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Latitudinal change of normal paraffin composition in the northwest Pacific sediments

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Abstract

We analyzed normal saturated paraffins (*n*-paraffins) in 70 surface sediments in the northwest Pacific to examine the spatial distribution of organic materials. All sediments show bimodal *n*-paraffin abundance patterns against carbon number with maxima at C₁₆ and C₃₁, indicating that *n*-paraffins in marine sediments are a mixture of long-chain *n*-paraffins from land-based higher plant waxes and short ones from marine organisms. We observed in this study a significant change of carbon preference index (CPI) from 2.5 in low latitudes to 4.5 in mid–high latitudes around 19–25°N. The following influences are discussed as the cause of CPI offset between low and mid–high latitudes: (1) meteorological conditions, (2) *n*-paraffin composition of higher land plants, (3) contribution of petroleum components, and (4) mixing ratio of higher land plants and marine organisms. However, none of them can be the possible cause of the CPI offset. Because *n*-paraffin content and composition vary significantly according to the species of a bacterium, difference of the species of bacterial communities between low and mid–high latitudes may be a possible reason for the CPI offset found in sediment from the northwest Pacific.

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1. Introduction

Marine sediments are an important reservoir of organic carbon, and contain various kinds of organic material (Killops and Killops, 1993; Hunt,

1995). Major components of the organic matter, normal saturated paraffins (*n*-paraffins), are considered to be relatively inert under normal environmental conditions. Marine sediments contain *n*-paraffins which originate from terrestrial higher plants and those of marine organism origin; the former mainly contain long-chain *n*-paraffins with a strong odd carbon predominance, whereas the latter consist mainly of short-chain *n*-paraffins, usually with a high carbon preference index

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(CPI) (e.g. Simoneit, 1977a; Giger et al., 1980). *N*-paraffins released from fuel combustion show a wide range of carbon number with no odd/even carbon predominance (Simoneit, 1984). Analyses of *n*-paraffins in marine sediments, therefore, may give important information on terrestrial organic input to the marine environment, on the input of anthropogenic carbon into the marine environment, and on the circulation of organic matter on the Earth's surface (e.g. Venkatesan and Kaplan, 1982).

The importance of airborne transport of terrestrial materials to the marine environment has been highlighted by mineralogical, isotopic and organic studies of pelagic sediments (e.g. Blank et al., 1985; Asahara et al., 1999; Gagosian and Peltzer, 1986). In contrast to riverine transport of terrestrial materials to marine environments, however, the airborne transport is not evaluated in the global carbon cycle presented by Killops and Killops (1993). This is partly due to the following: (1) previous studies of marine organics have focused on localized areas and the spatial distribution of organic matter in surface sediments is not well known, (2) the contribution of terrestrial organics by airborne transport in the marine reservoir has not been estimated quantitatively.

As a first step to evaluate the importance of airborne transport of terrestrial organics to marine environments, the relationship between *n*-paraffin composition of sediments and their sedimentary environments is discussed in this study. We analyzed *n*-paraffins in 70 surficial marine sediments from a wide area in the northwest Pacific. In order to estimate the contribution of *n*-paraffins contained in higher land plant waxes to Pacific marine environments, we also analyzed *n*-paraffins of leaf waxes of tropical plants from southeastern Asia and central America and those of temperate–subarctic plants from Japan.

2. Experimental

2.1. Samples

Samples for this study are surface sediments collected during cruises GH79-2, GH80-3,

NH90-1, NH91-1, and NH93-1 (Fig. 1 and Table 1). Analyzed sample numbers of the respective cruise are shown in Table 1. Mineralogical composition of samples (Fig. 1) is governed mainly by distance from land, biogenic activity, and water depth. Pelagic NH91-1 and NH93-1 samples are mostly fine-grained yellowish or dark brown clays. Many GH79-2 samples contain scoria and pumice provided probably from active Bonin Islands. GH80-3 samples are sandy silts reflecting proximity of sites to the Japan Islands. Calcareous oozes are recovered from all cruises, except for GH80-3, reflecting shallower water depths than carbonate compensation depth ($CCD \cong 4500$ m).

In addition to the surface sediments, core samples of different burial depths from 4 to 57 cm collected in the southern Philippine Sea (NGC26 during NH91-1; 3°00'N, 135°01'E) were analyzed to evaluate the possible influence of early diagenesis on *n*-paraffin abundance. The core samples are composed mainly of yellowish brown–dark brown clays.

Leaves of tropical plants were provided by Higashiyama Botanical Gardens, Nagoya City, and those of temperate–subarctic plants were provided by the Botanic Garden and Museum, Hokkaido University.

2.2. Analytical method

All samples were dried in a chamber evacuated by a rotary pump without heating and ground into <115 mesh with an agate mortar. The following analytical methods are essentially the same as those of Sugisaki and Mimura (1994) and Yamamoto et al. (1997).

N-paraffins in each 2-g sample were extracted twice by ultrasonication with 15 ml of benzene–methanol (3:2 by volume). After reducing the volume by rotary evaporator, the extract was applied to a silica gel column. A fixed amount of mixed standard containing dodecyl acetate (105 ng), octadecyl acetate (108 ng), and triacontyl acetate (112 ng) was added to the *n*-paraffin fraction eluted by 5 ml hexane. The fraction was condensed by rotary evaporator and analyzed by a Shimadzu GC-9A FID gas chromatograph

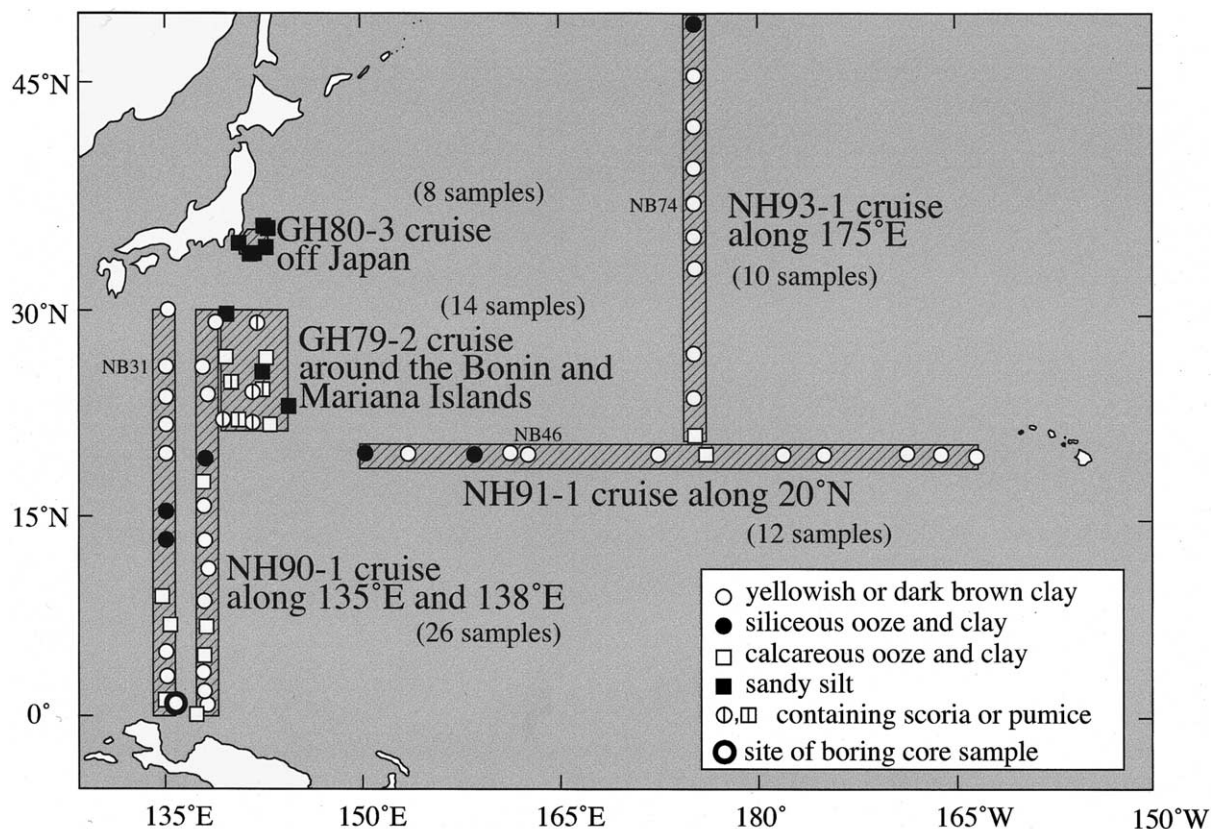


Fig. 1. Location map of surface marine sediments from the north Pacific. Samples were collected by box and piston corers during GH79-2 and GH80-3 by Geological Survey of Japan, and NH90-1, NH91-1, and NH93-1 by New Energy and Industrial Technology Development Organization.

equipped with a 30-m \times 0.25-mm capillary column with a 0.25- μ m layer of TC-5 (5% diphenyl, 95% dimethyl polysiloxane). The temperature program was from 80°C for 10 min to 320°C at 5°C/min followed by 25 min at 320°C. Relative response factors of *n*-paraffins against octadecyl acetate (internal standard) were determined using mixed standard solutions containing octadecyl acetate and applied to the determination of *n*-paraffins. The identification was based on relative retention times against dodecyl, octadecyl and triacontyl acetate obtained by gas chromatography and fragmental patterns obtained by gas chromatography–mass spectrometry (Shimadzu GCMS QP2000). Concentrations of *n*-paraffins with carbon numbers from 11 to 38 and two isoprenoids, pristane and phytane, were analyzed in this study.

N-paraffins with carbon numbers less than 16 can be lost during sample preparation because of their relatively high volatility; a recovery test using mixed standard solutions showed that about 50% of *n*-C₁₁ (*n*-paraffin with carbon number of 11) and about 10% of *n*-C₁₅ were lost during the procedure. In the following discussion, these losses were not corrected for because of the lack of reproducibility of the recovery test. Since we focus mainly on CPI values calculated for *n*-paraffins with carbon numbers from 24 to 34, the volatility of short-chain *n*-paraffins is not a serious problem.

N-paraffins in leaf waxes were extracted by washing with double-distilled hexane. After reducing the volume by rotary evaporator, the extract was applied to a silica gel column. The subsequent

Table 1
Sampling locations, water depths, and average *n*-paraffin compositions

| | NH90-1 | NH91-1 | NH93-1 | GH79-2 | GH80-3 |
|---------------------------------------|-----------------|---------------------|----------------------|---|--|
| Covering area | Philippine Sea | transect along 20°N | transect along 175°E | boundary area of the Mariana and Bonin arcs | northern margin of the Bonin Arc off Japan |
| Number of samples | 26 | 12 | 10 | 14 | 8 |
| Latitude | 0–30°N | 20°N | 21–48°N | 22–30°N | 34–36°N |
| Longitude | 135°E and 138°E | 150°E–164°W | 175°E | 139–143°E | 141–143°E |
| Water depth (m) | 2990–5850 | 3450–5580 | 2510–5910 | 830–3850 | 1890–7190 |
| Total <i>n</i> -paraffin ^a | 430 ± 270 | 390 ± 130 | 550 ± 180 | 160 ± 56 | 670 ± 300 |
| LPs ^a | 210 ± 150 | 200 ± 57 | 390 ± 150 | 94 ± 48 | 390 ± 150 |
| SPs ^a | 170 ± 150 | 170 ± 94 | 120 ± 58 | 48 ± 31 | 210 ± 160 |
| LP/SP ratio | 1.8 ± 1.5 | 1.9 ± 2.1 | 4.4 ± 3.0 | 2.8 ± 2.2 | 2.6 ± 2.1 |
| CPI | 3.2 ± 1.3 | 4.5 ± 1.2 | 4.5 ± 0.9 | 3.8 ± 1.2 | 4.3 ± 0.4 |

The LPs, SPs, and CPI are the mean total amounts of long-chain *n*-paraffins (C₂₄–C₃₄), that of short-chain ones (C₁₄–C₂₃), and carbon preference index, respectively. Sedimentation rate varies largely reflecting the morphology, distance from land, organic activities, etc. of the sampling site on each cruise.

^a Presented in ng/g dry sediment.

procedures are the same as those for marine sediments.

A gas chromatographic record of total procedure blank is shown in Fig. 2. Phthalate esters (P.E. in Fig. 2) and anonymous compounds are contaminated during the analytical procedure. However, most of these have different retention times from those of *n*-paraffins. Contaminants having possibility of interference for the *n*-paraffin determination are shown by asterisks in Fig. 2. From the intensities of these peaks relative to the internal standard, the detection limits can be estimated to be 2 ng *n*-paraffin/g dry sediment.

3. Results

3.1. Abundance patterns of *n*-paraffins

Gas chromatographic records of selected samples from different sedimentary environments are shown in Fig. 2. All samples contain *n*-paraffins with a highest peak at *n*-C₃₁. Lower molecular weight *n*-paraffins show no clear odd-to-even number predominance, whereas higher ones show a strong predominance. All samples show a hump of unresolved complex mixture of paraffins to a greater or lesser extent.

Table 1 and Fig. 3 show averaged analytical

results and abundance patterns of *n*-paraffins against carbon number, respectively, for each sampling cruise. The patterns show a bimodal distribution characterized by two highest peaks at C₁₆ and C₃₁ (Fig. 3).

3.1.1. Long-chain *n*-paraffins (LPs; C₂₄–C₃₄)

Since terrestrial higher plant waxes are generally characterized by LPs with a strong predominance of odd carbon numbers (e.g. Simoneit, 1977a; Giger et al., 1980), the LPs observed in the marine samples may originate from land plants. They could be transported to the sampling site by the atmosphere or rivers (e.g. Gagosian and Peltzer, 1986; Schlünz and Schneider, 2000). The importance of airborne transport of organic materials has been assessed by analyses of *n*-paraffins and fatty acids in aerosols and marine sediments (Gagosian and Peltzer, 1986; Ohkouchi et al., 1997). An airborne transport of Asian loess to the Central Pacific sediment was also suggested by Sr isotopic data (Asahara et al., 1999).

3.1.2. Short-chain *n*-paraffins (SPs; C₁₄–C₂₃)

The SPs have usually been attributed to marine organisms. According to Blumer et al. (1971) and Hunt (1995), marine plants and algae are characterized by SPs with a strong odd carbon number predominance. Since present samples do not show

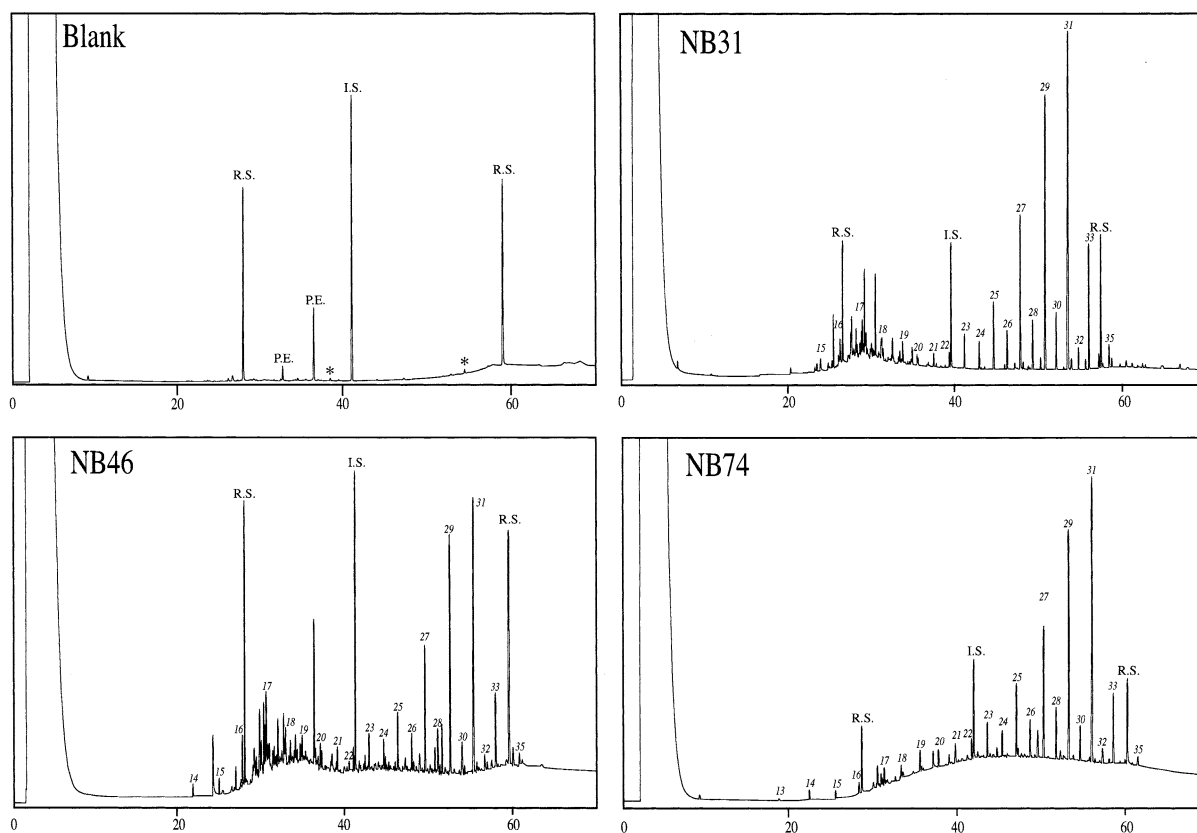


Fig. 2. Chromatograms of total blank and selected samples. I.S. denotes internal standard and R.S. reference standard for check of retention times of analyzed *n*-paraffins. Numbers in the chromatogram show chain length of *n*-paraffins. Asterisks in blank chromatogram show peaks having potential of interference for *n*-paraffin determination. Sampling location of each sample is shown in Fig. 1.

the odd carbon number predominance and many of them have a highest peak at C₁₆, the SPs in these samples cannot be attributed only to such marine organisms. Marine sediments with the highest peak at C₁₆ have also been reported from the Indian Ocean, the coast of Chile and other regions (Littke et al., 1991; Kvenvolden et al., 1995).

On the other hand, the occurrence of C₁₄–C₂₀ *n*-paraffins with even carbon preference has been recognized in the Gulf of Mexico and Davis Strait (Nishimura and Baker, 1986; Grimalt and Albaigés, 1987). On the basis of compositional features of *n*-paraffin, *n*-fatty acid and *n*-alcohol distributions, Nishimura and Baker (1986) concluded that the even-predominant *n*-paraffins are derived directly from marine bacteria. The

smooth abundance peak in the short-chain range for the present samples may suggest that the SPs are derived from bacteria as well as algae, as discussed in detail later.

3.2. Distribution of *n*-paraffins in the northwest Pacific

The northwest Pacific sediments show total amounts of *n*-paraffins ranging from 50 to 1000 ng/g. Sediment samples from the central Philippine Sea and around the Bonin Islands have low *n*-paraffin concentrations (Fig. 4A). In the latter region, volcanic fragments such as pumice and scoria are scattered in sediments (Fig. 1). These volcanic materials contain scarce amounts of *n*-paraffins. Therefore, the low abundance of

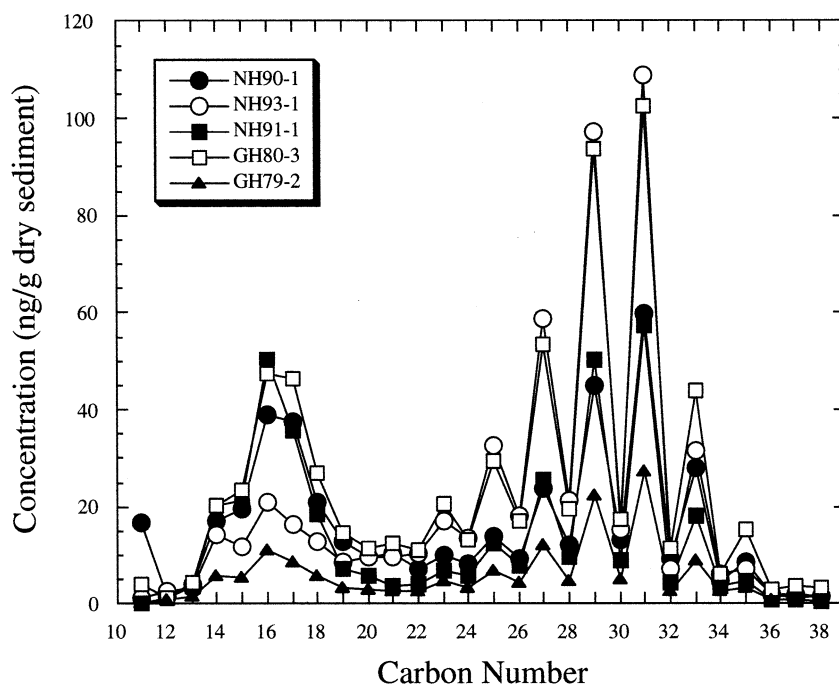


Fig. 3. Abundance patterns of *n*-paraffin in sediments from the northwest Pacific Ocean. Analytical data were averaged and plotted for each cruise. Note that all patterns show a bimodal distribution with peaks at C_{16} and C_{31} .

n-paraffins can be ascribed to the dilution effect by volcanic materials. In contrast, the reason for the low content of *n*-paraffins in sediments from the central Philippine Sea could not be clarified in this study.

Marine *n*-paraffins can mainly be derived from higher land plants and marine organisms. In order to estimate the relative contribution of these two sources, the lateral distribution of the LP/SP ratio was plotted (Fig. 4B). Since the sediments from the northern Pacific and off Japan show high ratios of LPs/SPs, the high *n*-paraffin concentrations in these areas are attributed to the large contribution of land-derived *n*-paraffins (e.g. Kawamura, 1995). In contrast, sediments off Papua New Guinea show high *n*-paraffin concentrations, but they have low LP/SP ratios. Therefore, the high concentrations are probably caused by high productivity of marine organisms. This inference is consistent with the fact that the equatorial area off Papua New Guinea shows high sedimentation rates due to high organic productivity (Geological Survey of Japan, 1984). Relatively high *n*-paraffin

concentrations found in sediments along 20°N are also ascribed to a large contribution of marine organisms because of the low LP/SP ratio.

The total amount of *n*-paraffins was plotted against the sampling latitude (Fig. 5); the higher the sampling latitude, the higher the total *n*-paraffin concentration, except for a small area near the equator. In Fig. 3, LPs with odd carbon numbers (C_{27} , C_{29} , and C_{31}) show extremely high abundances. The total amount of LPs clearly correlates with that of all *n*-paraffins ($\gamma=0.902$). This shows that the increase in the total amount of *n*-paraffins toward high latitudes is caused mainly by the increase of LPs. Ohkouchi et al. (1997) also reported an increase of LPs toward high latitudes.

3.3. Influence of early diagenesis on *n*-paraffin composition

In order to observe the influence of early diagenesis on *n*-paraffin composition, four boring core samples with different burial depths from 4

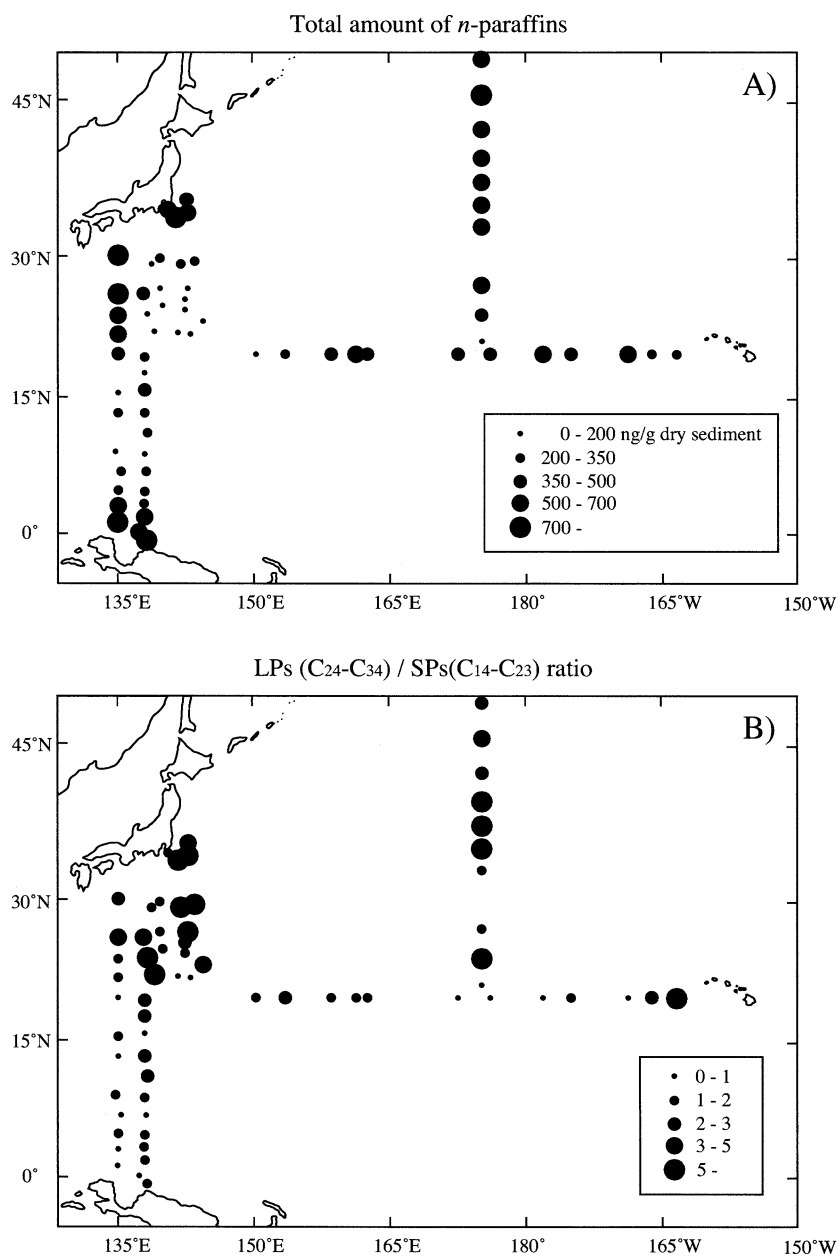


Fig. 4. Lateral distribution of (A) the total amounts of *n*-paraffins and (B) the LP/SP ratio.

to 57 cm were analyzed and chromatograms are shown in Fig. 6. Abundance patterns of *n*-paraffin in the core samples are similar to each other, though concentrations of both LPs and SPs and the LP/SP ratio tend to be higher toward deeper horizons. Nishimura and Baker (1986) reported

that as *n*-paraffins with a striking odd carbon number predominance suffer diagenetic alteration at the early stage of the sedimentation process, the odd predominance disappears and the ratio of odd-to-even *n*-paraffins generally tends to approach unity. Then, the odd predominance must

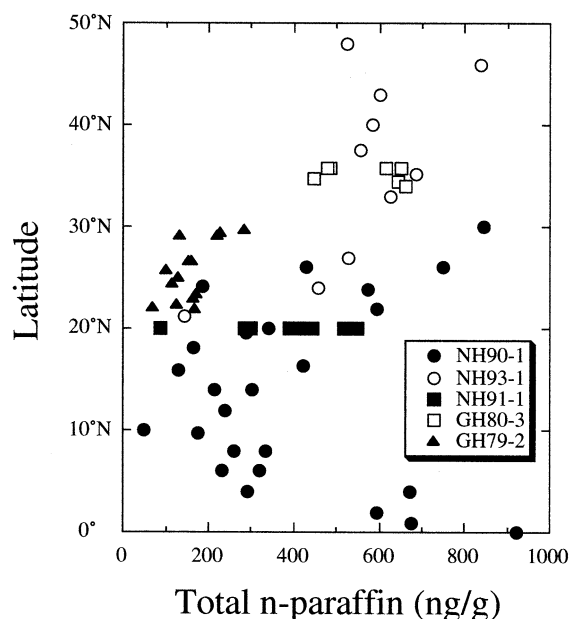


Fig. 5. Latitudinal distribution of the total amount of *n*-paraffins.

be lowered with increasing burial depth. CPIs (defined below) of the samples range from 2.04 to 2.92, but show no clear decreasing trend toward deep horizons. This suggests that severe modifications of *n*-paraffin composition have not occurred in these samples probably because of shallow burial depth. Then we will discuss the distribution and origin of *n*-paraffins in surface sediments from the northwest Pacific without considering modification of *n*-paraffin composition by early diagenetic processes.

4. Discussion

4.1. Variation of CPI value against latitude

The CPI is a useful parameter to discuss the origin of *n*-paraffins and the maturation degree of organic materials (e.g. Anders and Robinson, 1973; Simoneit, 1977a). In order to investigate the latitudinal variation of CPI values, the value for LPs (C_{24} – C_{34}) is calculated by the following equation and is plotted against latitude in Fig. 7:

$$CPI = 2 \times \sum_{n=12}^{16} C_{2n+1} \div \left(\sum_{n=12}^{16} C_{2n} + \sum_{n=13}^{17} C_{2n} \right)$$

The averaged value of samples collected from latitudes below 19°N is 2.52 ± 0.65 , whereas those higher than 25°N have a CPI of 4.47 ± 0.53 (Table 2). The value in the intermediate region from 19°N to 25°N is between the two values and shows a large fluctuation (4.14 ± 1.38). If we postulate two end member components for the *n*-paraffins, we can regard *n*-paraffins in the intermediate region as a mixture of one component with high CPI found in high latitudes and another with low CPI in low latitudes. But what causes the gap in the CPI value between low latitude and middle–high latitude?

The following influences may cause the CPI difference between low and mid–high latitudes: (1) meteorological conditions, (2) *n*-paraffin composition of higher land plants, (3) contribution of petroleum components, and (4) mixing ratio of higher land plants and marine organisms. We discuss these possibilities below.

4.2. Meteorological conditions

A large offset of CPI values has also been reported to occur between 19°N and 15°N in the central Pacific along the 175°E transect (open triangles in Fig. 7; Ohkouchi et al., 1997). Because the area where the offset occurs corresponds to the boundary between westerly and trade wind regimes, Ohkouchi et al. (1997) ascribed the offset to the difference in meteorological conditions. Since westerlies over the north Pacific transport continental materials from Asia and trade winds from North and Central America (Gagosian and Peltzer, 1986), *n*-paraffin composition in aerosols from Asia may be different from those from the Americas.

This interpretation cannot be applied to the NH90-1 sediments from the Philippine Sea. Schlünz and Schneider (2000) reported that much terrestrial organic carbon is transported into the Philippine Sea through rivers from the Asian Continent. However, the same increase in CPI values is found in the NH90-1 samples (closed circles in Fig. 7) as in central Pacific sedi-

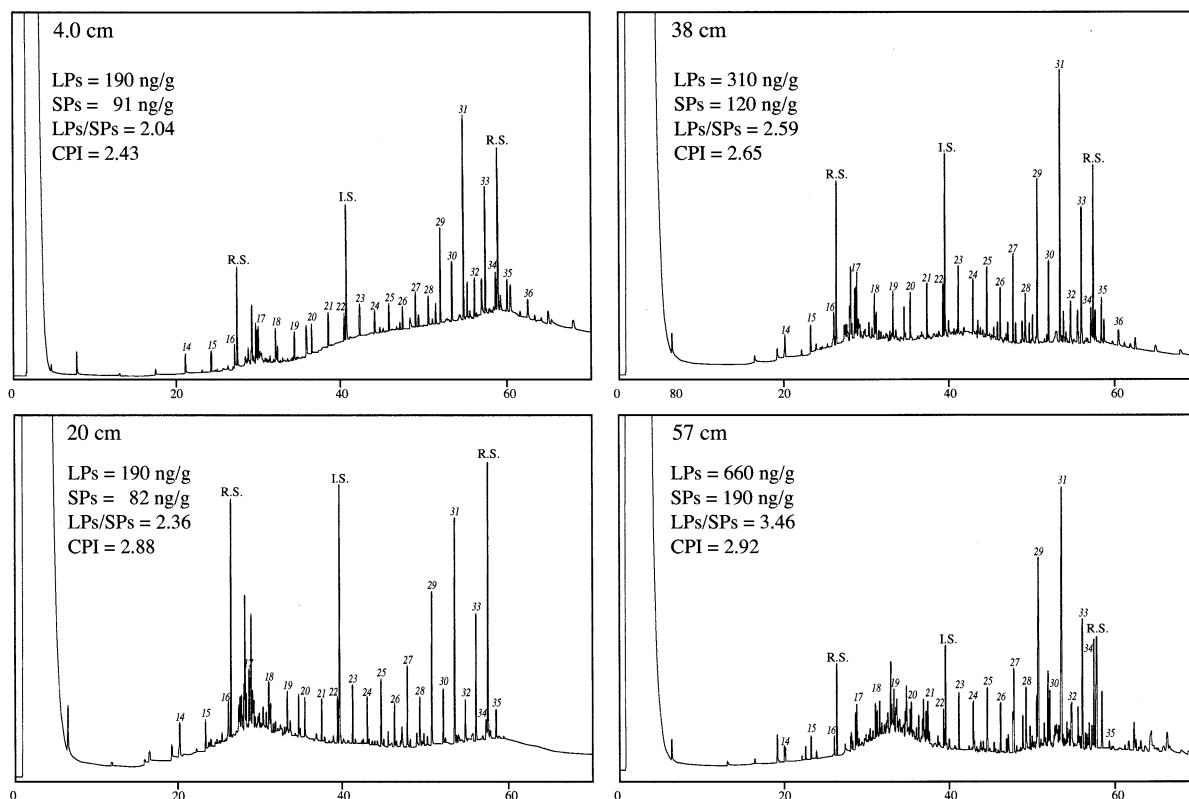


Fig. 6. Chromatograms of core samples with burial depths from 4 to 57 cm. This core is located in the southern Philippine Sea and has a high sedimentation rate of about 100 mm/kyr. LPs indicate total amounts of *n*-paraffins with chain lengths from 24 to 34, SPs are total amounts of *n*-paraffins with chain lengths from 14 to 23. The CPI value is calculated by the equation indicated in the text. I.S. denotes internal standard and R.S. reference standard for check of retention times of analyzed *n*-paraffins. Numbers in the chromatogram show chain lengths of *n*-paraffins.

ments. Therefore, the difference of *n*-paraffin composition of aerosols from Asia and from the Americas cannot explain the CPI offset found in NH90-1 samples. These facts may suggest that the CPI offset is caused by the difference of wax *n*-paraffin composition of hinterland higher plants between tropical and temperate-subarctic areas.

4.3. Composition of land plant waxes

Source variation in *n*-paraffin composition of higher land plants must be taken into account for the present case. The source variation likely results from environmental differences; generally, the lower latitudes show higher temperature and humidity than do the higher latitudes. According to Simoneit (1977b) and Simoneit et al. (1991),

the molecular weights of the *n*-paraffins synthesized by plants tend to be higher as the ambient temperature increases; *n*-paraffin compositions of our samples may thus reflect differences in vegetation. To decide if this is true, we analyzed *n*-paraffins in leaf waxes of tropical and temperate-subarctic plants (Table 3). All plant waxes show a strong odd carbon predominance with maximum abundance at C₂₉ or C₃₁, except for two subarctic pine trees with a maximum at C₂₃ (*Picea jazoensis* var. *jazoensis* and *Abies sachalinensis* Mast.). Eight tropical plants having their main habitat in northern Brazil, central America, and southeastern Asia show a range of CPI value from 3.50 to 10.62 (average = 6.27), whereas three temperate-subarctic plants in Japan are in the range from 2.84 to 4.26 (average = 3.52). On the

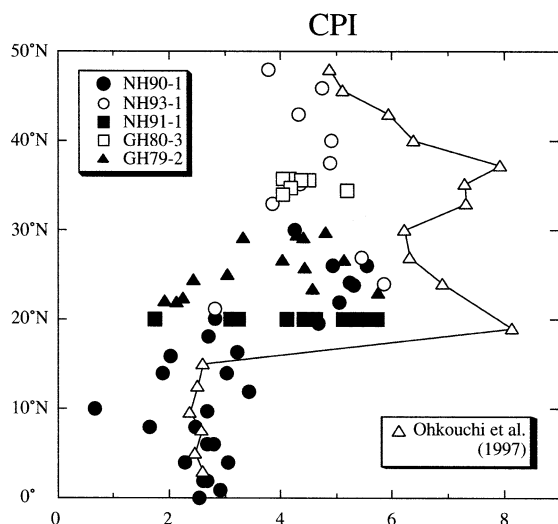


Fig. 7. Latitudinal distribution of CPI for long-chain *n*-paraffins (C_{24} – C_{34}). The CPI value is calculated by the equation indicated in the text. Data for sediments along 175°E shown by open triangles are quoted from Ohkouchi et al. (1997). Both data in this study and Ohkouchi et al. (1997) show a significant change of CPI around 20 – 25°N . The difference of CPI values between this study and Ohkouchi et al. (1997), especially for that found at 19 – 50°N , may be caused by differences in the analytical method such as extracting solvent and saponification.

basis of the present results as well as data reported by Hunt (1995), no significant difference in CPI value can be found between tropical and temperate–subarctic plants. Hence, the difference of *n*-paraffin compositions of terrestrial plants appears not to be responsible for the CPI difference.

4.4. Contribution of the petroleum component

Simoneit et al. (1991 and references therein) studied extractable organic matter in aerosols

and reported that a petroleum combustion component is contained in aerosols from various localities. In contrast, Venkatesan and Kaplan (1982) proposed petroleum seepage from deeper to surface sediments in the Bering Sea. Since *n*-paraffins of both petroleum components generally have a CPI of about unity, the contribution of the petroleum component to marine sediments lowers the CPI values. If the degree of contribution is different between low and mid–high latitudes, the petroleum component may be the cause of the CPI gap.

Westerlies over the north Pacific transport continental materials from Asia (Gagosian and Peltzer, 1986). Eastern Asia, especially Japan and China, is a mass consumption area of petroleum. During airborne transport, organic matter is enriched in smaller aerosol particles usually less than $1\ \mu\text{m}$ (Zenchelsky et al., 1976), whereas mineral aerosols are reported to be larger and its median is several micrometers (Duce et al., 1983). Because of this difference in aerosol size, smaller size lipid-rich particles stay in the atmosphere longer than the mineral particles (Slinn and Slinn, 1980). Ohkouchi et al. (1997) concluded that the fine organic aerosols from eastern Asia are transported to the higher latitudes up to the Arctic and subarctic regions whose ambient temperatures are low enough to act as a cold sink. These observations suggest that the petroleum combustion component from eastern Asia is delivered to high latitudes of the Pacific Ocean. If this were the case, sediments from higher latitudes should show lower CPI values than samples from lower latitudes, because the contribution of petroleum *n*-paraffins lowers the CPI values of sediments. This is apparently in contrast to the present results. On the other hand, the difference

Table 2
N-paraffin compositions according to the depositional latitude (D.L.)

| | D.L. $\leq 19^{\circ}\text{N}$ | $19^{\circ}\text{N} < \text{D.L.} \leq 25^{\circ}\text{N}$ | $25^{\circ}\text{N} < \text{D.L.}$ |
|---------------------------------------|--------------------------------|--|------------------------------------|
| Total <i>n</i> -paraffin ^a | 390 ± 280 | 310 ± 170 | 520 ± 280 |
| LP _s ^a | 170 ± 110 | 170 ± 95 | 340 ± 170 |
| SP _s ^a | 190 ± 170 | 120 ± 90 | 130 ± 110 |
| LP/SP ratio | 1.24 ± 0.65 | 2.29 ± 2.5 | 3.53 ± 2.2 |
| CPI | 2.52 ± 0.65 | 4.14 ± 1.38 | 4.47 ± 0.53 |

^a Presented in ng/g dry sediment.

Table 3
Analytical results of leaf wax *n*-paraffins of tropical and temperate plants

| Botanical name | Main habitat | C ₁₇ | C ₁₈ | C ₁₉ | C ₂₀ | C ₂₁ | C ₂₂ | C ₂₃ | C ₂₄ | C ₂₅ | C ₂₆ | C ₂₇ | C ₂₈ | C ₂₉ | C ₃₀ | C ₃₁ | C ₃₂ | C ₃₃ | C ₃₄ | C ₃₅ | C ₃₆ | C ₃₇ | C ₃₈ | CPI | |
|---|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------|------|
| <i>Asclepias curassaviaca</i> L. | central America | | | | | | | | | 1.2 | 3.6 | 3.6 | 1.2 | 16.9 | 4.5 | 45.3 | 3.6 | 17.0 | | 3.3 | | 1.4 | | 9.02 | |
| <i>Aristolochia gigantea</i> Mart and Zucc. | northern Brazil | | 1.4 | 2.9 | 1.4 | 3.6 | 1.5 | 21.0 | 2.9 | 41.3 | 3.0 | 19.3 | | | | | | | | | | | | 10.62 | |
| <i>Bruguiera gymnorrhiza</i> Lam. | southeastern Asia | | | | | | | | | | 23.4 | 6.8 | 42.4 | 7.6 | 17.3 | 1.0 | | | | | | | | | 5.59 |
| <i>Ficus microcarpa</i> L.f. | southeastern Asia | | | | | | | | | | 20.3 | 3.5 | 46.2 | 6.8 | 22.1 | | | | | | | | | | 8.65 |
| <i>Terminalia catappa</i> L. | southeastern Asia | | | | | | | | | 1.3 | 3.1 | 4.0 | 19.4 | 6.8 | 36.0 | 9.6 | 17.2 | | | | | | | | 3.50 |
| <i>Barringtonia asiatica</i> (L.) Kurz | southeastern Asia | | | | | | | | | 1.6 | 2.9 | 8.3 | 6.5 | 22.0 | 4.2 | 40.2 | 3.0 | 10.2 | | | | | | | 4.95 |
| <i>Mangifera indica</i> L. | southeastern Asia | | | | | | | | 1.1 | 3.1 | 1.1 | 5.4 | 1.8 | 11.7 | 3.4 | 19.1 | 6.1 | 16.1 | 4.2 | 12.3 | 2.9 | 8.5 | 2.4 | | 3.83 |
| <i>Ficus benjamina</i> L. | southeastern Asia | | | | | | | | | | | 2.9 | 1.4 | 18.0 | 4.5 | 41.2 | 7.8 | 24.3 | | | | | | | 6.29 |
| <i>Camellia japonica</i> L. | Ryukyu, Japan | | | | | | | | | 1.1 | 4.6 | 4.9 | 10.9 | 8.5 | 31.3 | 9.3 | 23.2 | 2.2 | 2.8 | | | | | | 2.84 |
| <i>Picea jazoensis</i> var. <i>jazoensis</i> | Hokkaido, Japan | 1.9 | 3.0 | 2.8 | 2.9 | 8.2 | 5.5 | 29.7 | 4.5 | 14.0 | 2.9 | 7.9 | 2.1 | 8.6 | 1.1 | 2.6 | | | | | | | | | 3.99 |
| <i>Abies sachalinensis</i> (F. Schmidt) Mast. | Hokkaido, Japan | 1.0 | 1.7 | 2.0 | 1.9 | 8.2 | 8.4 | 32.5 | 5.8 | 14.7 | 3.0 | 10.0 | 1.5 | 5.6 | | 1.6 | | | | | | | | | 4.26 |

The values shown are the percentages of total *n*-paraffins. Values less than 1.0% are not shown.

in the contribution of petroleum seepage from deeper horizons to surface sediments is unlikely to be the reason for the offset of CPI values between low and mid–high latitudes, though no data are available at this moment. Hence, the difference in contribution degree of the petroleum component is probably not responsible for the present CPI difference.

4.5. Mixing of *n*-paraffins from marine organisms and land plants

4.5.1. Algal source

In normal marine environments, marine algae and higher land plants are considered to be the main source of *n*-paraffins in sediments. Damsté et al. (1995) calculated the composition of molecular markers contributing to the organic matter of marl beds in an Italian Messinian evaporitic basin, and reported that marine algae and higher land plants are the dominant contributors and account for >75% of the total.

As shown in Table 2, sediments with low CPI values from low latitudes contain more SPs and fewer LPs than do sediments with high CPI values from high latitudes. It is therefore possible that a large contribution of marine organic matter lowers the CPI values. If this were the case, a positive correlation between CPI value and LP/SP ratio must be found, because LPs and SPs are mainly derived from terrestrial higher plant and marine organisms, respectively (Simoneit, 1977a; Giger et al., 1980; Killops and Killops, 1993; Hunt, 1995). However, we can find no clear correlation between them (Fig. 8A). Sediments with high CPI values from 4 to 6 show a wide variation of the LP/SP ratio from 1 to 9. This means that the gap of CPI value cannot be explained by a difference of mixing degree between terrestrial *n*-paraffins and algal ones.

4.5.2. Bacterial source

The CPI value positively correlates with C₃₁/C₂₂ ratio (Fig. 8B), especially for NH90-1 samples (closed circles; $\gamma=0.908$). The C₃₁ originates mainly from higher plants, whereas the C₂₂ is scarcely contained in marine algae and higher plants (e.g. Hunt, 1995; Blumer et al., 1971), ex-

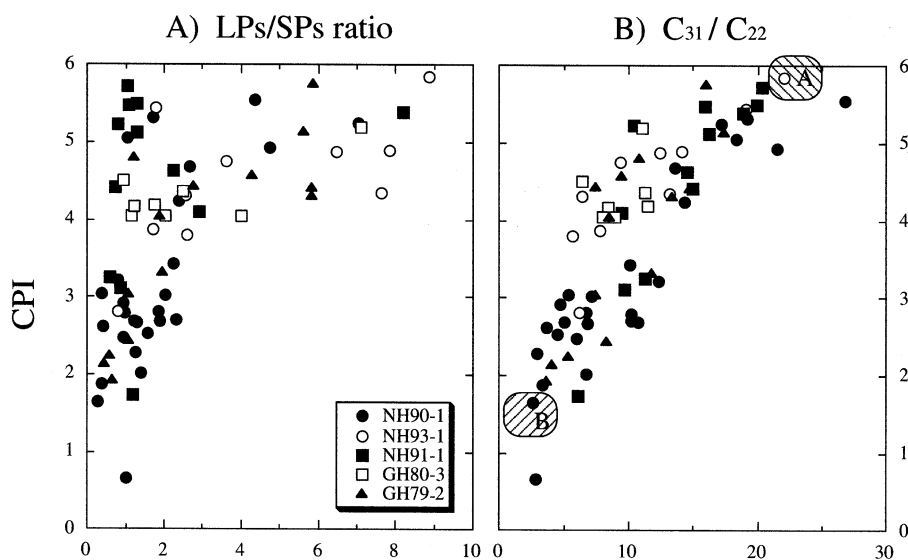


Fig. 8. Correlation diagrams of CPI value against (A) LP/SP ratio and (B) C_{31}/C_{22} ratio. The C_{31}/C_{22} ratio shows a stronger correlation with the CPI value than does the LP/SP ratio. Shaded areas A and B in panel B show the ideal compositions of end members, when the linear trend is regarded as a result of mixing of two components.

cept for two pine trees analyzed in this study. Sediments in this study, however, show high C_{22} concentrations ranging from 0.73 to 27.3 ng/g (average = 6.73 ± 5.83 ng/g), which are about one-tenth of the C_{31} concentrations (64.7 ± 43.8 ng/g). These facts suggest that the marine sediments under consideration contain other n -paraffin components than those from land-based higher plants and marine algae, and that a third component contributes to the CPI value.

If we regard the linear trend in Fig. 8B as a result of mixing of two components, one has high CPI values and C_{31}/C_{22} ratios about 6 and 25, respectively (component A), and the other has low values and ratios about 1.5 and 3, respectively (component B). Higher land plants may be responsible for the former component (A). What then is responsible for the latter component?

Hayakawa et al. (1996) and Ternois et al. (1998) reported that marine sinking particles at Freid Bay and Southern Ocean, respectively, contain n -paraffins distributed from C_{20} to C_{35} with low CPI values from 1.0 to 1.9. Hayakawa et al. (1996) suggested that the major source of the n -paraffins in the sinking particles is marine organisms such as algae and bacteria living in surface

waters. Since marine algae are known to produce odd-numbered short-chain n -paraffins such as C_{15} and C_{17} , Ternois et al. (1998) proposed a marine source other than algae.

Some species of bacteria may be candidates for the latter component (component B in Fig. 8B). According to Davis (1968), Han and Calvin (1969) and Hunt (1995), some bacteria contain LPs with no odd–even predominance, though the LP content varies significantly according to the species of a bacterium. Our sediments apparently contain SPs not only from an algal source, but also from a bacterial source. Bacterial input of LPs with no odd–even predominance to sediments must simultaneously lower the CPI value and the C_{31}/C_{22} ratio. Hagström and Larsson (1984) and Lovejoy et al. (2000) reported that the growth rate and productivity of bacteria are positively correlated with water temperature in the euphotic zone. The average temperature of surface seawater at low latitudes is about 10°C higher than that at mid latitudes (Libes, 1992), giving rise to a higher growth rate and productivity of bacteria at low latitudes. The difference in productivity of bacterial communities between tropical and temperate–subarctic ocean environ-

ments may thus cause the offset of CPI values. However, average temperatures of surface seawater decrease gradually toward high latitudes from the equatorial region and do not show an abrupt change around 19–25°N, suggesting a gradual decrease in bacterial activity toward higher latitudes. Therefore, the difference in productivity of bacterial communities is unlikely to be the reason for the CPI offset.

From the above discussion, we could not clarify the cause of the CPI offset found around 19–25°N. On the contrary, the LP composition and content vary significantly according to the species of a bacterium (Davis, 1968; Han and Calvin, 1969; Hunt, 1995). Though the detailed distribution of bacterial species in the Pacific region has not been reported to date, it can be considered that species of bacterial communities are different between tropical and temperate–subarctic ocean environments as is the case for land higher plants. If this is the case, *n*-paraffins supplied from bacterial communities to sediments are different between tropical and temperate–subarctic oceans. However, this is only a possibility that can explain the CPI offset. To ascertain this, the distribution of bacterial communities and their *n*-paraffin composition must be clarified in the future.

5. Conclusion

In this study, we analyzed 70 surface marine sediments from a wide area of the north Pacific to find the distribution of *n*-paraffins in the marine region. The following patterns in the latitudinal distribution of *n*-paraffins emerged from this study: (1) *n*-paraffin contents of sediments increase from low latitudes toward high latitudes, owing to the increase of land-derived long-chain *n*-paraffins; (2) a significant change of CPI of long-chain *n*-paraffins from 2.5 to 4.5 is found around 19–25°N.

This change of CPI values between low and mid latitudes can be explained neither by a change in mixing ratio of *n*-paraffins from terrestrial sources and algal sources, nor by the different meteorological conditions. The offset found in sediments from the Philippine Sea may be as-

cribed to the difference of leaf wax *n*-paraffin composition of land-based higher plants between tropical and temperate–subarctic areas because of a large contribution of terrestrial materials. Analyses of leaf waxes of higher land plants from both areas, however, show no significant difference in CPI value.

The CPI value positively correlates with the C_{31}/C_{22} ratio in the sediments analyzed here. This suggests a contribution of a source rich in $n-C_{22}$ that is neither terrestrial nor algal in origin. This component probably contains LPs with a wide range of carbon numbers and without odd–even carbon predominance and can derive from some species of marine bacteria. The difference in species of bacterial communities between tropical and temperate–subarctic ocean environments may be the cause for the offset in CPI value found in sediments of the Pacific Ocean.

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