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# Detection of mono- and bicyclic alkanes and their characteristics in Neogene sediments of the Shinjo basin, Japan

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Forty five mono- and 12 bicyclic alkanes were detected in a sedimentary sequence from Miocene to Pliocene in the Shinjo basin, northeastern Japan. The monocyclic alkanes included polyalkylcyclohexanes ($C_9$, $C_{10}$, $C_{11}$, and $C_{13}$), a series of *n*-alkylcyclohexanes ($C_9$–$C_{26}$) and a series of *n*-alkylcyclopentanes ($C_{12}$–$C_{26}$). The bicyclic alkanes were from $C_9$ to $C_{12}$, including *cis*- and *trans*-hydrindanes, *cis*- and *trans*-decalins, and methyl- and dimethyldecalins. These cyclic alkanes were detected at a level of 0.01–1 nmol $g^{-1}$. Concentrations of 2-alkyl-1,1,3-trimethylcyclohexanes ($C_{11}$ and $C_{13}$), a major portion of *n*-alkylcyclohexanes ($C_{11}$–$C_{26}$), all *n*-alkylcyclopentanes, and methyl- and dimethyldecalins showed a maximum in the lower part of the sequence which has been known to be an oil generation zone. *n*-Alkane ($C_{15}$–$C_{38}$) concentration as well as that of pristane and phytane also showed a maximum in the lower part. Concentrations of 1,1,3-trimethyl-, and 1,1,2,3-tetramethylcyclohexanes, a minor portion of *n*-alkylcyclohexanes ($C_9$ and $C_{10}$), *cis*-hydrindane, *cis*- and *trans*-decalin showed a maximum in the middle part of the sequence. Only *trans*-hydrindane showed a maximum concentration in the upper part of the sequence, as did perylene. The molecular distributions of series of *n*-alkylcyclohexanes ($C_{15}$–$C_{26}$) and *n*-alkylcyclopentanes ($C_{15}$–$C_{26}$) showed a predominance in a range from $C_{15}$ to $C_{18}$ in the upper part of the sequence, whereas that of *n*-alkanes did from $C_{27}$–$C_{31}$ in the part. However, the distributions of the three series became relatively smooth in the lower part, reflecting the further progress of diagenetic maturation resulting from the oil generation in the part.

## INTRODUCTION

A large number of organic geochemical studies on hydrocarbons in sediments and crude oils has been reported, since the study by Smith (1952). A general background of those hydrocarbon studies was summarized from a viewpoint of their origin and diagenesis by Killops and Killops (1993), and of their petroleum geochemistry by Hunt (1996). Cyclic alkanes are one of the major classes of hydrocarbons which are commonly present in sediments and crude oils. A large portion of cyclic alkane studies in these geochemical materials has dealt with tri-, tetra-, and pentacyclic alkanes such as steranes and hopanes mainly because of the interest in molecular biomarkers in relation to their sources and maturity parameters on organic diagenesis. On the other hand, studies of mono- and bicyclic alkanes have been reported infrequently, probably because many of these compounds are rather volatile (therefore, partially lost in sediment and/or during analysis), or cannot be easily linked to specific precursors compared to tri-, tetra- and pentacyclic alkanes. Therefore, it remains important to study mono- and bicyclic alkanes in sediments and to understand their characteristics in relation to sediment diagenesis as well as their precursors.

Neogene sediments of the Shinjo basin, Japan provide a suitable sedimentary sequence for a geochemical study of cyclic alkanes as well as many other organic compounds, because the

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sediments are in an old oil field and intense oil generation occurred in the lower part of the sequence (Taguchi *et al.*, 1986). As to cyclic alkanes, several steranes and hopanes were detected in the sediments, and the *S*/*R* ratios of $C_{29}$ sterane isomers and $C_{32}$ hopane isomers were shown in relation to the sediment diagenesis (Taguchi *et al.*, 1986).

Therefore, we analyzed the mono- and bicyclic alkanes in the Neogene Shinjo sediments to determine their characteristic distributions over the sedimentary sequence. Here we report the detection of 45 monocyclic and 12 bicyclic alkanes in the sediments and the determination of their absolute (30 components) and relative concentrations (27 components). Furthermore, using these data, we describe characteristics of their depth and molecular distributions over the stratigraphic sequence, including comparison with those of the *n*-alkanes, pristane, phytane, tetralin, and perylene analyzed in the same extracts from the sediment samples.

## EXPERIMENTAL

### *Samples*

Sediment samples were aliquots of common samples collected for the joint study on the diagenesis of organic and inorganic constituents in the Neogene Shinjo basin, Yamagata Prefecture, northeastern Japan (Taguchi *et al.*, 1986). The samples are chiefly marine shales and mudstones of the Nakawatari and Noguchi Formations (Pliocene), and the Furukuchi and Kusanagi Formations (Late to Middle Miocene), in stratigraphic descending order. The rock facies of the sediments were shown in the stratigraphic and lithologic sections of these formations (Taguchi *et al.*, 1986). In this study we analyzed 18 sediment samples numbered from 83110 to 90105 representing the top and bottom, respectively, of the 1600 m thick sedimentary sequence.

### *Analyses*

For each analysis, a pulverized sediment sample (2 g) was extracted with hexane (5 ml) by sonication (30 min) and the supernatant after centrifugation was recovered. This extraction and centrifugation process was repeated 6 times. The supernatants were combined, concentrated under reduced pressure, and applied to a silica gel column (220 mm × 10 mm i.d.; Keiselgel-60, Merk). From the column, cyclic and acyclic alkanes were eluated with hexane (15 ml) and then aromatic hydrocarbons with benzene (15 ml). The hexane and benzene eluates were concentrated to 50 $\mu$l individually under a nitrogen flow for analysis by a gas chromatography (GC)-mass spectrometry (GC-MS) (Hewlett Packard G1800 GCD System). The gas chromatograph was equipped with a HP-5 capillary column (30 m × 0.32 mm i.d.). For cyclic and acyclic alkanes, the GC oven temperature was programmed to hold at 40°C for 10 min, and to increase from 40 to 65°C at a rate of 1°C $\text{min}^{-1}$, from 65 to 160°C at a rate of 4°C $\text{min}^{-1}$, and from 160 to 300°C at a rate of 6.5°C $\text{min}^{-1}$. For aromatic hydrocarbons, it was programmed to hold at 40°C for 5 min, and to increase from 40 to 100°C at a rate of 6°C $\text{min}^{-1}$, from 100 to 130°C at a rate of 3°C $\text{min}^{-1}$, and from 130 to 300°C at a rate of 4°C $\text{min}^{-1}$. The mass spectra were acquired every 0.5 s over *m*/*z* 45 to 425 in an electron impact ionization mode at 70 eV. Identification and quantification of compounds were made by comparison of peak retention times on mass chromatograms and mass spectra, and peak areas, respectively, with those of standard compounds. For compounds without standard compounds, identification was made by comparison of mass spectra with library data of the National Institute of Standards and Technology (NIST), USA (1992) or data reported by Yamamoto *et al.* (1990). Relative concentrations of isomers and homologous series were obtained by comparison of peak areas on their mass chromatograms.

Hexane and benzene (analytical grade, Wako Pure Chem.) were distilled twice before use. All glassware was heated at 500°C for at least 3 h before use to eliminate organic contaminants. A procedural blank was carried out with pre-ignited sea sand powder (1 g) and it was found that there was no significant contamination during the analysis. A recovery test of cyclic alkanes was also carried out with 13 standard compounds mixed with sea sand (1 g) under the same procedure as employed in the analysis of the sediments.

## RESULTS AND DISCUSSION

### *Identification*

Figure 1 shows partial mass chromatograms (retention time 5–45 min) of *m*/*z* 69, 83, 97, and 111, which are major fragment ions for monocyclic alkanes (Fig. 2), and *m*/*z* 67 and 81 for bicyclic alkanes recovered from the sediment 83002. These fragment ions are of an olefin fragment from a cyclohexyl ring and/or a cyclopentyl ring (*m*/*z* 69), a cyclohexyl ring (*m*/*z* 83), and alkyl cyclohexanes (*m*/*z* 97 and 111) formed upon the electron impact ionization. The molecular ions of monocyclic alkanes were not intense and often less than 10 percent of those of base ions, which varied depending on the kind of polyalkylcyclohexanes, i.e., *m*/*z* 111 vs. 126 for 1,1,3-trimethylcyclohexane (peak 1 in Fig. 2), and *m*/*z* 97 vs. 126 for 1-ethyl-4-methylcyclohexane (peak 4 in Fig. 2). For bi-

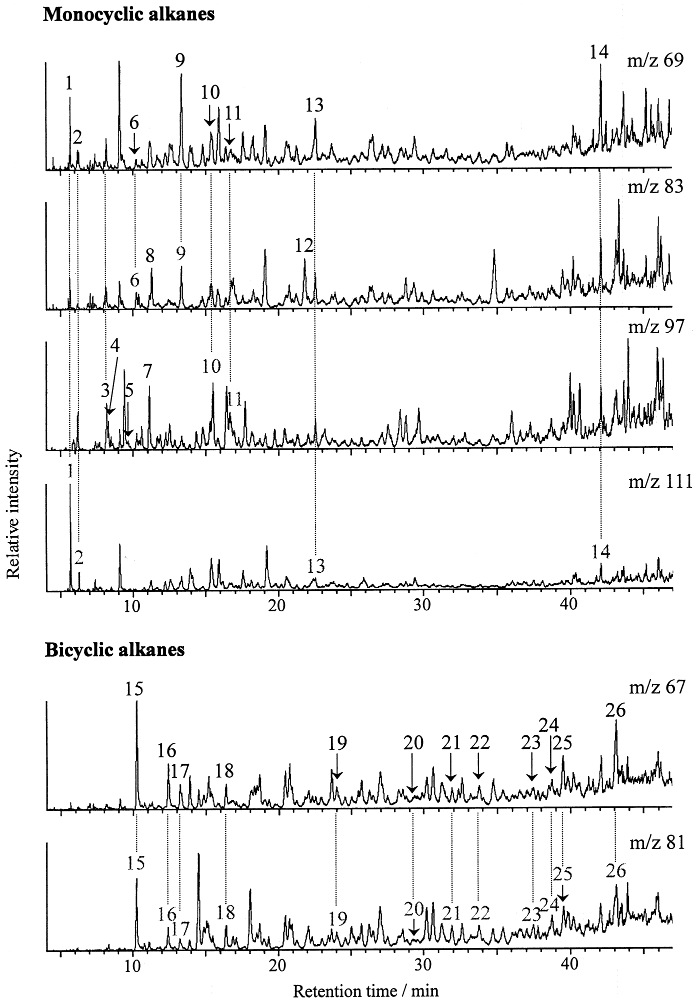

*Fig. 1. Mass chromatograms of m/z 69, 83, 97, and 111 for monocyclic alkanes, and m/z 67 and 81 for bicyclic alkanes in the Shinjo sediment 83002. Peak numbers correspond to those in Table 1.*

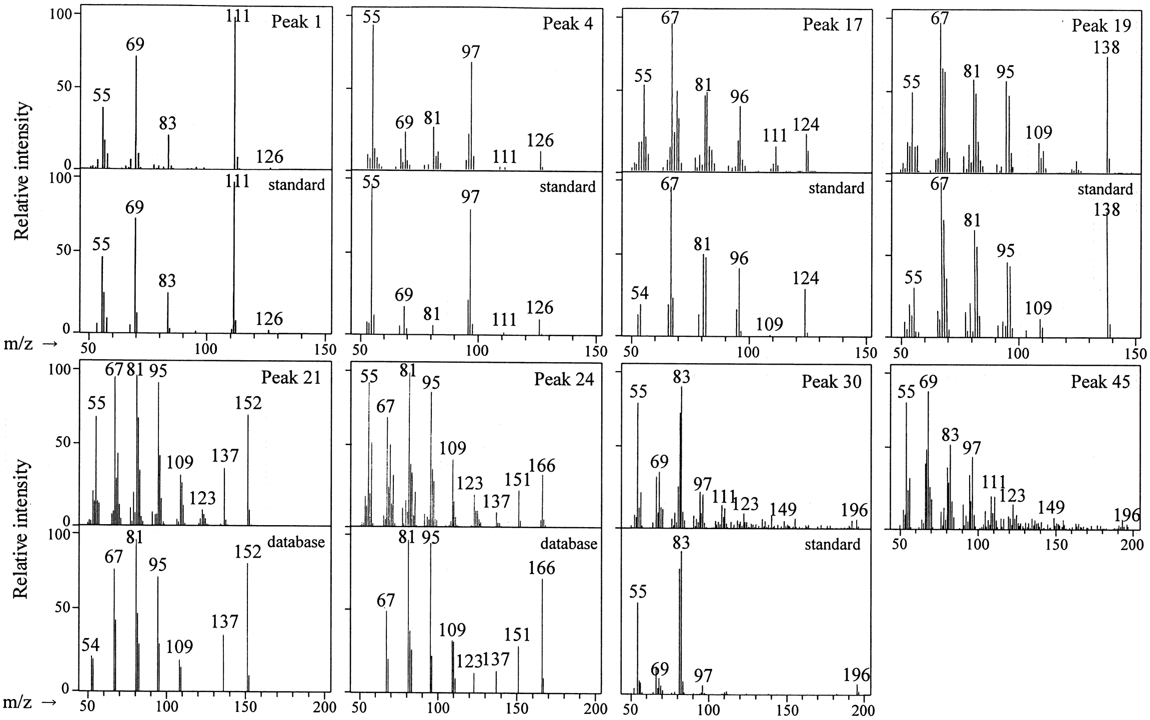

*Fig. 2. Mass spectra of cyclic alkanes in the Shinjo sediment 83002. Peak numbers correspond to those in Fig. 1 and Table 1.*

cyclic alkanes, base ions of *m*/*z* 67 and 81 were used to obtain their mass chromatograms (Fig. 1). Mass spectra of the peaks 17, 19, 21, and 24 in Fig. 2 showed that the intensities of the two base ions were large and those of molecular ions were strong compared with those of monocyclic alkanes.

Figure 3 shows the later parts of mass chromatograms (retention time 30–85 min) of *m*/*z* 83 (*n*-alkylcyclohexanes), *m*/*z* 69 (*n*-alkylcyclopentanes), and *m*/*z* 57 (a major ion for *n*-alkanes, pristane, and phytane) recovered from the sediment 83002. *n*-Alkylcyclohexanes were detected from $C_9$ to $C_{26}$ and *n*-alkylcyclopentanes from $C_{12}$ to $C_{26}$. The mass chromatograms of *m*/*z* 69 indicated the presence of alkylcyclohexanes as shown in the earlier part (Fig. 1), but also showed the presence of a series of *n*-alkylcyclopentanes. The peaks of *n*-alkylcyclohexanes, *n*-alkylcyclopentanes and *n*-alkanes were clearly recognized. Individual peaks of *n*-alkylcyclohexanes and *n*-alkylcyclopentanes with the same carbon numbers were noted by expanding parts of the two mass chromatograms and the total ion chromatogram (TIC) (Fig. 4), although the retention times of some members of the two series were very close to each other in Fig. 3. Their mass spectra (Fig. 2) were also distinguishable from each other by the intensity ratio of the *m*/*z* 83 to 69, i.e., the ratio of *n*-alkylcyclohexane (peak 30) was larger than 1, and that of *n*-alkylcyclopentane (peak 45) was less than 1. In addition, identification of tetralin (1,2,3,4-tetrahydronaphthelene) and perylene (58 and 59, respectively, in Appendix) in benzene eluate were identified by mass chromatograms of their molecular ions, *m*/*z* 132 and 252, respectively.

In summary, 45 monocyclic alkanes were identified (Table 1). Among these compounds, 26 were identified using standard compounds. These included two trimethylcyclohexanes (1 and 2; Ta-

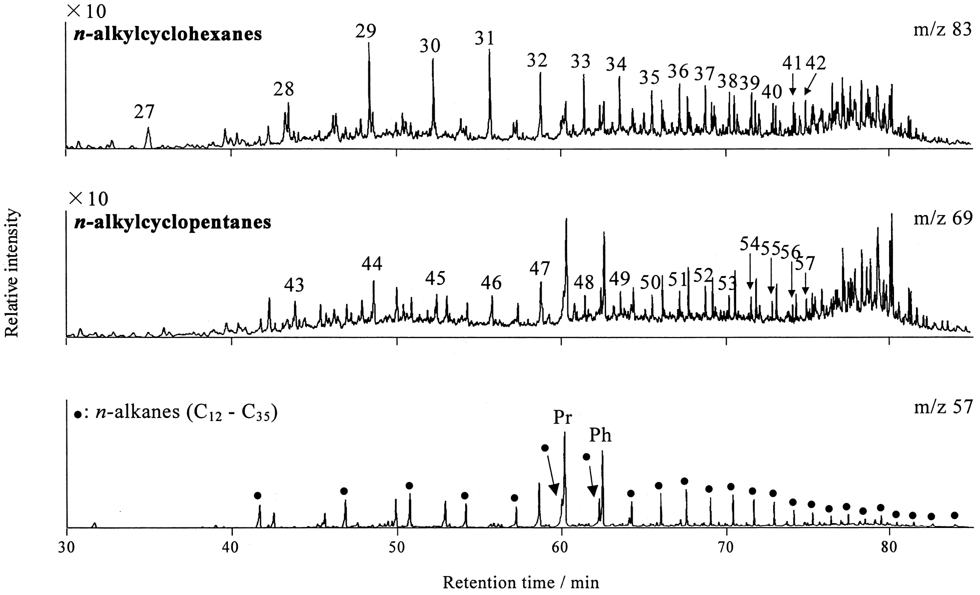

*Fig. 3. Mass chromatograms of m/z 83 for n-alkylcyclohexanes, m/z 69 for n-alkylcyclopentanes, and m/z 57 for n-alkanes (●), pristane (Pr), and phytane (Ph) in the Shinjo sediment 83002. Peak numbers correspond to those in Table 1.*

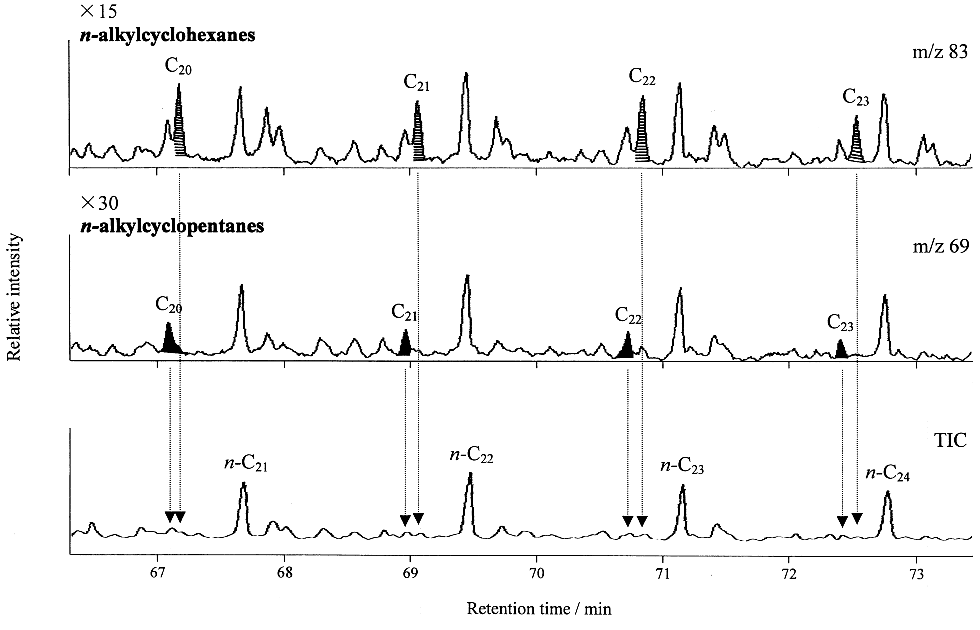

*Fig. 4. Expanded parts of mass chromatograms of m/z 83 for n-alkylcyclohexanes, m/z 69 for n-alkylcyclopentanes, and TIC (total ion chromatogram) over retention time of 68–73 min in the Shinjo sediment 83002.*

*Table 1. Cyclic alkanes identified in the Neogene Shinjo sediments*

| Peak number | Compound | Base *m*/*z* | Standard |
|---|---|---|---|
| 1 | 1,1,3-Trimethylcyclohexane | 69, 111 | * |
| 2 | 1,2,4-Trimethylcyclohexane | 69, 111 | * |
| 3 | 1-Ethyl-3-methylcyclohexane | 97 | * |
| 4 | 1-Ethyl-4-methylcyclohexane (*trans*) | 97 | * |
| 5 | 1-Ethyl-4-methylcyclohexane (*cis*) | 97 | * |
| 6 | *iso*-Propylcyclohexane | 69, 83 | * |
| 7 | 1-Ethyl-2-methylcyclohexane | 97 | * |
| 8 | *n*-Propylcyclohexane | 83 | * |
| 9 | 1,1,2,3-tetramethylcyclohexane | 69, 83 | |
| 10 | 1-Methyl-4-isopropylcyclohexane | 69, 97 | * |
| 11 | 1-Methyl-propylcyclohexane | 69, 97 | |
| 12 | *n*-Butylcyclohexane | 83 | * |
| 13 | 2-Ethyl-1,1,3-trimethylcyclohexane | 69, 83, 97, 111 | |
| 14 | 2-Butyl-1,1,3-trimethylcyclohexane | 69, 83, 97, 111 | |
| 15 | Bicyclo[3.3.1]nonane | 67, 81, 124 | |
| 16 | Methylbicyclo[3.3.0]octane | 67, 81, 124 | |
| 17 | Hydrindane (*trans*) | 67, 81, 124 | * |
| 18 | Hydrindane (*cis*) | 67, 81, 124 | * |
| 19 | Decalin (*trans*) | 67, 81, 138 | * |
| 20 | Decalin (*cis*) | 67, 81, 138 | * |
| 21 | Methyldecalin | 67, 81, 152 | |
| 22 | Methyldecalin | 67, 81, 152 | |
| 23 | Dimethyldecalin | 67, 81, 166 | |
| 24 | Dimethyldecalin | 67, 81, 166 | |
| 25 | Dimethyldecalin | 67, 81, 166 | |
| 26 | Dimethyldecalin | 67, 81, 166 | |

ble 1), four ethyl-methylcyclohexanes (3, 4, 5, and 7), isopropylcyclohexane (6), 1-methyl-4-isopropylcyclohexane (10), and a series of 18 *n*-alkylcyclohexanes from $C_9$ to $C_{26}$ (8, 12, and 27–42). In addition, four polyalkylcyclohexanes (9, 11, 13, and 14) were identified using the NIST library data, and a series of 15 *n*-alkylcyclopentanes from $C_{12}$ to $C_{26}$ (43–57) using the data of Yamamoto *et al.* (1990). As to bicyclic alkanes, 12 compounds were identified (Table 1) using standard compounds of *trans*- and *cis*-isomers of hydrindane (17 and 18) and those of decalin (19 and 20), and the NIST library data of bicyclo[3.3.1]nonane (15), methylbicyclo[3.3.0]-octane (16), two isomers of methyldecalin (21 and 22), and four isomers of dimethyldecalin (23–26). However, methyl positions on the bicyclo[3.3.0]-octane and the decalin structure could not be determined. Structures of these mono- and bicyclic alkanes are shown in Appendix. In addition to those cyclic alkanes, a series of *n*-alkanes ($C_{12}$–$C_{35}$), pristane, phytane, tetralin, and perylene were identified, although they are not listed in Table 1.

### *Concentrations*

The recovery experiment showed about 20–40% of polyalkylcyclohexanes ($C_9$), and *trans*- and *cis*-decalins ($C_{10}$), and 50–80% of *n*-alkylcyclohexanes ($C_{11}$–$C_{20}$ except $C_{15}$ and $C_{19}$) (Table 2). In spite of these rather low recoveries, concentrations of the 30 cyclic alkanes for which we have standard compounds and relative concentrations of the other 27 components were estimated. Therefore, the test indicated that the concentrations estimated were roughly a half or less of the concentrations in the sediments, especially for compounds with lower molecular weight because of their rather high volatility. Nevertheless, those values enable their approximate concentration levels to be determined. In addition, they are

*Table 1. (continued)*

| Peak number | Compound | Base *m*/*z* | Standard |
|---|---|---|---|
| 27 | *n*-Pentylcyclohexane | 83 | * |
| 28 | *n*-Hexylcyclohexane | 83 | * |
| 29 | *n*-Heptylcyclohexane | 83 | * |
| 30 | *n*-Octylcyclohexane | 83 | * |
| 31 | *n*-Nonylcyclohexane | 83 | * |
| 32 | *n*-Decylcyclohexane | 83 | * |
| 33 | *n*-Undecylcyclohexane | 83 | * |
| 34 | *n*-Dodecylcyclohexane | 83 | * |
| 35 | *n*-Tridecylcyclohexane | 83 | * |
| 36 | *n*-Tetradecylcyclohexane | 83 | * |
| 37 | *n*-Pentadecylcyclohexane | 83 | * |
| 38 | *n*-Hexadecylcyclohexane | 83 | * |
| 39 | *n*-Heptadecylcyclohexane | 83 | * |
| 40 | *n*-Octadecylcyclohexane | 83 | * |
| 41 | *n*-Nonadecylcyclohexane | 83 | * |
| 42 | *n*-Eicosylcyclohexane | 83 | * |
| 43 | *n*-Heptylcyclopentane | 69 | |
| 44 | *n*-Octylcyclopentane | 69 | |
| 45 | *n*-Nonylcyclopentane | 69 | |
| 46 | *n*-Decylcyclopentane | 69 | |
| 47 | *n*-Undecylcyclopentane | 69 | |
| 48 | *n*-Dodecylcyclopentane | 69 | |
| 49 | *n*-Tridecylcyclopentane | 69 | |
| 50 | *n*-Tetradecylcyclopentane | 69 | |
| 51 | *n*-Pentadecylcyclopentane | 69 | |
| 52 | *n*-Hexadecylcyclopentane | 69 | |
| 53 | *n*-Heptadecylcyclopentane | 69 | |
| 54 | *n*-Octadecylcyclopentane | 69 | |
| 55 | *n*-Nonadecylcyclopentane | 69 | |
| 56 | *n*-Eicosylcyclopentane | 69 | |
| 57 | *n*-Heneicosylcyclopentane | 69 | |

**; compound with standard.*

useful for comparing the depth profiles and molecular distributions of the three homologous series over the stratigraphic sequence, because the comparison was made on the basis of the same compounds (therefore, similar recoveries) among different sediments. Concentrations of *n*-alkanes from $C_{12}$ to $C_{14}$ were not estimated, although they were detected, because they are highly volatile compared to *n*-$C_{15}$ and longer *n*-alkanes. Their abundances among the sediments were not particularly important in this study.

Polyalkylcyclohexanes ($C_9$ and $C_{10}$) were detected at a concentration level of 0.01–1 nmol $g^{-1}$ (Table 3). Most of these compounds were present in the middle part of the sequence (upper part of the Kusanagi Formation), and absent or nearly absent in the upper part (Nakawatari and Noguchi Formations) and the bottom two sediments of the sequence (lower part of the Kusanagi Formation). *n*-Alkylcyclohexanes from $C_9$ to $C_{17}$ were detected also at a level of 0.01–1 nmol $g^{-1}$, whereas those from $C_{18}$ to $C_{26}$ were present at one order of magnitude less than those from $C_9$ to $C_{17}$ (Table 4). Compounds from $C_{15}$ to $C_{18}$ were present in all of the 18 sediments. However, those from $C_9$ to $C_{13}$ and from $C_{22}$ to $C_{26}$ were not detected in the top two sediments (Nakawatari Formation).

The bicyclic alkanes, hydrindanes and decalins, were detected at a level of 0.01–1 nmol $g^{-1}$ (Table 5). *trans*-Hydrindane was present

*Table 2. Recovery of cyclic alkanes in the analytical procedure*

| Peak number | Compound | Amount/nmol/$\mu$l | After the recovery test | Recovery/% |
|---|---|---|---|---|
| 2 | 1,2,4-Trimethylcyclohexane | 0.19 | 0.04 | 22 |
| 6 | *iso*-Propylcyclohexane | 0.22 | 0.07 | 30 |
| 7 | 1-Ethyl-2-methylcyclohexane | 0.21 | 0.08 | 36 |
| 19 | *trans*-Decalin | 0.20 | 0.07 | 33 |
| 20 | *cis*-Decalin | 0.18 | 0.07 | 39 |
| 27 | *n*-Pentylcyclohexane | 0.20 | 0.10 | 52 |
| 28 | *n*-Hexylcyclohexane | 0.18 | 0.10 | 55 |
| 29 | *n*-Heptylcyclohexane | 0.17 | 0.10 | 61 |
| 30 | *n*-Octylcyclohexane | 0.17 | 0.11 | 64 |
| 32 | *n*-Decylcyclohexane | 0.14 | 0.10 | 73 |
| 33 | *n*-Undecylcyclohexane | 0.16 | 0.12 | 74 |
| 34 | *n*-Dodecylcyclohexane | 0.19 | 0.15 | 77 |
| 36 | *n*-Tetradecylcyclohexane | 0.13 | 0.10 | 80 |

in all the sediments except the top sediment of the sequence (Nakawatari Formation), while the *cis*-isomer was found mainly in the middle part (upper part of the Kusanagi Formation). *trans*-Decalin was present over most of the sequence except for a few of the top most sediments (Nakawatari and Noguchi Formations) and the bottom sediment (lower part of the Kusanagi Formation), while *cis*-decalin was detected in greatest concentration in the sediment 83003 (upper part of the Kusanagi Formation).

The concentrations of most polyalkylcyclohexanes, *n*-alkylcyclohexanes, and bicyclic alkanes in the sediments from 83110 to 83103 (Nakawatari to Furukuchi Formation) in the upper part of the sequence were generally at the same level or less than those of *n*-alkanes from $C_{15}$ to $C_{38}$, pristane, and phytane, which were present at a level of 0.01–1 nmol $g^{-1}$ (Table 6). Their concentrations in the sediments from 83102 to 90105 (upper to lower part of the Kusanagi Formation) in the lower part of the sequence were one order of magnitude lower than those of *n*-alkanes, pristane, and phytane which were present at a level of 0.1–10 nmol $g^{-1}$. These relative compositions of mono- and bicyclic alkanes to *n*-alkanes in sediments are roughly similar to those in crude oils (Rubinstein and Strausz, 1979; Kissin, 1990). Perylene was present at a level of 0.01 or 0.1 nmol $g^{-1}$. The other cyclic alkanes including a series of *n*-alkylcyclopentanes, methyl- and dimethyldecalins, and tetralin were present at most at a level of 1.0 or sub-nmol $g^{-1}$, judging from their peak areas on the mass chromatograms (e.g., Fig. 1).

### *Depth profiles*

The absolute and relative concentrations of cyclic alkanes were plotted with depth of the sediments down the sequence. Based on the depth of maximum concentrations, these cyclic alkanes could be divided into three groups.

The first group includes 39 cyclic alkanes, such as *n*-alkylcyclohexanes ($C_{11}$–$C_{26}$), *n*-alkylcyclopentanes ($C_{12}$–$C_{26}$), 2-alkyl-1,1,3-trimethylcyclohexanes ($C_{11}$ and $C_{13}$), and methyl- and dimethyldecalins (Figs. 5a, b, and c). Absolute or relative concentrations of this group started increasing at the depth of the sediment 83102 (upper part of the Kusanagi Formation), maximised at the sediment 90103 (middle part of the Kusanagi Formation), and then decreased in the bottom two sediments. Similar depth profiles were observed with *n*-alkanes ($C_{15}$–$C_{38}$), pristane plus phytane (Fig. 5d), and the reported EOC/TOC ratio (Fig. 5e; Shimoyama and Matsubaya, 1985).

The second group comprises 17 cyclic alkanes, such as 10 polyalkylcyclohexanes ($C_9$ and $C_{10}$), *n*-alkylcyclohexanes ($C_9$ and $C_{10}$), *cis*-hydrindane, *cis*- and *trans*-decalins, bicyclo[3.3.0]nonane, and methylbicyclo[3.3.0]octane (Fig. 6). Their concentrations started increasing at the depth of the sedi-

*Table 3. Concentrations of polyalkylcyclohexanes in the Neogene Shinjo sediments*

| Formation | Sample No. | Concentrations/nmol g$^{-1}$ Rock | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1,1,3-Trimethyl-cyclohexane | 1,2,4-Trimethyl-cyclohexane | 1-Ethyl-2-methyl-cyclohexane | 1-Ethyl-3-methyl-cyclohexane | 1-Ethyl-4-methyl-cyclohexane (*trans*) | 1-Ethyl-4-methyl-cyclohexane (*cis*) | *iso*-Propyl-cyclohexane | 1-Methyl-4-isopropyl-cyclohexane |
| Nakawatari | 83110 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83109 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Noguchi | 83108 | 0.25 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83107 | 0.03 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83106 | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Furukuchi | 83105 | 0.11 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83104 | 0.23 | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83103 | 0.07 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Kusanagi (upper) | 83102 | 0.60 | 0.18 | 0.02 | 0.19 | 0.15 | n.d. | 0.01 | 0.19 |
| | 83101 | 0.45 | 0.17 | 0.09 | 0.18 | 0.18 | n.d. | 0.03 | 0.25 |
| | 83003 | 2.25 | 0.87 | 1.36 | 1.56 | 1.18 | 0.58 | 0.66 | 2.60 |
| | 83002 | 1.81 | 0.57 | 0.78 | 1.07 | 0.73 | 0.37 | 0.38 | 1.55 |
| | 83001 | 1.02 | 0.33 | 0.24 | 0.44 | 0.34 | n.d. | 0.15 | 0.88 |
| (middle) | 90101 | 1.33 | 0.55 | 0.34 | 0.58 | 0.39 | 0.18 | 0.25 | 1.08 |
| | 90102 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 90103 | 0.08 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.12 |
| (lower) | 90104 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 90105 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

*n.d.; not detected.*

*Table 4. Concentrations of n-alkylcyclohexanes ($C_9$–$C_{26}$) in the Neogene Shinjo sediments*

| Formation | Sample No. | Concentrations/nmol $g^{-1}$ Rock | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{17}$ | $C_{18}$ | $C_{19}$ | $C_{20}$ | $C_{21}$ | $C_{22}$ | $C_{23}$ | $C_{24}$ | $C_{25}$ | $C_{26}$ |
| Nakawatari | 83110 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.01 | 0.02 | 0.03 | 0.05 | 0.02 | 0.01 | 0.00 4 | n.d. | n.d. | n.d. | n.d. | n.d. |
| | 83109 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.01 | 0.03 | 0.04 | 0.02 | 0.01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Noguchi | 83108 | 0.05 | 0.06 | 0.07 | 0.09 | 0.09 | 0.08 | 0.11 | 0.08 | 0.04 | 0.03 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | n.d. |
| | 83107 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.03 | 0.06 | 0.11 | 0.13 | 0.07 | 0.02 | 0.01 | 0.01 | 0.004 | n.d. | n.d. | n.d. | n.d. |
| | 83106 | n.d. | n.d. | n.d. | 0.02 | 0.03 | 0.03 | 0.06 | 0.10 | 0.08 | 0.05 | 0.02 | 0.01 | 0.004 | 0.004 | 0.003 | 0.003 | 0.002 | n.d. |
| Furukuchi | 83105 | 0.01 | 0.002 | n.d. | n.d. | 0.009 | 0.02 | 0.03 | 0.04 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.004 | 0.003 | 0.003 | n.d. | n.d. |
| | 83104 | 0.01 | 0.01 | n.d. | n.d. | 0.004 | 0.03 | 0.04 | 0.05 | 0.04 | 0.03 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.004 | n.d. |
| | 83103 | 0.11 | 0.06 | 0.04 | 0.04 | 0.05 | 0.05 | 0.07 | 0.08 | 0.07 | 0.05 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | n.d. |
| Kusanagi<br>(upper) | 83102 | 0.38 | 0.14 | 0.20 | 0.11 | 0.13 | 0.12 | 0.17 | 0.15 | 0.12 | 0.10 | 0.06 | 0.05 | 0.03 | 0.03 | 0.02 | 0.02 | 0.02 | n.d. |
| | 83101 | 0.42 | 0.14 | 0.18 | 0.08 | 0.01 | 0.08 | 0.09 | 0.08 | 0.05 | 0.04 | 0.03 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | n.d. |
| | 83003 | 2.31 | 0.46 | 0.66 | 0.30 | 0.50 | 0.51 | 0.78 | 0.48 | 0.43 | 0.40 | 0.25 | 0.30 | 0.23 | 0.25 | 0.23 | 0.19 | 0.19 | 0.20 |
| | 83002 | 0.51 | 0.04 | 0.35 | 0.21 | 0.36 | 0.48 | 0.63 | 0.36 | 0.24 | 0.21 | 0.09 | 0.09 | 0.06 | 0.06 | 0.06 | 0.06 | 0.03 | n.d. |
| | 83001 | 0.05 | 0.08 | 0.27 | 0.21 | 0.19 | 0.22 | 0.24 | 0.15 | 0.11 | 0.09 | 0.07 | 0.06 | 0.03 | 0.03 | 0.03 | 0.02 | 0.02 | n.d. |
| (middle) | 90101 | 0.12 | 0.40 | 0.39 | 0.83 | 0.64 | 0.76 | 0.81 | 1.02 | 0.80 | 0.61 | 0.55 | 0.32 | 0.26 | 0.17 | 0.14 | 0.13 | 0.09 | 0.08 |
| | 90102 | n.d. | n.d. | 0.02 | 0.06 | 0.16 | 0.30 | 0.45 | 0.53 | 0.52 | 0.52 | 0.39 | 0.28 | 0.20 | 0.20 | 0.17 | 0.14 | 0.12 | 0.11 |
| | 90103 | 0.13 | 0.21 | 1.18 | 0.81 | 0.74 | 0.86 | 1.10 | 0.75 | 0.63 | 0.49 | 0.35 | 0.29 | 0.31 | 0.26 | 0.25 | 0.22 | 0.22 | n.d. |
| (lower) | 90104 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.15 | 0.76 | 0.76 | 0.59 | 0.69 | 0.73 | 0.62 | 0.34 | 0.32 | 0.26 | 0.19 | 0.19 | 0.15 |
| | 90105 | n.d. | n.d. | n.d. | n.d. | 0.04 | 0.10 | 0.30 | 0.49 | 0.54 | 0.50 | 0.32 | 0.32 | 0.22 | 0.21 | 0.17 | 0.15 | 0.13 | 0.11 |

*n.d.; not detected.*

*Table 5. Concentrations of bicyclic alkanes in the Neogene Shinjo sediments*

| Formation | Sample No. | Concentrations/nmol $g^{-1}$ Rock | | | |
|---|---|---|---|---|---|
| | | Hydrindane (*trans*) | Hydrindane (*cis*) | Decalin (*trans*) | Decalin (*cis*) |
| Nakawatari | 83110 | n.d. | n.d. | n.d. | n.d. |
| | 83109 | 0.81 | n.d. | n.d. | n.d. |
| Noguchi | 83108 | 1.89 | n.d. | n.d. | n.d. |
| | 83107 | 1.59 | n.d. | 0.46 | n.d. |
| | 83106 | 2.19 | n.d. | n.d. | n.d. |
| Furukuchi | 83105 | 0.44 | n.d. | n.d. | n.d. |
| | 83104 | 0.29 | n.d. | 0.76 | n.d. |
| | 83103 | 0.50 | n.d. | n.d. | n.d. |
| Kusanagi | 83102 | 1.04 | 0.13 | 1.38 | 0.02 |
| (upper) | 83101 | 0.76 | 0.27 | 0.37 | n.d. |
| | 83003 | — | 2.13 | 2.05 | 2.70 |
| | 83002 | 0.07 | 1.53 | 3.42 | 0.03 |
| | 83001 | 0.26 | 1.01 | 1.17 | 0.05 |
| (middle) | 90101 | 1.01 | 0.41 | 1.37 | 0.12 |
| | 90102 | 0.15 | n.d. | 0.12 | n.d. |
| | 90103 | 0.22 | n.d. | 0.56 | n.d. |
| (lower) | 90104 | 0.09 | n.d. | 1.87 | n.d. |
| | 90105 | 0.22 | n.d. | n.d. | n.d. |

*n.d.; not detected, —; not determined.*

ment 83102 (upper part of the Kusanagi Formation), maximised at the sediment 83003 or 83002 (upper part of the Kusanagi Formation), decreased down to the sediment 90102 (middle part of the Kusanagi Formation), and were not detected below. This depth profile resembles those of naphthalenes (Shimoyama *et al.*, 2000).

The third group consists of only one cyclic alkane, *trans*-hydrindane (Fig. 7). Its concentration started increasing at the depth of the sediment 83109 (lower part of the Nakawatari Formation), became relatively high in the sediments 83108 and 83107 (Noguchi Formation), and maximised at 83106 (lower part of the Noguchi Formation). The concentration generally decreased with depth except in the sediments 83102 and 83101 (upper part of the Kusanagi Formation), and 90101 (middle part of the Kusanagi Formation) where it was higher than those of sediments just above and below. Perylene analyzed in this study also showed a similar depth profile.

The fact that the cyclic alkanes in the first group showed a similar depth profile to those of acyclic alkanes, revealed that the major portion of cyclic alkanes had been formed around the same diagenetic stage as those of acyclic alkanes. The horizon at the sediment 83101 is known to be at the beginning of the intense oil generation zone in the sedimentary sequence as shown by stratigraphic profiles of TOC and EOC (Shimoyama and Matsubaya, 1985), the vitrinite reflectance, $T_{max}$ value, and the ratios of $20S/20R$ of $C_{29}$ steranes and of $22S/22R$ of $C_{32}$ hopanes (Taguchi *et al.*, 1986).

The cyclic alkanes in the second group were relatively abundant just above the oil generation zone. They had been formed in the oil generation zone, and probably volatilized or diffused to horizons higher than the sediment 90103 (maximum concentration horizon of the first group) because

*Table 6. Concentrations of n-alkanes ($C_{15}$–$C_{38}$), pristane, and phytane in the Neogene Shinjo sediments*

| Formation | Sample No. | Concentrations/nmol $g^{-1}$ Rock | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $n$-$C_{15}$ | $n$-$C_{16}$ | $n$-$C_{17}$ | $n$-$C_{18}$ | $n$-$C_{19}$ | $n$-$C_{20}$ | $n$-$C_{21}$ | $n$-$C_{22}$ | $n$-$C_{23}$ | $n$-$C_{24}$ | $n$-$C_{25}$ | $n$-$C_{26}$ | $n$-$C_{27}$ |
| Nakawatari | 83110 | 0.31 | 0.28 | 0.07 | 0.03 | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.02 | 0.04 |
| | 83109 | 0.01 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Noguchi | 83108 | 0.13 | 0.09 | 0.06 | 0.06 | 0.05 | 0.07 | 0.09 | 0.08 | 0.10 | 0.09 | 0.11 | 0.09 | 0.10 |
| | 83107 | 0.03 | 0.05 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.02 | 0.04 | 0.03 | 0.05 | 0.03 | 0.06 |
| | 83106 | 0.36 | 0.27 | 0.18 | 0.15 | 0.13 | 0.14 | 0.18 | 0.18 | 0.30 | 0.21 | 0.38 | 0.24 | 0.59 |
| Furukuchi | 83105 | 0.27 | 0.24 | 0.12 | 0.10 | 0.13 | 0.10 | 0.14 | 0.11 | 0.16 | 0.13 | 0.22 | 0.15 | 0.43 |
| | 83104 | 0.16 | 0.28 | 0.16 | 0.13 | 0.13 | 0.14 | 0.19 | 0.18 | 0.26 | 0.23 | 0.31 | 0.21 | 0.39 |
| | 83103 | 0.21 | 0.18 | 0.18 | 0.18 | 0.20 | 0.23 | 0.30 | 0.32 | 0.46 | 0.34 | 0.43 | 0.29 | 0.42 |
| Kusanagi (upper) | 83102 | 1.66 | 1.38 | 2.27 | 1.83 | 2.16 | 2.82 | 3.93 | 3.54 | 4.81 | 3.93 | 4.54 | 3.10 | 3.37 |
| | 83101 | 1.95 | 1.49 | 1.59 | 1.40 | 1.24 | 1.37 | 1.55 | 1.31 | 1.36 | 1.09 | 1.09 | 0.80 | 0.72 |
| | 83003 | 6.19 | 5.15 | 5.93 | 4.31 | 4.48 | 4.87 | 5.03 | 4.93 | 4.88 | 4.44 | 3.90 | 2.70 | 2.37 |
| | 83002 | 2.82 | 2.64 | 2.97 | 2.39 | 1.88 | 2.13 | 3.01 | 2.02 | 2.24 | 1.87 | 1.84 | 1.19 | 1.16 |
| | 83001 | 2.30 | 1.75 | 2.63 | 1.78 | 1.41 | 1.60 | 1.86 | 1.55 | 1.58 | 1.32 | 1.15 | 0.83 | 0.65 |
| (middle) | 90101 | 10.9 | 9.14 | 14.3 | 11.7 | 6.87 | 8.22 | 7.86 | 8.63 | 7.44 | 7.80 | 6.41 | 4.41 | 3.70 |
| | 90102 | 5.33 | 5.20 | 6.05 | 6.69 | 3.89 | 4.35 | 5.22 | 3.73 | 3.19 | 3.32 | 2.87 | 1.93 | 1.34 |
| | 90103 | 18.3 | 17.4 | 33.2 | 23.8 | 13.6 | 18.6 | 18.1 | 15.2 | 12.9 | 11.4 | 11.6 | 7.25 | 5.18 |
| (lower) | 90104 | 8.78 | 12.1 | 17.1 | 11.6 | 9.86 | 12.6 | 12.8 | 10.6 | 9.01 | 8.70 | 9.05 | 5.74 | 4.15 |
| | 90105 | 4.15 | 5.40 | 9.08 | 7.16 | 6.90 | 7.01 | 7.24 | 6.29 | 5.86 | 5.03 | 4.66 | 3.29 | 2.62 |

| Formation | Sample No. | Concentrations/nmol $g^{-1}$ Rock | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $n$-$C_{28}$ | $n$-$C_{29}$ | $n$-$C_{30}$ | $n$-$C_{31}$ | $n$-$C_{32}$ | $n$-$C_{33}$ | $n$-$C_{34}$ | $n$-$C_{35}$ | $n$-$C_{36}$ | $n$-$C_{37}$ | $n$-$C_{38}$ | pristane | phytane |
| Nakawatari | 83110 | 0.02 | 0.07 | 0.02 | 0.05 | 0.02 | 0.03 | 0.02 | 0.01 | n.d. | n.d. | n.d. | 0.18 | 0.10 |
| | 83109 | 0.01 | 0.02 | 0.01 | 0.02 | 0.007 | 0.02 | 0.01 | 0.004 | n.d. | n.d. | n.d. | 0.09 | 0.05 |
| Noguchi | 83108 | 0.06 | 0.15 | 0.03 | 0.02 | 0.03 | 0.06 | 0.03 | 0.02 | n.d. | n.d. | n.d. | 0.44 | 0.45 |
| | 83107 | 0.03 | 0.10 | 0.03 | 0.08 | 0.02 | 0.03 | 0.004 | 0.008 | n.d. | n.d. | n.d. | 0.37 | 0.11 |
| | 83106 | 0.30 | 1.02 | 0.27 | 0.84 | 0.15 | 0.29 | n.d. | n.d. | n.d. | n.d. | n.d. | 1.14 | 0.37 |
| Furukuchi | 83105 | 0.16 | 0.72 | 0.15 | 0.51 | 0.09 | 0.17 | 0.04 | 0.07 | n.d. | n.d. | n.d. | 0.75 | 0.37 |
| | 83104 | 0.21 | 0.56 | 0.18 | 0.39 | 0.10 | 0.18 | 0.04 | 0.05 | n.d. | n.d. | n.d. | 1.53 | 0.63 |
| | 83103 | 0.23 | 0.50 | 0.18 | 0.37 | 0.09 | 0.13 | 0.03 | 0.04 | n.d. | n.d. | n.d. | 1.18 | 0.37 |
| Kusanagi | 83102 | 1.94 | 3.65 | 1.33 | 1.94 | 0.55 | 0.72 | n.d. | n.d. | n.d. | n.d. | n.d. | 6.42 | 2.47 |
| (upper) | 83101 | 0.53 | 0.66 | 0.41 | 0.57 | 0.25 | 0.28 | 0.18 | 0.13 | n.d. | n.d. | n.d. | 6.97 | 2.25 |
| | 83003 | 1.42 | 1.87 | 1.48 | 1.82 | 0.86 | 1.17 | 1.02 | 0.93 | 0.27 | 0.23 | 0.31 | 18.1 | 9.10 |
| | 83002 | 0.60 | 0.69 | 0.65 | 0.70 | 0.36 | 0.43 | 0.56 | 0.55 | 0.16 | n.d. | n.d. | 10.8 | 7.03 |
| | 83001 | 0.43 | 0.45 | 0.35 | 0.42 | 0.18 | 0.22 | 0.22 | 0.20 | n.d. | n.d. | n.d. | 6.80 | 2.82 |
| (middle) | 90101 | 2.36 | 2.19 | 1.90 | 1.87 | 0.86 | 0.81 | 0.93 | 0.90 | 0.64 | 1.48 | 1.29 | 16.1 | 17.0 |
| | 90102 | 1.05 | 0.84 | 0.84 | 0.89 | 0.44 | 0.69 | 0.91 | 0.88 | n.d. | n.d. | n.d. | 9.44 | 7.90 |
| | 90103 | 4.06 | 4.14 | 3.85 | 3.93 | 2.34 | 3.03 | 3.21 | 2.81 | 0.66 | 1.75 | 2.28 | 31.7 | 34.6 |
| (lower) | 90104 | 3.34 | 2.78 | 3.00 | 2.69 | 1.63 | 1.61 | 3.27 | 2.84 | 0.87 | 3.56 | 3.30 | 21.1 | 16.2 |
| | 90105 | 1.83 | 2.01 | 1.40 | 1.58 | 0.82 | 0.84 | 1.60 | 0.84 | 0.78 | 0.80 | 0.66 | 10.4 | 5.38 |

*n.d.; not detected.*

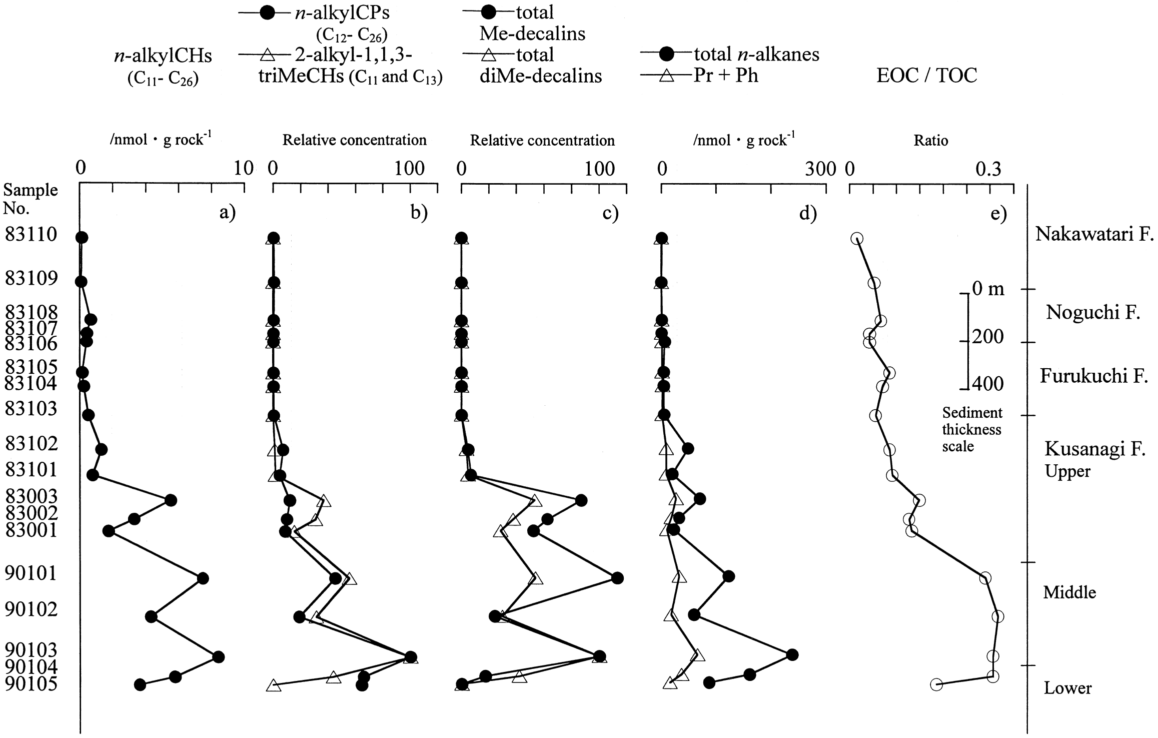

*Fig. 5. Depth profiles of a) concentrations of total n-alkylCHs (cyclohexanes, $C_{11}$–$C_{26}$), b) relative concentrations of total n-alkylCPs (cyclopentanes, $C_{12}$–$C_{26}$) and total 2-alkyl-1,1,3-triMe (trimethyl) CHs ($C_{11}$ and $C_{13}$), c) total Me (methyl)-decalins and total diMe (dimethyl)-decalins, d) concentrations of total n-alkanes ($C_{15}$–$C_{38}$), and Pr (pristane) plus Ph (phytane), and e) ratios of EOC (extractable organic compounds) to TOC (total organic carbon) in the Neogene Shinjo basin. Relative concentration in the Shinjo sediment 90103 was set to 100.*

of their lower molecular weights than those in the first group. Although carbon skeletons of 2-alkyl-1,1,3-trimethylcyclohexanes are specific to carotenoids (Anders and Robinson, 1971; Hall and Douglas, 1983; Jiang and Fowler, 1986), their depth profiles differed depending on their molecular weights. 1,1,3-Trimethyl- and 1,1,2,3-tetramethylcyclohexanes belonged to the second group (Figs. 6a and b), while 2-ethyl- and 2-butyl-1,1,3-trimethylcyclohexanes showed profiles of the first group (Fig. 5b). Likewise, *n*-alkylcyclohexanes ($C_9$ and $C_{10}$) and decalin belonged to the second group (Figs. 6a and d), whereas *n*-alkylcyclohexanes longer than $C_{10}$ and methyl- and dimethyldecalins belonged to the first (Figs. 5a and c). In addition, water solubility of *n*-alkanes becomes significantly higher around $C_{10}$ as their molecular weights become lower (McAuliffe, 1980). This suggests that cyclic alkanes ($C_9$ and $C_{10}$) in this group are also more water soluble than those ($C_{11}$–$C_{26}$) in the first group, and therefore, they might have migrated to upper horizons as sediment interstitial water migrated. A similar interpretation has been reported for the depth profiles of naphthalenes in the Shinjo sediments (Shimoyama *et al.*, 2000). Tetralin analyzed in this study also showed a depth profile of the second group, which seems to be reasonable from similarities in molecular weight and structure among decalin, tetralin, and naphthalene. In addition, water solubility of aromatic hydrocarbons is higher than those of *n*-alkanes (McAuliffe, 1980), and therefore, the same explanation by water migration is possible for why tetralin belongs to the second group.

The occurrence of the third group, comprising

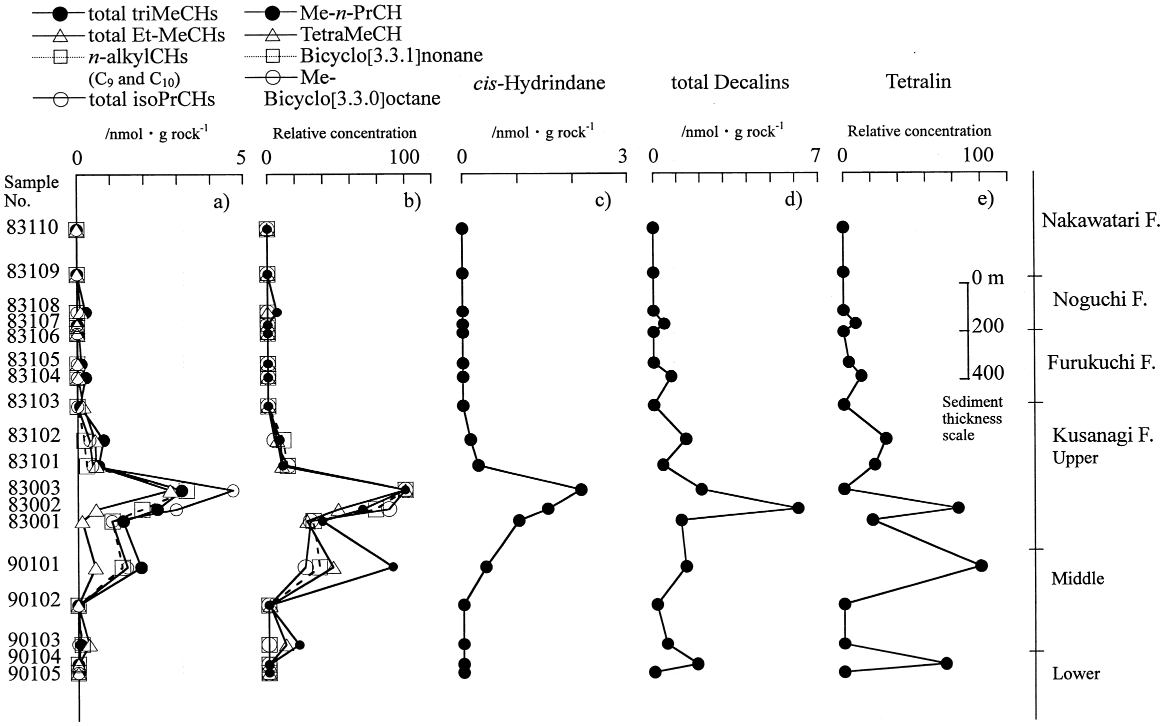

*Fig. 6. Depth profiles of concentrations or relative ones of a) total triMeCHs (trimethylcyclohexanes), total EtMeCHs (ethylmethylcyclohexanes), n-alkylCHs (alkylcyclohexanes) ($C_9$ and $C_{10}$), and total isoPrCHs (isopropylcyclohexanes), b) Me-n-PrCH (methyl-n-propylcyclohexane), tetraMeCH (tetramethylcyclohexane), bicyclo[3.3.1]nonane, and Mebicyclo[3.3.0]octane (methylbicyclo[3.3.0]octane), c) cis-hydrindane, d) total (cis- plus trans-) decalins, and e) tetralin in the Neogene Shinjo sediments. Maximum concentration was set to 100 in b) and e).*

*trans*-hydrindane only, seems to be unrelated to those of the first and second groups. A relatively large input of land derived organic matter into the sediments from the Noguchi to the Furukuchi Formation has been proposed, because of relatively high concentrations of perylene (Taguchi *et al.*, 1970; Suzuki and Taguchi, 1982), high ratios of $C_{29}/(C_{27} + C_{28})$ of steranes (Suzuki and Shimada, 1983), and low L/H ratios ($\Sigma C_{13-19}/\Sigma C_{20-38}$) for *n*-alkanes (Ishiwatari and Shioya, 1986). In this study, relatively high concentrations of perylene and low L/H ratios (<1) of $\Sigma C_{15-19}/\Sigma C_{27-31}$ for *n*-alkanes were also observed in the two formations compared to those in the lower part of the sequence (Fig. 7). Thermal cracking of longer chain *n*-alkanes to shorter ones makes the L/H ratios higher. However, the cracking takes place mainly in the oil generation zone which is located below the two formations, and therefore, the cracking effect was insignificant from the lower ratios in the two formations. Accordingly, it is suggested that *trans*-hydrindane detected had been derived from land derived organic matter.

### *Molecular distributions of n-alkylcycloalkanes*

The molecular distributions of *n*-alkylcyclohexanes ($C_{15}$–$C_{26}$), *n*-alkylcyclopentanes ($C_{15}$–$C_{26}$), and *n*-alkanes ($C_{15}$–$C_{38}$) in the sediments are shown in Fig. 8. The distributions of *n*-alkylcyclohexanes showed a maximum in composition at $C_{18}$ in the sediment 83110 and at $C_{16}$ in 83109 (Nakawatari Formation), and exhibited relatively large amounts of $C_{15}$, $C_{16}$, $C_{17}$, and $C_{18}$ from 83107 to 83102 (Noguchi to the top of the Kusanagi Formation) in the upper part of the sequence. The distribution of *n*-

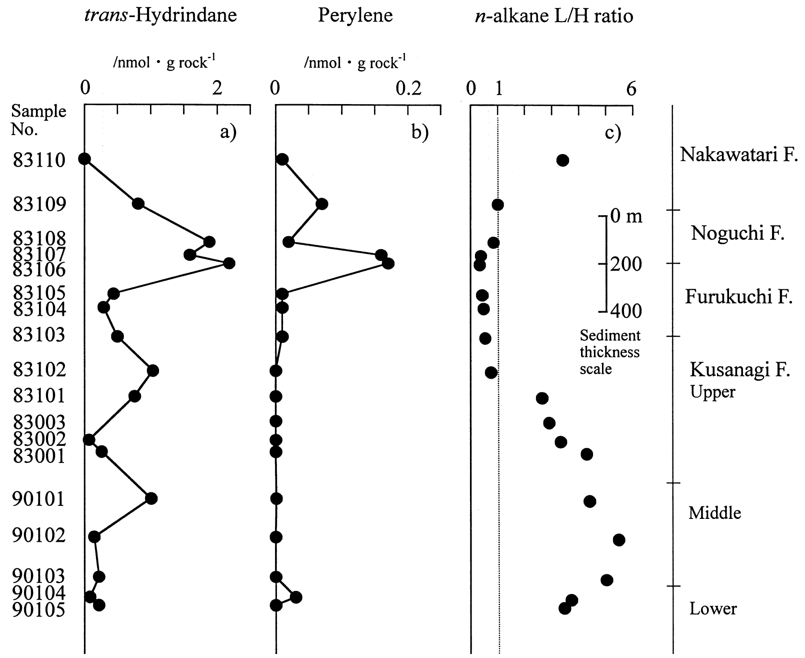

*Fig. 7. Depth profiles of concentrations of a) trans-hydrindane and b) perylene, and c) n-alkane L/H ratios (L/H = $\Sigma C_{15-19}/\Sigma C_{27-31}$) in the Neogene Shinjo sediments.*

alkylcyclohexanes longer than $C_{18}$ began to increase downward from the sediment 83105 (top of the Furukuchi Formation). An exception in the region is the sediment 83108 (top of the Noguchi Formation), which showed a smooth molecular distribution from $C_{15}$ to $C_{25}$ with a maximum in composition at $C_{15}$. Most of the sediments from 83101 to 90105 (upper to lower part of the Kusanagi Formation) in the lower part of the sequence showed relatively smooth molecular distributions from $C_{15}$ to $C_{26}$ compared to those in the upper part of the sequence. The molecular distributions of *n*-alkylcyclopentanes over the sequence showed roughly similar patterns as those of *n*-alkylcyclohexanes (Fig. 8).

The molecular distributions of *n*-alkanes in the sediments from 83110 to 83108 seem to be a composite of two end members, one with a maximum around $C_{15}$ to $C_{18}$ and the other with a maximum around $C_{27}$ to $C_{31}$. However, the compositions around $C_{15}$ to $C_{18}$ decreased in the sediments from 83107 to 83102, and began to increase in 83101. The increase in composition continued downward. On the other hand, the compositions around $C_{27}$ to $C_{31}$ increased to the sediment 83105 and decreased to 83102. The decreased composition continued downward. The molecular distributions showed a remarkable predominance of odd carbon number molecules in the sediments from 83110 to 83102 in the upper part of the sequence, and then, the predominance disappeared downward from 83101. Finally, the molecular distributions became smooth from $C_{15}$ to $C_{26}$ and showed a decreased relative amount from $C_{27}$ to $C_{38}$ in the sediments from 83101 to 90105 in the lower part of the sequence. The change in these molecular distributions of *n*-alkanes along the sequence is similar to that reported by Ishiwatari and Shioya (1986).

*n*-Alkylcyclohexanes have been detected in various crude oils and source rocks (Johns *et al.*, 1966; Anders and Robinson, 1971; Fowler and Douglas, 1984; Fowler *et al.*, 1986; Summons *et al.*, 1988). It has been suggested that they were produced by cyclization of *n*-carboxylic acids during diagenesis (Rubinstein and Strausz, 1979;

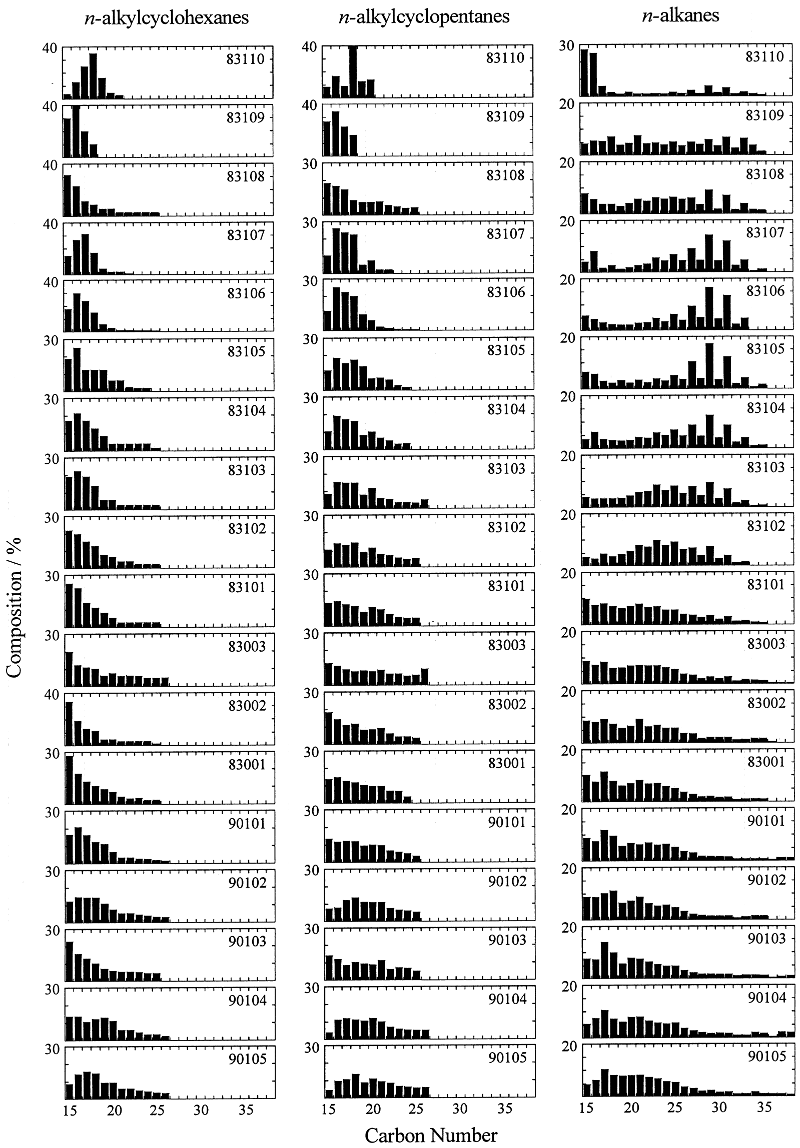

*Fig. 8. Molecular distributions with carbon number of n-alkylcyclohexanes, n-alkylcyclopentanes, and n-alkanes in the Neogene Shinjo sediments.*

Hoffmann *et al.*, 1987; Kissin, 1990), or decarboxylation of *ω*-cyclohexyl carboxylic acids in thermoacidophilic bacterial products (De Rosa *et al.*, 1972; Oshima and Ariga, 1975; Suzuki *et al.*, 1981). *n*-Alkylcyclohexanes in the upper part of the sequence could have been derived mainly from *n*-carboxylic acids by cyclization because of the predominance of *n*-alkylcyclohexanes from $C_{15}$ to $C_{18}$ and that of *n*-carboxylic acids with $C_{16}$ and $C_{18}$ in these sediments (Ishiwatari and Shioya, 1986). Similarly, *n*-alkylcycloalkanes longer than $C_{18}$ might have been produced from longer chain carboxylic acids than $C_{18}$. Contribution from thermoacidophilic bacteria, if any, is insignificant because of the Neogene Shinjo sedimentary environment. The occurrence of *n*-alkylcyclopentanes in sediments has been less reported than those of *n*-alkylcyclohexanes (Ingram *et al.*, 1983;

Yamamoto *et al.*, 1990). It has been suggested that these compounds might have been formed by the intramolecular cyclization of unsaturated carboxylic acids during diagenesis (Philp, 1980).

The molecular distributions of *n*-alkylcyclohexanes, *n*-alkylcyclopentanes, and *n*-alkanes were roughly similar to each other in the sediments from 83101 to 90105 in the lower part of the sequence. This suggests that these distributions reflect the further progress of diagenetic maturation in the sequence as observed in the case of *n*-alkanes. An experimental study was reported for the isomerization of *n*-alkylcyclohexanes and *n*-alkylcyclopentanes during an intense oil generation stage (Kissin, 1990), although the applicability of this study to the two series of the alkylcycloalkanes in the Shinjo sediments is debatable.

## CONCLUSION

Eighteen sediments over a stratigraphic sequence of the Neogene Shinjo basin were analyzed for mono- and bicyclic alkanes. As a result, 45 mono- and 12 bicyclic alkanes were detected at a concentration level of 0.01–1 nmol $g^{-1}$. These cyclic alkanes could be divided into three groups. The first group showed a maximum concentration in the lower part of the sequence (middle part of the Kusanagi Formation), and a depth profile similar to those of *n*-alkanes, pristane plus phytane, and the reported EOC/TOC ratio. This fact indicates a close relation between the cyclic and acyclic alkanes in petroleum formation in the sequence. The second group showed a maximum in the middle part (upper part of the Kusanagi Formation). However, the cyclic alkanes in this group might have been formed at the same diagenetic stage as those of the first group. Later, they probably volatilized or diffused to the upper horizon because of their lower molecular weights, and/or migrated together with water because of their relatively high water solubility. The third group, although it is necessary to find more compounds for this group, showed a maximum in the upper part (the Noguchi Formation) and apparently was not related to the first and second groups in the process of petroleum formation. Further studies are necessary to elucidate precursors and their diagenetic paths to these mono- and bicyclic alkanes in order to obtain a better understanding of the diagenesis of these compounds.

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## REFERENCES

Anders, D. E. and Robinson, W. E. (1971) Cycloalkane constituents of the bitumen from Green River Shale. *Geochim. Cosmochim. Acta* **35**, 661–678.

De Rosa, M., Gambacorta, A. and Minale, L. (1972) The formation of ω-cyclohexyl-fatty acids from shikimate in an acidophilic thermophilic bacillus. *Biochem. J.* **128**, 751–754.

Fowler, M. G. and Douglas, A. G. (1984) Distribution and structure of hydrocarbons in four organic-rich Ordovician rocks. *Org. Geochem.* **6**, 105–114.

Fowler, M. G., Abolins, P. and Douglas, A. G. (1986) Monocyclic alkanes in Ordovician organic matter. *Org. Geochem.* **10**, 815–823.

Hall, P. B. and Douglas, A. G. (1983) The distribution of cyclic alkanes in two lacustrine deposits. *Advances in Organic Geochemistry 1981* (Bjoroy, M. *et al.*, eds.), 576–587, Wiley, Chichester.

Hoffmann, C. F., Foster, C. B., Powell, T. G. and Summons, R. E. (1987) Hydrocarbon biomarkers from Ordovician sediments and the fossil alga *Gloeocapsomorpha priska* Zalessky 1917. *Geochim. Cosmochim. Acta* **51**, 2681–2697.

Hunt, J. M. (1996) *Petroleum Geochemistry and Geology*. 2nd ed., W. H. Freeman & Company, New York.

Ingram, L. L., Ellis, J., Crisp, P. T. and Cook A. C. (1983) Comparative study of oil shales and shale oils from the Mahogany Zone, Green River Formation (U.S.A.) and Kerosene Creek Seam, Rundle Formation (Australia). *Chem. Geol.* **38**, 185–212.

Ishiwatari, R. and Shioya, M. (1986) Diagenetic change of organic compounds in relation to generation of petroleum hydrocarbons. *Contributions to Petroleum Geoscience, dedicated to professor Kazuo Taguchi on the occasion of his retirement 1986*, 357–377 (in Japanese).

Jiang, Z. S. and Fowler, M. G. (1986) Carotenoid-derived alkanes in oils from north-western China. *Advances in Organic Geochemistry 1985* (Leythaeuser, D. and Rullkotter, J., eds.), 831–839, Pergamon Journals, Oxford.

Johns, R. B., Belsky, T. B., McCarthy, E. D., Burlingame A. L., Haug, P., Schnotes, H. K., Richter, W. and Calvin, M. (1966). The organic geochemistry of ancient sediments—Part II. *Geochim. Cosmochim. Acta* **30**, 1191–1222.

Killops, S. D. and Killops, V. J. (1993) *An Introduction to Organic Geochemistry*, Longman Scientific & Technical, U.K.

Kissin, Y. V. (1990) Catagenesis of light cycloalkanes in petroleum. *Org. Geochem.* **15**, 575–594.

McAuliffe, C. D. (1980) The multiple gas-phase equilibration method and its application to environmental studies. *Adv. Chem. Ser.* **1980**, 193–218.

Oshima, M. and Ariga, T. (1975) Cyclohexyl fatty acids in acidophilic thermophilic bacteria. *J. Biol. Chem.* **250**, 6963–6968.

Philp, R. P. (1980) Comparative organic geochemical studies of recent algal mats and sediments of algal origin. *Biogeochemistry of Ancient and Modern Environments*, 173–187, Australian Academy of Science, Canberra, A.C.T.

Rubinstein, I. and Strausz, O. P. (1979) Geochemistry of the thiourea adduct fraction from an Alberta petroleum. *Geochim. Cosmochim. Acta* **43**, 1387–1392.

Shimoyama, A. and Matsubaya, O. (1985) Stable carbon isotopes of organic matter in the Neogene sediments of the Shinjo basin. *Geochem. J.* **19**, 175–179.

Shimoyama, A., Hagiwara, M. and Nomoto, S. (2000) Naphthalenes in Neogene sediments of the Shinjo basin, Japan. *Geochem. J.* **34**, 333–340.

Smith, P. V. (1952) The occurrence of hydrocarbons in recent sediments from the Gulf of Mexico. *Science* **116**, 437–439.

Summons, R. E., Powell, T. G. and Boreham, C. J. (1988) Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, northern Australia; III. *Geochim. Cosmochim. Acta* **52**, 1747–1763.

Suzuki, K., Saito, K., Kawaguchi, A., Okuda, S. and Komagata, K. (1981) Occurrence of $\omega$-cyclohexyl fatty acids in *Curtobacterium pusillum* strains. *J. Gen. Appl. Microbiol.* **27**, 261–266.

Suzuki, N. and Shimada, I. (1983) Considerations in epimerization of sterane and triterpane as indicators of thermal history of sedimentary rocks. *Studies on Diagenesis of Sedimentary Rocks* (Taguchi, K., ed.), 47–55, Tohoku Univ., Sendai.

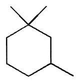
Suzuki, N. and Taguchi, K. (1982) Diagenesis of fatty acids related to sedimentary environment in Neogene sediments of the Shinjo basin, Japan. *Journal of the Geological Society of Japan* **88**, 185–198 (in Japanese).

Taguchi, K., Sasaki, K. and Ushijima, N. (1970) Porphirins of Neogene Tertiary sediments in the Shinjo basin, Yamagata, Japan. *Journal of the Geological Society of Japan* **76**, 559–566 (in Japanese).

Taguchi, K., Shimoda, S., Ichihara, Y., Imoto, N., Ishiwatari, R., Shimoyama, A., Akiyama, M. and Suzuki, N. (1986) Relationship of organic and inorganic diagenesis of Neogene Tertiary rocks, Northeastern Japan. *Soc. Econ. Paleon. Miner. Sp. Publ.* **38**, 47–64.

Yamamoto, S., Ishiwatari, R., Machihara, T. and Morinaga, S. (1990) Characterization of hydrocarbons from sediments of the Panama Basin (ODP Hole 677A and 678B). *Res. Org. Geochem.* **7**, 41–44.

## APPENDIX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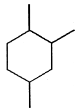
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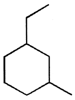
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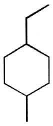
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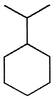
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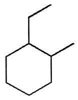
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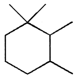
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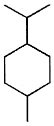
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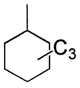

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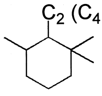

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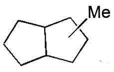

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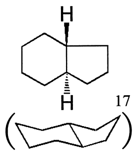

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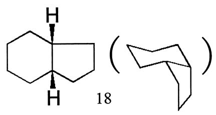

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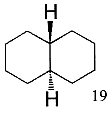

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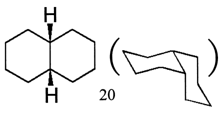

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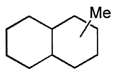

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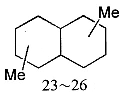

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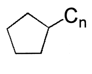

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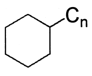

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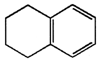
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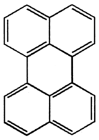
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