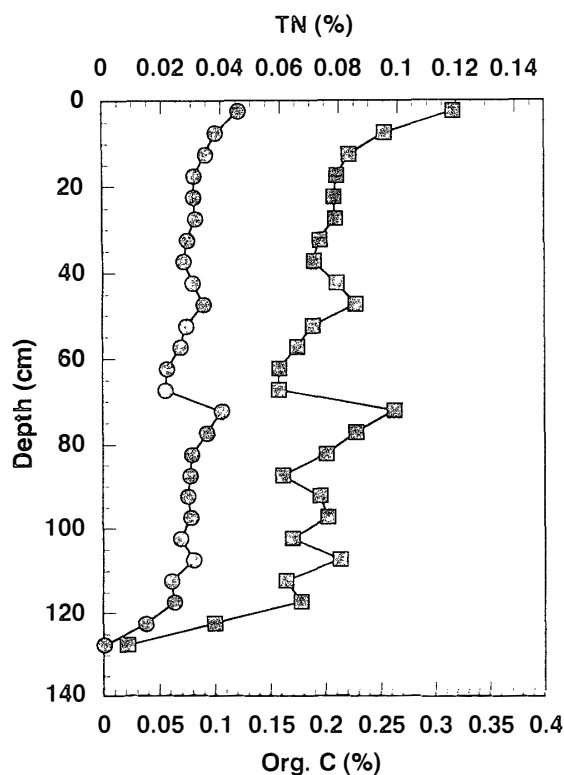


Fig. 2. Vertical profiles of organic carbon (■) and total nitrogen content (●) by weight percent in the sediment core (Lh-2).

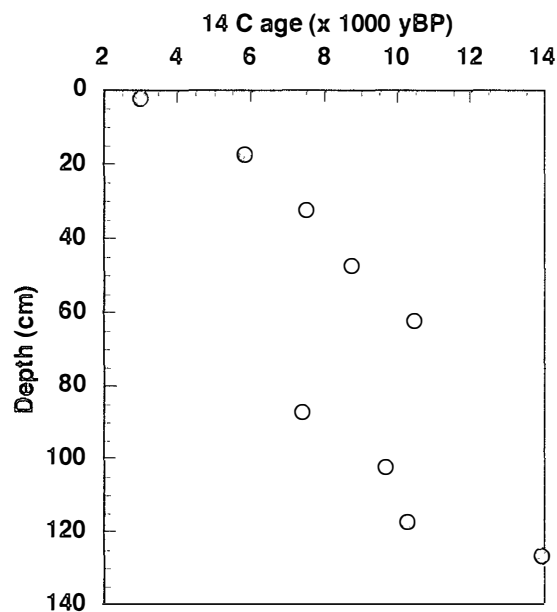


Fig. 3. Vertical profile of  $^{14}\text{C}$  age in the sediment core (Lh-2).

gap at this stage, which in all probability may be related to some major geological event such as slide or slump which occurred over a geological time scale. The profiles of organic carbon and total nitrogen content which depict the unusually high values at 70 cm in the core also support the view that some major geological event occurred during this period. Since this age gap observed in the present study has not been reported from other research on sediment samples in Lützow-Holm Bay, it seems likely that this geological event could have been a very localized phenomenon in this area.

Radiocarbon age estimates of marine derived materials from the Antarctic generally appear older in comparison with those of terrestrial derived materials as a result of significantly depleted  $^{14}\text{C}$  concentrations in Antarctic seas (BROECKER, 1963; OMOTO, 1983). This depletion of  $^{14}\text{C}$  concentration in sea-water is generally referred to as the "reservoir effect". It is necessary to correct the observed ages for marine organisms. GORDON and HARKNESS (1992) reviewed measurements of  $^{14}\text{C}$  concentrations in modern Antarctic marine life from Antarctic coastal areas and suggested that correction factors of *ca.* 1400 years were required to relate radiocarbon measurements on fossil marine materials from the Antarctic region to the conventional radiocarbon time scale. In the Syowa Station area, which is close to the continental margin, age anomalies are expected to be greater in sea water samples than those in the offshore area, since the low  $^{14}\text{C}$  concentration in sea-water could be caused by dilution of sea-water due to the inflow of fresh water from the submarine melting of icebergs, ice shelves and glaciers in which carbon dioxide has been packed during the geological time period. In order to correct the observed ages for marine sediment samples in this study on reservoir effect using a correction factor, an accurate correction factor is necessary, but only a few observations of sea water samples undertaken during earlier studies (1969–1970) in an area that was close to East Ongul Island showed widely different radiocarbon ages of  $2860 \pm 125$  and  $880 \pm 115$  yBP (OMOTO, 1972). Due to these widely varying  $^{14}\text{C}$  age estimates and, therefore, lack of a suitable correction factor for the "reservoir effect" on marine materials from the vicinity of Syowa Station in Lützow-Holm Bay, no corrections were applied in the present study to the  $^{14}\text{C}$  determined age of bulk organic matter in the marine sediment. Taking all these shortcomings into consideration, the estimates of  $^{14}\text{C}$  age in this study could be older than the real calendar age by *ca.* 1000 to 3000 years.

### 3.3. *The contents and compositions of normal alkanes*

Normal-alkane contents in the sediment core varied from 0.16 to 12.2  $\mu\text{g/g}$  dry sediment (Fig. 4). These values are similar to those reported for marine sediments from other regions in the Antarctic and sub-Antarctic (KVENVOLDEN *et al.*, 1987; MACKIE *et al.*, 1978), but are considerably larger than those detected by MATSUMOTO *et al.* (1992) in the vicinity of Syowa Station. Sediment sections at depths of both 45–50 and 90–95 cm in the core which correspond to calculated  $^{14}\text{C}$  ages of *ca.* 8000–9000 yBP (6000–7000 yBP if an age correction factor of *ca.* 2000 yr is applied) had a remarkably high content (11.8  $\mu\text{g/g}$  and 12.2  $\mu\text{g/g}$  respectively) of *n*-alkanes.

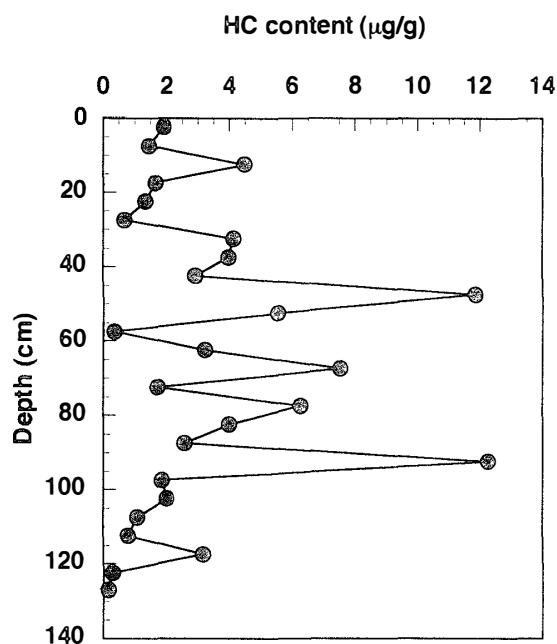


Fig. 4. Vertical profile of hydrocarbon content in the sediment core (Lh-2).

On a geological time scale, the age period of these sediment sections corresponds to the time of rapid warming following the Younger Dryas. It is possible that the productivity of phytoplankton such as diatoms might have dramatically increased during this geological period due to extinction of the thick sea ice covering the ocean surface and due to several other factors related to climate warming.

Since large differences were observed in the *n*-alkane contents within various sections of the sediment core, we compared the relative weights (%) of individual *n*-alkanes between high *n*-alkane-containing sections at depths of 45–50 cm and 90–95 cm with those from the low *n*-alkane-containing sections at depths of 0–5 cm, 55–60 cm and 120–125 cm. Figure 5a shows the relative weights (%) of characteristic *n*-alkanes with chain lengths ranging from  $C_{15}$  to  $C_{33}$ . In the surface sediments (0–5 cm),  $C_{21}$  was dominant, long-chain *n*-alkanes ( $C_{25}$ ,  $C_{27}$ ,  $C_{29}$  etc.) were minor constituents. In the high *n*-alkane-containing section (45–50 cm),  $C_{22}$  and  $C_{23}$  were the dominant *n*-alkanes (Fig. 5b). This unique feature of *n*-alkane distribution was also conspicuous in the other high hydrocarbon-containing section (90–95 cm) of the core. The *n*-alkanes composition of the other low hydrocarbon-containing sections (55–60 cm, 120–125 cm) likewise had a similar pattern of distribution to the surface sediment section.

The contemporary Antarctic region however lacks vegetation like that found in the temperate and tropical zones. Two species of vascular plants have been reported to occur on the Antarctic Peninsula but their distribution is quite sparse (GREENE *et al.*, 1967). Mosses, on the other hand, constitute the major terrestrial vegetation. MATSUMOTO and KANDA (1985) presented an inventory of hydrocarbons in two Antarctic mosses, *Pottia heimii* and *Sarconeurum glaciale*, collected from the McMurdo Sound region. The major hydrocarbon in *Pottia heimii* was  $C_{21}$ . Long-chain *n*-alkanes such as  $C_{27}$  and  $C_{29}$  were also predominant. Although mosses can be

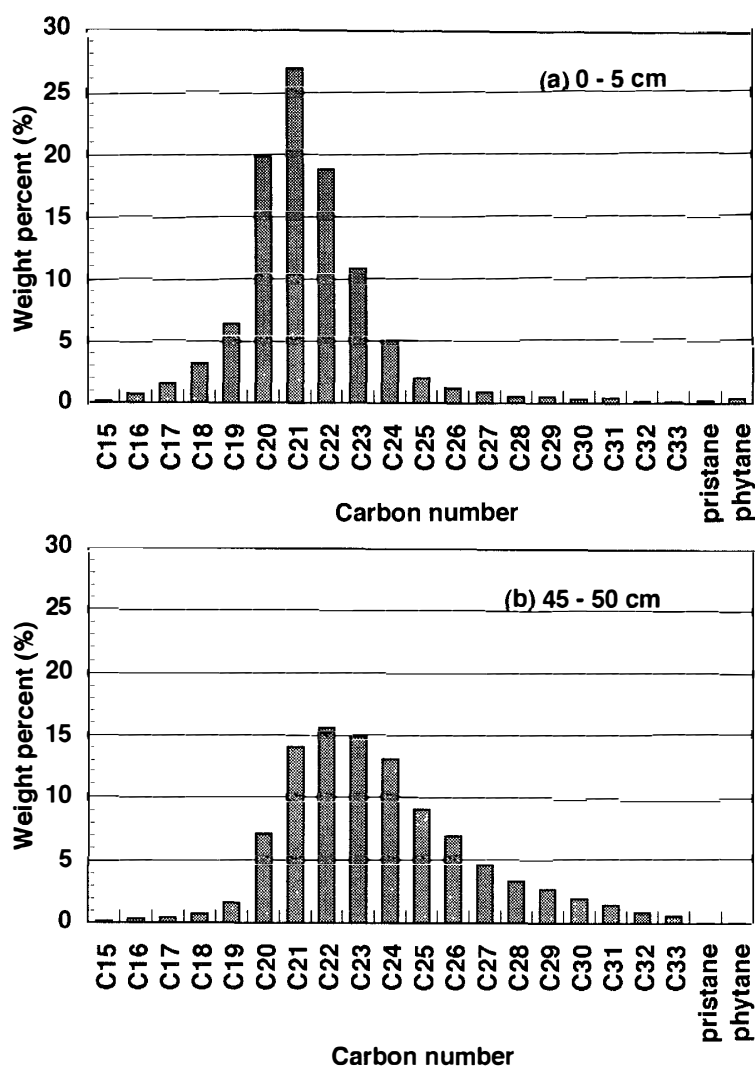


Fig. 5. Relative composition of *n*-alkanes (a) 0–5 cm and (b) 45–50 cm sections in the sediment core (Lh-2).

found in exposed areas of the Antarctic continent close to the present study site, their contribution to the long-chain *n*-alkanes in the sediment is unlikely because they are available only during a limited period of the year, *i.e.* the short summer period, and in very small areas.

In aquatic plants, BLUMER *et al.* (1970, 1971) reported that the diatom *Rhizosolenia setigera*, which is normally found in the coastal regions of high latitude seas, also contains a higher proportion of C<sub>21</sub>, presumably derived from C<sub>21:6</sub> by hydrogenation. Although this species in particular has not been found in Lützow-Holm Bay, the presence of other species of *Rhizosolenia* has been reported from this area (HOSHIAI, 1982). If these *Rhizosolenia* species had a higher proportion of C<sub>21</sub> like *Rhizosolenia setigera*, these marine organisms could likely be the source of *n*-alkanes in certain sections of this sediment core.

In general, marine organisms (phyto and zoo plankton) preferentially synthesize short-chain and odd-carbon numbered *n*-alkanes such as C<sub>15</sub> and C<sub>17</sub> (BLUMER

*et al.*, 1971; CLARK and BLUMER, 1967; GELPI *et al.*, 1970), while terrestrial higher plants contain characteristically long-chain *n*-alkanes with odd-carbon numbers ranging from C<sub>25</sub> to C<sub>33</sub> (CORRIGAN *et al.*, 1973; KVENVOLDEN *et al.*, 1987; MATSUMOTO and KANDA, 1985). On the other hand, it is recognized that bacteria indicate a remarkable even-carbon number preference on short-chain *n*-alkane distribution (NISHIMURA and BAKER, 1986). However, the relative distributions of *n*-alkanes in both high and low hydrocarbon content sections observed in the present study conspicuously did not indicate a significant odd and even-carbon number dominance on *n*-alkane distribution. JOHNSON and CALDER (1973) also reported a similar distribution pattern of *n*-alkanes to our results, and noted that these compounds had undergone significant modification upon being deposited in sediment. According to these authors, the main change in hydrocarbon by diagenesis during geological time was not only alternation of the distribution pattern of *n*-alkanes, but also decrease in the concentration of unsaturated components. KVENVOLDEN *et al.* (1987) also observed the dominance of *n*-alkanes in the range of C<sub>13</sub>–C<sub>22</sub> having only a slight odd-carbon number in marine sediment samples from Antarctica, and attributed this to mixing of primary and recycled compounds derived primarily from marine organisms such as phytoplankton.

In our Antarctic sediment samples, despite the presence of a higher proportion of long-chain *n*-alkanes such as C<sub>27</sub> and C<sub>29</sub> in the high hydrocarbon-containing sections, it seems most likely that the major source of *n*-alkanes in the high hydrocarbon-containing sections is phytoplankton and not mosses. The *n*-alkane distribution in both high and low hydrocarbon-containing sections probably represents a mixture of original *n*-alkanes derived from marine organisms, especially diatoms such as *Rhizosolenia setigera* which have a relatively high proportion of C<sub>21</sub>, and from recycled *n*-alkanes derived from older sediment which have undergone some degree of alternation. This explanation on the source of *n*-alkanes undergoing diagenetic changes is also supported by evidence as follows: (1) unsaturated hydrocarbon components such as branched isoprenoid-C<sub>25</sub> 4 components which are relatively weaker during early diagenesis as compared to *n*-alkanes, have been detected in particulate matter samples in Lützow-Holm Bay, but not in the sediment core sample (Fig. 6), (2) organic carbon, total nitrogen content and <sup>14</sup>C age vertical profiles indicate the occurrence of geological events over geological time.

### 3.4. Isoprenoid alkanes

It is generally believed that isoprenoid hydrocarbons in Antarctic sediments probably come mainly from marine organisms (MATSUMOTO *et al.*, 1992). Pristane (*i*-C<sub>19</sub>; isoprenoid hydrocarbon of carbon number 19) and phytane (*i*-C<sub>20</sub>), two of the most common isoprenoids recorded during previous studies in the Antarctic (VENKATESAN, 1988), were also detected in the sediment core samples of the present study. KVENVOLDEN *et al.* (1987) observed a strong relationship between pristane/phytane ratios and the organic carbon and extractable organic material content of the sediments. KVENVOLDEN *et al.* (1987) reported that the larger ratios of pristane/phytane in sediments which were richer in organic material reflected the



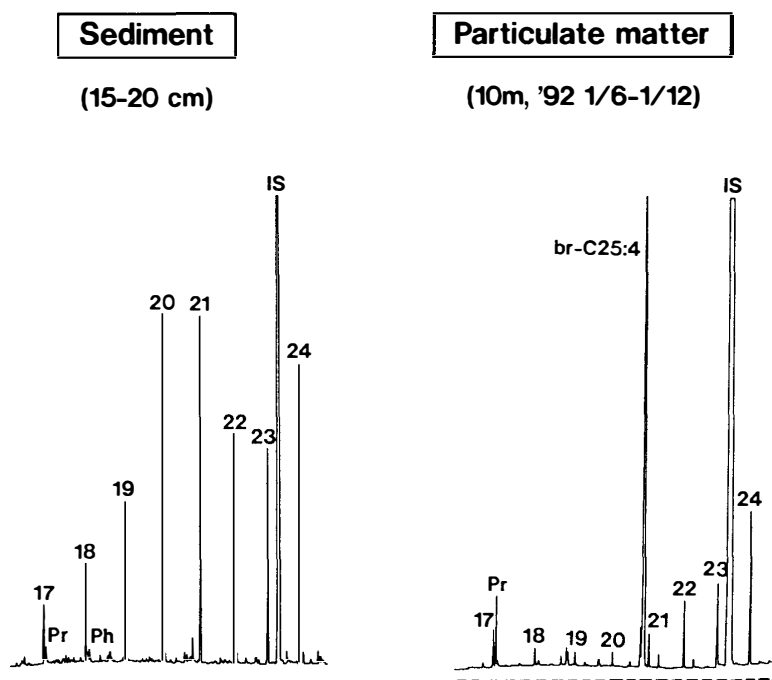


Fig. 6. Partial gas chromatograms of n-alkanes and isoprenoid alkanes in the sediment core (depth of 15–20 cm) and particulate matter sample. Particulate matter sample was obtained by a sediment trap which was settled at 10 m of the water depth in Ongul Strait (69°00'09.4''S, 39°37'37.0''E, water depth: 219 m, sampling period: 1/6/92–1/12/92). The number of each peak indicates the carbon number of each n-alkane. Abbreviations: Pr: Pristane, Ph: Phytane, IS: internal standard, br-C<sub>25:4</sub>: branched isoprenoid alkene of C<sub>25:4</sub>.

preferential input of pristane relative to phytane derived from biomolecules such as phytadienes and chlorophyll. In the water column, MATSUEDA (1986) observed that the pristane/phytane ratios of sinking particles (water depth 1060 m) and suspended particles in a sea water column were 2.1 and 3.3, respectively. These ratios are much higher than the value of 0.8 recorded for marine sediments, suggesting that the pristane/phytane ratio is a useful indicator of the relative degree of alternation or degradation of organic materials during precipitation or sedimentation processes at different depths within the water column and in sea floor sediments.

In Fig. 7, pristane/phytane ratios recorded in the present study seem relatively constant (unity) with depth in the sediment core except for a few lower values at the surface and an unusually high value between 30 and 35 cm. The positive correlation of these ratios with sediment organic carbon content observed by KVENVOLDEN *et al.* (1987) was not seen in the present study. In separate studies it has been reported that pristane and phytane can also be derived from fuel oil sources (MACKIE *et al.*, 1978) and from the degradation of chlorophyll under oxic palaeoenvironmental conditions (DIDYK *et al.*, 1978). These authors provided evidence that anoxic conditions preserve phytane, giving pristane/phytane ratios < 1. On the other hand, it was observed that oxic conditions preserve pristane because pristane is formed

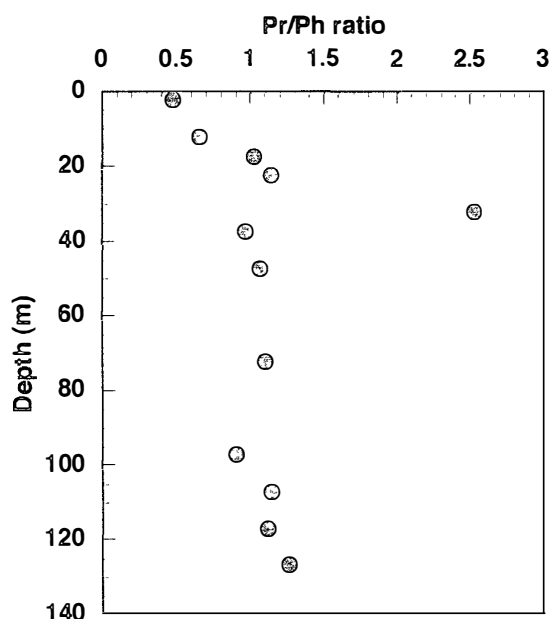


Fig. 7. Vertical profile of Pristane/Phytane ratio in the sediment core (Lh-2).

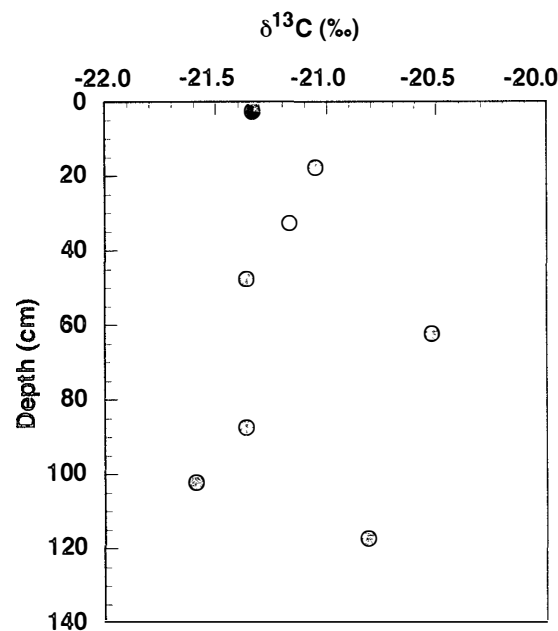


Fig. 8. Vertical profile of  $\delta^{13}\text{C}$  in the sediment core (Lh-2).

from phytol by an oxidative pathway, while phytane is generated through various reductive paths, leading to  $>1$  pristane/phytane ratios. Since the  $n$ -alkane components of Lh-2 sediments (Fig. 5) are very different from those of the fuel oil (MACKIE *et al.*, 1978) it is highly improbable that either pristane or phytane is derived from fuel oil. It is also highly unlikely that any drastic change of oxic and anoxic condition of sediment could have occurred during the past *ca.* 14000 years on account of the close to unity values of the pristane/phytane ratios.

### 3.5. $\delta^{13}\text{C}$ of the bulk organic matter and $n$ -alkanes

Figure 8 shows the vertical distribution of  $\delta^{13}\text{C}$  in bulk organic matter contained in the present sediment core.  $\delta^{13}\text{C}$  found in various organisms are typical of each organism and therefore can be useful to recognize the source of sinking and suspended particles in the water column. Almost all terrestrial  $\text{C}_3$  plants have generally a lower  $\delta^{13}\text{C}$  ( $-26\text{‰}$ ) than most marine phytoplankton ( $-20\text{‰}$ ) (LIBES, 1992).  $\delta^{13}\text{C}$  values in the present study varied from  $-20.5$  to  $-21.6\text{‰}$ , indicating that the major source of organic material was marine. The relatively larger  $\delta^{13}\text{C}$  values of bulk organic carbon in the low hydrocarbon-containing sections as compared to the high hydrocarbon-containing sections may suggest a relatively greater contribution of marine phytoplankton to organic materials in these sections as compared to that in the high hydrocarbon-containing sections of the sediment core.

Table 1 summarizes a comparison of  $\delta^{13}\text{C}$  values of individual  $n$ -alkanes from the high (45–50cm) and low (55–60cm) hydrocarbon-containing sections.  $\delta^{13}\text{C}$  values ranged from  $-26.2$  to  $-28.5\text{‰}$  in the high hydrocarbon-containing section and from  $-26.0$  to  $-28.0\text{‰}$  in the low hydrocarbon-containing sections. Differ-

Table 1.  $\delta^{13}\text{C}$  results of *n*-alkanes in the sediment core (Lh-2).

<i>n</i> -alkane	Depth of section (cm)	
	45–50	60–65
	$\delta^{13}\text{C}^*$ (‰)	
C <sub>17</sub>	–27.3	–27.8
C <sub>18</sub>	–26.4	–26.0
C <sub>19</sub>	–28.2	–29.1
C <sub>20</sub>	–27.3	–27.2
C <sub>21</sub>	–27.5	–27.3
C <sub>22</sub>	–27.7	–27.6
C <sub>23</sub>	–28.0	–28.0
C <sub>24</sub>	–28.2	–27.7
C <sub>25</sub>	–28.3	–27.1
C <sub>26</sub>	–28.2	—
C <sub>27</sub>	–28.0	—
C <sub>28</sub>	–28.5	—
C <sub>29</sub>	–28.0	—
C <sub>30</sub>	–27.4	—
C <sub>31</sub>	–26.2	—
C <sub>32</sub>	–27.0	—
Average	–27.6	–27.5

\*  $\delta^{13}\text{C}$  values of individual *n*-alkanes are measured with the standard error of  $\pm 0.4\text{‰}$ .

ences in  $\delta^{13}\text{C}$  values in the high and low hydrocarbon-containing sections of the sediment core were not appreciable. While the range of  $\delta^{13}\text{C}$  in individual *n*-alkanes indicates that the major source of these compounds is marine organisms, the lack of significant differences in the high and low hydrocarbon-containing sections also means that the biological source of the hydrocarbons in the low and the high hydrocarbon-containing sections of the sediment core are the same. In recent studies, it has been observed that carbon isotopic composition of hexane eluent (hydrocarbon) from total extractable organic material in shale or sinking particles in the Japan Trench is generally lower by 5–6‰ relative to the values for the total extractable organic material (R. ISHIWATARI, pers. commun.). SCHOELL *et al.* (1994) also reported values of carbon isotope compositions of C<sub>27</sub> sterane, which are derived from shallow photic-zone organisms, of –25.4‰. On the other hand, ISHIWATARI *et al.* (1994) reported that the carbon isotope composition of long-chain *n*-alkanes (C<sub>25</sub>–C<sub>33</sub>), which are essentially of higher-plant origin from marine sediment at 171–174 cm depth of the core on the Oki Ridge in the Japan Sea, were in the range from –30.2 to –31.8‰. In the present study,  $\delta^{13}\text{C}$  values recorded for *n*-alkanes are also lower than those recorded for bulk organic carbon and are also well within the range of those recorded for individual *n*-alkanes in marine organisms (ISHIWATARI *et al.*, 1994; HAYES *et al.*, 1987; SCHOELL *et al.*, 1994). Therefore, molecular level  $\delta^{13}\text{C}$  records suggest that the major source of *n*-alkanes both in high and low hydrocarbon-containing sections is marine organisms. Although at present we do not have any data on the carbon isotope composition of *n*-alkanes in Antarctic mosses, we believe that  $\delta^{13}\text{C}$  values of *n*-alkanes in Antarctic mosses are

probably lower relative to those of marine organisms as well as other higher plants and therefore their contribution to hydrocarbons in the sediments of this region is not likely to be large.

#### 4. Summary

Based on OC, TN and hydrocarbon content and  $^{14}\text{C}$  age profiles in the sediment core from Lützow-Holm Bay, we found that a remarkably high content of organic material occurred at 6000–7000 yBP, corresponding to a geological period of global warming.

In previous geochemical studies, short-chain *n*-alkanes included in marine sediments have been generally derived from marine organisms. Long-chain *n*-alkanes, on the other hand, are believed to originate from terrestrial higher plants via river water or aeolian transportation. This conventional interpretation is based on observations of marine sediments in Antarctica (MATSUMOTO *et al.*, 1992) and from observations of world ocean sediments summarized by MATSUEDA (1986). The distributions of *n*-alkanes in this study showed that the source of *n*-alkanes in marine sediment in Lützow-Holm Bay could be a mixture of primary and alternated compounds derived mainly from marine organisms such as diatoms. In addition, on the basis of observations on the carbon isotope composition of *n*-alkanes in the present study, it is evident that the most important source of hydrocarbons in the sediment is most probably marine organisms with a negligible contribution from terrestrial plants such as moss. Since the organic carbon isotope signatures of biomarkers such as hydrocarbons are generally not affected by diagenesis, as long as the basic carbon skeleton and the biological structure of the molecule is preserved, carbon isotope analysis of these compounds can be reliably used to advance our knowledge of the palaeoenvironment.

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