Probable fungal origin of perylene in Late Cretaceous to Paleogene terrestrial sedimentary rocks of northeastern Japan as indicated by stable carbon isotopes

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ABSTRACT

Perylene is present in high concentration in Paleogene sediments from the Sanriku-oki borehole of the Ministry of International Trade and Industry (MITI), northeastern Japan. The borehole penetrates a thick sequence of Late Cretaceous to Neogene sediments deposited under a range of conditions including fluvial-deltaic and shallow marine environments. Organic petrological and geochemical data show the sediments to be rich in organic matter derived from higher plants. Biomarker analysis of aliphatic and aromatic hydrocarbons confirms a significant input from higher plants, with extracts dominated by numerous gymnosperm- and angiosperm-derived biomarkers such as diterpanes, oleanenes, des-A-triterpanes, and their aromatized counterparts. The highest concentration of perylene occurs in Middle Eocene sediments deposited in a relatively reducing environment. Stable carbon isotope compositions show ^{13}C enrichment in perylene compared to gymnosperm and angiosperm biomarkers, suggesting a fungal origin. This elevated abundance of sedimentary perylene could relate to a Paleogene continental climate where fungi flourished.

Keywords: perylene, carbon isotope ratio, fungal biomarker, fungi, PAH, Eocene

1. Introduction

Perylene is a typical polyaromatic hydrocarbon (PAH) that occurs in sediments. Although numerous studies have sought to clarify its origin, both its precursors and formation mechanism remain uncertain. Previous investigations have agreed that it can be formed from combustion of organic matter (OM) and fossil fuels in a similar manner to other PAHs. However, unlike anthropogenic PAHs, perylene generally increases in abundance with depth (Orr and Grady, 1967; Aizenshtat, 1973; Ishiwatari et al., 1980; Wakeham et al., 1980; Gschwend et al., 1983; Silliman et al., 1998, 2000), leading researchers to infer that it forms within the rock mass. This conclusion has, in turn, led to the proposition that it forms through diagenetic alteration of natural precursors under anaerobic conditions (Aizenshtat, 1973; Orr and Grady, 1967; Hites et al., 1977; Garrigues et al., 1988; Silliman et al., 1998). Possible precursors include perylenequinones derived from black pigments of modern plants (Thomson, 1976), insects (Cameron et al., 1964), fungi (Hardil et al., 1989; Hashimoto et al., 1994) and crinoids (De Riccardis et al., 1991). Although such precursors are largely terrestrial in origin, it is still not apparent whether perylene is generated in terrestrial or aquatic environments.

There are numerous reports on the existence of perylene in terrestrial sediments (Taguchi et al., 1970; Aizenshtat, 1973; Ishiwatari et al., 1980; Hites et al., 1980; White and Lee, 1980; Garrigues et al., 1988; Jiang et al., 2000; Grice et al., 2009), but it has also been found in marine sediments (Orr and Grady, 1967; Aizenshtat, 1973; Wakeham et al., 1979; Hites et al., 1980; Louda and Baker, 1984; Venkatesan, 1988). In these latter cases, diatoms have been proposed as the source of perylene (Hites et al., 1980;

Venkatesan, 1988), despite an absence of data showing the presence of perylene-related compounds in diatoms.

In this paper we report the distribution and stable carbon isotope ratio ($\delta^{13}C$) of perylene in terrestrial sediments of various lithology and depositional environment in the MITI Sanriku-oki borehole of northeastern Japan. Our objective is to ascertain if natural precursors of perylene can be identified.

2. Samples and methods

2.1. Samples and geological setting

The MITI Sanriku-oki borehole is located on the Pacific side of northeastern Japan (40˚ 40'N, 142˚ 17'E) in a water depth of 857 m (Fig. 1) close to Leg 57, Sites 438 and 439, of the Deep Sea Drilling Project (DSDP; DSDP Scientific Party, 1980). The borehole penetrates 3.64 km of Late Cretaceous to Early Miocene sediments to a depth of 4500 metres below sea level (mbsl). Downhole petrophysical log data, along with the results of seismic profiling have been summarized by the Japan National Oil Corporation (JNOC, 2000) and Osawa et al. (2002).

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Core and cuttings were recovered from depths between 1453 and 4500 mbsl. The geological age, lithology, fossil assemblage, paleoenvironmental record and extent of maturation of the sediments have been extensively investigated (JNOC, 2000). The fossil assemblage consists of higher plant pollen, trilete and monolete spores, dinoflagellate

cysts, nannoplankton and foraminifera. Ages of the sequences are based mainly on dinoflagellate stratigraphy. The whole sedimentary sequence is divided into four distinct lithostratigraphic units at the following depths: Unit A from 4500–3534 m; Unit B, 3534–2921 m; Unit C, 2921–1683 m; Unit D, 1683–1120 m; Unit E, 1120–857 m (Fig. 1).

Unit A is composed of Late Santonian, Early Campanian, Late Campanian, and Early Maastrichtian sediments, and is approximately 1000 m thick. The sediments consist of sandy siltstones, tuffaceous sandstones, and layers of alternating siltstones, volcanoclastic sandstones, conglomerates and claystones, deposited in shallow marine and fluvial environments. Unit A is subdivided into four members, A1, A2, A3, and A4 on the basis of lithology and fossil assemblages.

Unit B is a Paleocene sequence, ca. 600 m thick, comprising variable sequences of mudstones, sandstones, siltstones, tuffaceous sandstones, conglomerates and coaly mudstones deposited in fluvial, lacustrine and bay environments. The unit is divided into two members, B1 and B2, on the basis of lithology. The lower (B1) consists of marine mudstones while the upper (B2) is characterized by alternating coal, tuffaceous rocks, sandstones and mudstones.

Units C and D are separated from one another by an Oligocene erosional unconformity. A major change in lithology towards fine-grained sediments, including mudstones, occurs in the lower part of Unit C, which is exclusively of Eocene age. This lower section is subdivided into C1 and C2 members on the basis of microfossil assemblages. The upper portion (Unit C) of Eocene to Oligocene age, is composed of coarse-grained sediments with intercalations of relatively thick coal layers (C3) and

massive siltstones with coaly particles (C4). The sediments in Unit C were deposited in shallow marine, fluvial and deltaic environments and have a total thickness of ca. 1200 m.

Approximately 600 m of Late Oligocene to Early Miocene sediments make up Unit D. Only its lower portion was investigated. In this portion, the sequence is dominated by shallow marine, fine-grained clastic and volcanoclastic sediments.

JNOC (2000) reported that the core sediments have an average total organic carbon (TOC) content of 0.5–2.0%, with coals and coaly sediments having TOC of 40–60%. Sulfur content is generally around 0.2%. The maturity levels of the OM were estimated from measurements of vitrinite reflectance (R_o) that increased with depth from 0.3–0.6%, in agreement with estimates from thermal alteration index (TAI) and Rock Eval T_{max} values, which indicate that the maturity lies above the conventional oil window (JNOC, 2000).

2.2. Analyses

57 cuttings samples from the MITI Sanriku-oki borehole were analysed in this study. Each was extracted by ultrasonication for 15 min with CH_2Cl_2/MeOH (99:1). The extracts were separated using column chromatography into aliphatic and aromatic hydrocarbon fractions. To obtain suitable aromatic hydrocarbon fractions for compound-specific $\delta^{13}C$, the initial fractions were further separated using preparative high pressure liquid chromatography (HPLC) with a JASCO Gulliver series PU-986/UV-975 instrument fitted with a pressure-resistant glass column (29 cm x 8 mm i.d.) containing silica gel (WAKOGEL LP-20). A hexane/CH_2Cl_2 (95:5) solvent mixture was used as the

eluent at a constant flow of 2.0 ml/min. The cut points for fractionation were determined with an ultraviolet detector at 254 nm using a mixture of standard aromatic hydrocarbons (Yessalina et al., 2006).

The isolated hydrocarbons were analyzed using gas chromatography-mass spectrometery (GC/MS; HP6890/HP5973), equipped with a fused silica column (30 m x 0.25 mm i.d.) with a DB-5 stationary phase and employing He as a carrier gas at 1.5 ml/min. The oven temperature program was: 40˚C (2 min) to 300 ˚C (held 20 min) at a heating rate of 4 ˚C/min. The identification of components was made using MS library comparisons and data available in the literature.

The $\delta^{13}C$ values were measured using gas chromatography–combustion-isotope ratio mass spectrometry (GC–C/IR-MS; Finnigan MAT 252 or Thermo Quest DELTA V Advantage mass spectrometer), with a fused silica DB-5 column (60 m x 0.25 mm i.d.) and He as carrier gas at 1.1 ml/min. The combustion furnace (Finnigan MAT GC-combustion III Interface) was packed with CuO_2 and maintained at 850 °C. The $\delta^{13}C$ were determined vs. an internal standard ($C_{24}D_{50}$) and are reported in parts per thousand (‰) relative to Vienna Pee Dee Belemnite (VPDB). The error of the measurements was within ±0.3‰. Details of the measurements are described by Ratnayake et al. (2006).

3. Results and discussion

3.1. Occurrence of perylene in Late Cretaceous to Paleogene sedimentary rocks

Analysis of the aromatic fraction of samples from the MITI Sanriku-oki borehole shows the presence of perylene in sediments of Late Cretaceous to mid-Eocene age from Units A, B, and C. In all of them, perylene occurs in much greater abundance than PAHs

formed by combustion such as pyrene, benzo[a]anthracenes, benzofluoranthenes, benzopyrenes and phenanthrenes (Fig. 2 and Table 1).

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The Late Cretaceous to Paleogene sediments were deposited in shallow-terrestrial and marine environments. Continental environments persisted in the lower part of the sequence (Units A and B), as reflected by the presence of freshwater algae (*Leiosphaeridia hyalina*, *Pediastrum* spp.) and the large proportions of coal-bearing strata and coarse grained material such as conglomerates, sandstones and siltstones (JNOC, 2000). Shallow marine sediments occur mainly in the upper part of the sequence from 2500–1565 m (Units C and D) and are represented exclusively by fine clastic sediments in the major portion of the Middle Eocene section from 2921–2000 m (Unit C). The highest relative abundance of perylene is found in these fine-grained sedimentary intervals (Fig. 3). Perylene is less significant in the Late Cretaceous intervals dominated by fine-grained lithology or containing significant coal-bearing strata.

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Although an increase in fine-grained lithologies is associated with the emergence of a more marine environment, the occurrence of perylene appears to be unrelated to marine conditions. Sedimentary layers with fine-grained lithology from marine-influenced sections show a general absence of perylene. The part of Unit D that shows an

increase in marine influence throughout its extent is indistinguishable from other portions in terms of Rock-Eval pyrolysis data. It does, however, contain significant marine algae and is characterized by a greater proportion of amorphous OM (JNOC, 2000).

The presence of perylene in the samples is not maturity dependent. Its relative abundance varies with age, lithology, depositional environment and OM content. It is more abundant in sediments of Paleogene age than in Late Cretaceous sediments, with the highest concentration in fine grained sediments deposited in fluvial-deltaic environments rather than in shallow marine environments.

3.2. Distribution of higher plant biomarkers

The major compounds in the hydrocarbon fractions are long chain *n*-alkanes with an odd carbon number predominance, pointing to an elevated input of material from higher plants (JNOC, 2000). This suggestion is supported by a general depletion of steranes, a predominance of C_{29} over C_{27} steranes and an enrichment in higher plant biomarkers (JNOC, 2000). The latter include various aromatic di- and triterpenoid hydrocarbons such as cadalene, dehydroabietin, dehydroabietane, simonellite, retene, trimethyltetrahydrochrysene, an 8,14-seco-oleanoid, pentamethylnonahydropicene, tetramethyloctahydropicene, tetraaromatic lupene and trimethyltetrahydropicenes, all of which were also detected in the present study (Fig. 2). The presence of dehydroabietin, dehydroabietane, simonellite and retene indicate contributions from gymnosperms (Simoneit, 1977; Barrick and Hedges, 1981; Richardson and Miller, 1982; Noble et al., 1985, 1986; Ellis et al., 1996; Bastow et al., 2001). An input from angiosperms is

apparent from the presence of the 8,14-seco-oleanoid, pentamethylnonahydropicene, tetramethyloctahydropicene, tetraaromatic lupene and trimethyltetrahydropicenes (Bendoraitis, 1974; Spyckerelle et al., 1977; Corbet et al., 1980; Chaffee an Johns, 1988).

Table 1 gives the relative abundances of the various higher plant biomarkers, and Fig. 3 presents their vertical distribution profiles. The vertical distributions show random variations that cannot be correlated with the thermal evolution of the OM. Rather, the differences reflect changes in the land plant vegetation as shown by palynological data. Fossil assemblages are mainly those of land plants, with palynological analysis showing both angiosperm and gymnosperm species to be major components of the Paleogene section (JNOC, 2000). In the Late Cretaceous samples, land plants are less dominant and there is an increased presence of trilete and monolete spores of ferns. The relative abundance of angiosperm vs. gymnosperm pollen changes slightly with depth. Angiosperm pollen dominates from 3500-2900 m (Unit B) and 2000-1500 m (Units C3 to D2). A greater angiosperm input is also seen in the greater abundance of aromatic non-hopanoid triterpenoids relative to aromatic diterpenoids in Unit B as confirmed by the ratio of the sum of aromatic non-hopanoid triterpenoids to the sum of aromatic diterpenoids and non-hopanoid triterpenoids (Fig. 3). The relative abundance of perylene vs. gymnosperm and angiosperm aromatic biomarkers was highest in Units C1 and C2. Perylene also significantly dominates in Unit B. Its distribution does not correlate with gymnosperm or angiosperm contributions.

3.3. Carbon isotope ratios of perylene and higher plant biomarkers

Table 2 shows the $\delta^{13}C$ values of perylene and higher plant biomarkers such as aromatic di- and triterpenoids in the same samples. sThe values for higher plant biomarkers range from -22.3 to -30.9‰, with values of -22.5 to -26.7‰ (ave. -24.6‰) for retene (compound D), -24.1 to -28.7‰ (ave. -26.0‰) for trimethyltetrahydrochrysene (compound E), -24.4 to -29.6‰ (ave. -26.3‰) for the seco-oleanoid (compound G), -22.3 to -29.6‰ (ave. -25.3‰) for pentamethylnonahydropicene (compound H), -23.9 to -30.9‰ (ave. -26.6‰) for tetramethyloctahydropicene (compound I), -25.0 to -29.6‰ (ave. -27.0‰) for tetraaromatic lupene (compound J), -25.1 to -28.3‰ (ave. -26.8‰) for 1,2,9-trimethyltetrahydropicene (compound K), and -24.4 to -28.1‰ (ave. -26.3‰) for 2,2, 9-trimethyltetrahydropicene (compound L).

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The $\delta^{13}C$ values for the higher plant biomarkers fall within reported ranges for similar compounds identified as higher plant biomarkers in other geological studies (Freeman et al., 1994; Tuo et al., 2003). Despite the large scatter in the $\delta^{13}C$ values, it is still possible to distinguish between biomarkers of angiosperms and gymnosperms, with the $\delta^{13}C$ values for triterpenoids tending to be more negative than those of diterpenoids. Murray et al. (1998) suggested that typical $\delta^{13}C$ values of gymnosperm and angiosperm resins are ca. -22.8 and -26.4‰, respectively. The average values found in the present study for di- and triterpenoids taken as biomarkers of angiosperms and gymnosperms, respectively, are broadly consistent with the trend in those values (Table 2). The comparatively large variation in $\delta^{13}C$ of the higher plant biomarkers can be linked to

differences in the isotopic signatures among the various species that contributed to their formation, including aquatic microphytes (Freeman et al., 1994). Significant variations in isotopic compositions have been observed not only between different species, but also within species (Lockheart et al., 1997 and references therein). On the other hand, the values for perylene range from -21.1 to -24.5‰ (ave. -23.1‰) and are clearly more positive than values for both the gymnosperm and angiosperm biomarkers (Table 2). In particular, the highest values for perylene in the Paleogene sediments from the borehole point to an origin that is distinct from higher land plant sources.

3.4. Origin of perylene in sedimentary rocks from Sanriku-oki borehole

The abundance of perylene in the MITI Sanriku-oki sediments suggests its diagenetic formation from biogenic precursors under reducing conditions. When the concentration of perylene exceeds 10% of the total unsubstituted PAHs, it is generally considered to be of diagenetic origin (Hites et al., 1980). Combustion is unlikely to be the cause of perylene formation when other combustion-derived PAHs occur in extremely low concentration, as in the present study (Fig. 2 and Table 1).

The presence of high perylene concentrations in 4.5 km-thick Late Cretaceous and Paleogene sedimentary rocks in this study is one of the rare cases of its occurrence in ancient sediments. As with other occurrences, the presence of perylene in sedimentary rocks appears to be controlled by the redox conditions of the depositional environment. The highest abundance of perylene occurs in sediments of Unit C that were deposited in relatively reducing conditions, as indicated by the lowest pristane/phytane (Pr/Ph) ratios in the range 0.97–2.31 (Table 1). In the underlying sequences of Units B2 and B1, higher

Pr/Ph values >3.0 are consistent with a sub-oxic to oxic depositional environment (Didyk et al., 1978; Hunt, 1996). The more reducing depositional environment of Unit C is also apparent from the predominance of fine-grained lithologies. Our data also show that the abundance of perylene fluctuates in response to changing redox conditions during early diagenesis, in agreement with previous investigations (Aizenshtat, 1973; Orr and Grady, 1967; Hites et al., 1977; Garrigues et al., 1988; Silliman et al., 1998). Any differences in the thermal maturity of samples within the 2 km thick sequence can be excluded from influencing the results, given the relatively narrow range of maturity (0.3–0.5%, R_o).

The presence of perylene in sediments dominated by terrestrial OM supports the suggestion that it is a diagenetic product derived from terrestrial sources. Its occurrence in sediments dominated by higher plants appears to support the suggestion of an origin from such higher plants (cf. Aizenshtat, 1973; Jiang et al., 2000). However, the $\delta^{13}C$ values of perylene do not support such a proposition, being more positive and different from the $\delta^{13}C$ values for both gymnosperm and angiosperm biomarkers (Table 2).

Fungi have been suggested as important sources of sedimentary perylene (Hardil et al., 1989; Hashimoto et al., 1994). They inhabit soil and play important roles in the terrestrial cycling of carbon and nitrogen. Their biomass often exceeds that of bacteria and Archea in soil. Studies of the isotopic composition of fungi have shown more than +3.0‰ ^{13}C enrichment for saprophytic fungi relative to their substrates (Hobbie et al., 1999; Kohzu et al., 1999). Further, Kohzu et al. (2005) demonstrated that ^{13}C enrichment in fungal aggregates, compared to decomposed wood, ranges from +1.2 to +6.3‰, although the degree of enrichment is affected by the fungal species, substrate and growth stage.

Perylene in the sediments analysed in this study tends to be enriched in $\delta^{13}C$ compared to associated gymnosperm and angiosperm biomarkers, with an enrichment of ca. +1.5‰ and +3.3‰, respectively (Table 2), in agreement with the enrichment found in fungi compared to decomposed wood by Kohzu et al. (2005). The results suggest that the MITI Sanriku-oki perylene is derived mainly from fungal sources. The absence of any direct correlation between perylene and angiosperm and gymnosperm biomarkers can be linked to changes in land plant species and/or to the influence of oxic conditions unfavorable for perylene formation. A remarkable correlation was found in the Eocene sediments of Unit C, where perylene has the highest relative abundance in the aromatic hydrocarbon fraction. These particular sediments represent a continental climatic environment where fungi flourished, suggesting that a high abundance of sedimentary perylene might be a useful indicator of moist and humid continental climatic conditions.

4. Conclusions

Perylene occurs in sediments from the MITI Sanriku-oki borehole and increases in concentration with depth among the intervals deposited in reducing environments and rich in terrestrial OM. This is consistent with previous suggestions that perylene is a diagenetic product of terrestrial OM, with anoxic conditions favoring its formation and/or preservation. Examination of the carbon isotope ratios of perylene and associated gymnosperm and angiosperm biomarkers shows perylene to be enriched in ^{13}C compared to the higher plant markers. This result points strongly to an origin from fungal sources, in which case a high abundance of sedimentary perylene might indicate a moist and humid continental climate in the depositional environment.

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Figure captions

Fig. 1. Location and lithostratigraphy of the MITI Sanriku-oki borehole in northeastern Japan.

Fig. 2. Representative total ion chromatograms (TIC) showing distribution of perylene and higher plant biomarkers in Paleogene sediment samples of the MITI Sanriku-oki borehole. A, dehydroabietin; B, dehydroabietane, C, simonellite; D, retene; E. trimethyltetrahydrochrysene; F, perylene; G, 8,14-seco-oleanoid; H, 2,2,4a,6a,9-pentamethyl-1,3,4,5,6,13,14,14a,14b-nonahydropicene; I, 1,2,4a,9-tetramethyl-1,2, 3,4,4a,5,6,14b-octahydropicene; J, tetraaromatic lupane; K, 1,2,9-trimethyl-1,2,3,4-tetrahydropicene; L, 2,2,9-trimethyl-1,2,3,4-tetrahydropicene; M, benzohopane ($C_{31}H_{46}$); N, 2,9-dimethylpicene; O, benzohopane ($C_{33}H_{50}$); P, benzohopane ($C_{34}H_{52}$); Q, benzohopane ($C_{35}H_{54}$)

Fig. 3. Distribution of pollen/spores, vitrinite reflectance (R_o%), carbon preference index (CPI), Pr/Ph ratio and relative abundance of perylene, angiosperm biomarkers, and gymnosperm biomarkers, vs. depth in the MITI Sanriku-oki borehole. Data for pollen/spores and vitrinite reflectance from JNOC (2000).

Table 1. *n*-Alkane CPI, pristane/phytane ratio and relative abundance (%) of aromatic biomarkers in sediments from MITI Sanriku-Oki

Depth (m)	CPI	Pr/Ph	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	Perylene[*1]	Angio.[*2]
1590	4.32	0.43	2.38	2.35	3.19	2.49	5.62	11.0	11.13	24.87	12.18	4.48	1.09	10.05	3.34	0.33	1.95	3.39	0.18	0.15	0.86
1690	2.52	n.d.	7.36	7.32	28.06	4.48	3.99	20.3	2.27	4.42	1.88	1.39	4.73	10.47	1.31	1.05	0.60	0.40	0.00	0.28	0.35
1790	3.09	n.d.	1.22	5.36	6.54	39.48	4.81	16.6	1.09	4.48	4.78	1.59	5.21	7.02	1.01	0.07	0.29	0.41	0.00	0.22	0.31
1890	3.55	n.d.	4.11	10.16	47.59	14.50	3.88	0.4	1.34	3.57	2.31	1.97	2.68	6.34	0.56	0.03	0.22	0.35	0.00	0.00	0.19
1990	3.39	1.58	2.08	4.93	7.23	2.32	3.48	60.8	0.60	5.40	2.84	0.97	2.52	5.07	0.73	0.26	0.32	0.41	0.07	1.79	0.51
2050	4.30	2.23	2.50	7.61	26.86	9.60	5.14	23.1	1.42	3.78	1.85	1.27	4.37	9.81	0.75	0.36	0.51	0.82	0.22	0.33	0.33
2090	3.27	0.97	2.40	5.78	8.10	2.42	3.83	59.0	0.72	5.59	2.67	1.02	2.34	4.77	0.55	0.19	0.29	0.35	0.00	1.65	0.48
2150	4.11	1.79	2.40	6.66	10.60	2.54	5.29	40.2	1.35	6.84	4.98	1.82	7.14	8.10	0.67	0.65	0.33	0.32	0.12	0.77	0.58
2190	4.98	1.41	2.12	4.27	24.33	2.02	13.72	33.9	0.30	3.04	2.82	1.03	4.85	5.61	0.73	0.39	0.40	0.37	0.14	0.67	0.35
2250	3.44	1.45	3.01	4.94	3.20	1.84	21.15	38.1	0.13	2.63	1.59	1.27	8.49	10.02	1.26	0.50	0.86	0.68	0.33	1.03	0.65
2290	4.54	1.08	2.05	3.00	2.60	2.10	18.20	46.0	0.62	1.77	1.58	1.05	8.28	8.89	1.57	0.50	0.79	0.67	0.33	1.44	0.69
2350	4.15	1.25	3.03	2.89	3.14	2.47	13.31	37.4	1.46	3.06	2.10	1.31	9.34	12.37	3.51	0.50	1.93	1.59	0.55	0.91	0.72
2390	4.48	1.51	2.99	2.06	3.09	3.16	12.45	56.1	1.36	1.43	1.11	0.64	3.79	6.59	2.34	0.12	1.30	1.06	0.45	2.14	0.57
2450	4.20	2.00	1.34	1.33	1.74	4.05	16.09	51.7	1.98	1.16	1.07	0.79	4.24	7.48	3.41	0.28	1.42	1.52	0.43	2.05	0.66
2490	4.02	1.84	2.90	2.68	3.14	4.99	19.36	44.6	1.87	2.05	0.98	0.47	3.54	5.79	3.38	0.21	1.80	1.64	0.58	1.57	0.52
2550	4.08	2.11	0.32	0.19	0.88	1.73	5.81	34.6	1.44	1.31	1.78	1.50	8.23	19.06	9.37	0.63	4.26	6.48	2.45	0.95	0.91
2590	4.05	1.52	2.48	2.07	3.59	14.38	13.80	40.6	1.62	1.96	1.04	0.53	2.64	5.42	4.40	0.20	2.30	2.24	0.77	1.14	0.37
2650	3.77	1.74	1.57	1.36	3.58	6.69	14.10	39.1	2.71	1.50	1.62	1.19	4.21	8.24	6.50	0.37	2.90	3.19	1.22	1.20	0.60
2690	3.65	1.99	2.08	2.01	2.98	10.81	18.94	32.6	4.34	2.43	1.23	0.67	3.29	6.10	5.53	0.21	2.99	2.53	1.23	0.91	0.50
2750	3.76	2.08	0.97	0.69	0.94	3.31	12.24	46.3	4.87	1.05	2.11	0.97	4.39	8.74	7.31	0.58	1.49	3.03	0.95	1.65	0.79
2790	3.94	2.29	2.39	1.48	2.72	3.92	18.56	27.1	6.01	3.37	1.75	0.65	4.50	7.02	9.70	0.32	4.29	4.37	1.81	0.80	0.69
2850	3.61	2.31	0.95	0.65	1.01	6.39	13.04	38.3	5.23	1.86	1.88	0.86	3.97	9.59	8.43	0.75	2.22	3.64	1.25	1.18	0.72
2890	3.42	2.23	1.12	0.74	2.24	15.75	5.50	27.2	4.03	10.86	2.74	9.90	3.14	12.64	1.52	0.70	0.74	0.89	0.28	0.43	0.69
2950	3.64	3.83	1.10	0.35	0.54	1.66	1.69	15.1	2.11	10.58	10.18	9.22	7.82	35.68	1.35	1.29	0.39	0.70	0.29	0.19	0.95
2990	3.30	3.08	4.76	1.75	4.45	4.49	6.17	16.3	5.86	15.35	7.14	7.58	3.62	19.55	0.80	0.54	0.66	0.71	0.26	0.22	0.79
3050	3.20	4.32	1.02	0.44	0.90	11.82	8.25	7.9	9.86	5.76	4.38	6.38	12.24	28.36	0.77	0.82	0.26	0.44	0.37	0.10	0.83
3090	2.90	4.56	4.57	2.23	4.22	5.04	38.93	9.3	4.27	4.72	8.13	3.28	6.76	2.46	1.47	1.20	1.87	1.28	0.33	0.20	0.65
3150	2.59	5.63	2.42	0.80	0.89	8.10	2.91	39.6	4.66	7.69	8.94	6.51	1.71	13.23	0.57	1.06	0.29	0.51	0.14	0.72	0.78
3190	2.45	n.d.	4.21	1.52	5.82	8.94	3.78	35.8	5.72	11.48	6.34	4.69	1.13	6.55	0.99	1.03	0.81	0.90	0.25	0.63	0.64
3250	2.35	4.79	3.69	1.83	3.28	5.25	5.37	20.2	9.10	11.94	8.67	9.47	1.94	8.25	2.96	1.45	2.96	2.63	1.06	0.32	0.78
3290	2.04	2.74	4.23	1.25	4.54	3.70	6.85	28.2	13.85	5.98	8.95	2.62	1.99	10.65	1.77	1.08	2.08	1.71	0.55	0.49	0.76
3350	3.28	5.15	3.24	0.97	4.73	3.74	11.65	18.2	11.70	7.23	5.71	5.08	3.00	15.50	2.29	1.80	2.04	2.41	0.69	0.30	0.79
3400	2.27	5.57	4.48	1.51	8.36	5.73	9.33	20.1	15.38	10.82	3.53	2.37	1.66	8.29	2.21	0.75	2.41	2.28	0.82	0.32	0.68
3450	2.03	5.04	2.98	1.98	5.20	42.53	8.09	1.8	12.65	1.78	5.69	0.83	4.29	9.19	0.49	0.76	0.34	1.26	0.13	0.02	0.40
3490	1.66	n.d.	9.03	1.40	23.80	37.72	5.01	4.9	4.55	0.97	2.58	0.97	1.29	4.48	0.62	0.25	1.00	1.43	0.00	0.06	0.17
3550	1.72	5.19	3.65	1.76	8.71	5.56	5.21	19.1	8.56	11.62	6.20	8.68	1.87	7.93	2.97	1.30	3.10	2.76	1.04	0.30	0.70
3690	1.67	2.16	21.22	8.68	21.94	20.45	1.87	10.6	2.97	1.59	1.41	1.41	0.55	2.15	1.28	1.14	0.94	1.50	0.31	0.13	0.12
3700	1.65	1.73	9.64	2.25	3.37	60.49	2.25	4.0	0.00	3.91	3.85	4.07	0.00	4.01	0.00	0.00	0.80	0.80	0.54	0.04	0.17
3880	1.64	1.30	6.93	1.76	1.89	72.15	2.39	1.9	0.00	3.78	3.47	0.32	1.58	1.89	0.50	0.00	0.57	0.50	0.38	0.02	0.12
4100	1.77	1.45	20.14	3.82	15.57	14.97	2.39	19.9	2.37	4.61	2.06	4.97	0.43	5.18	0.51	1.27	0.43	1.21	0.19	0.27	0.26
4250	1.34	2.07	18.06	7.90	6.21	43.91	0.00	4.4	0.00	3.95	5.53	1.41	0.00	6.09	0.85	0.00	0.85	0.68	0.17	0.05	0.18
4300	1.14	2.69	49.22	8.52	12.00	16.86	1.25	2.8	0.65	1.12	0.90	1.16	0.31	3.51	0.34	0.51	0.20	0.51	0.16	0.03	0.08

A; Dehydroabietin, B; Dehydroabietane, C; Simonellite, D; Retene, E; Trimethyltetrahydrochrysene, F; Perylene, G; 8, 14-Seco-oleanoid, H; 2, 2, 4a, 6a, 9-Pentamethyl-1, 3, 4, 5, 6, 13, 14, 14a, 14b-nonahydropicene, I; 1, 2, 4a, 9-Tetramethyl-1, 2, 3, 4, 4a, 5, 6, 14b-octahydropicene, J; Tetraaromatic lupine, K; 1, 2, 9-Trimethyl-1,2,3,4-tetrahydropicene, L; 2, 2, 9-Trimethyl-1,2,3,4-tetrahydropicene, M; Benzohopane (($C_{31}H_{46}$), N; 2, 9-Dimethylpicene, O; Benzohopane ($C_{33}H_{50}$), P; Benzohopane ($C_{34}H_{52}$), Q; Benzohopane ($C_{35}H_{54}$). *1; Perylene abundance as shown by F/{(A+B+C+D)+(G+H+I+J+K+L)}, 2; Angiosperm contribution as shown by (G+H+I+J+K+L)/{(A+B+C+D)+(G+H+I+J+K+L)}

Table 2. Carbon isotope ratios (‰ vs.VPDB) of perylene and higher plant biomarkers in sediments from MITI Sanriku-oki.
Carbon isotope ratio was not determined for compounds not present or present at low concentrations.

Depth (m)	Geologic Unit	F(Perylene)	Gymosperm D（Retene）	Angiosperm E	G	H	I	J	K	L
1840	Unit C	-23.3					-27.6	-27.3	-25.1	
1900	Unit C			-28.7						
1950	Unit C		-25.6	-25.6						
2100	Unit C			-26.4						
2300	Unit C	-22.9	-23.7	-24.4						
2350	Unit C	-22.4	-22.5	-25.4			-26.4	-29.6	-26.3	-26.3
2550	Unit C	-22.7								
2750	Unit C	-23.5	-25.6							
2850	Unit C		-25.1	-24.5			-26.4	-27.3		
2950	Unit B	-22.6					-30.9	-27.9		
3000	Unit B	-22.6			-25.4		-25.9	-27.4		-24.4
3020	Unit B	-22.6					-23.9			
3040	Unit B	-21.1	-26.7	-26.6	-26.4	-24.6				-25.5
3120	Unit B	-23.6	-23.7	-26.1	-29.6	-29.6	-27.6	-26.5		-28.1
3140	Unit B	-23.5	-23.8	-26.4	-24.4	-22.3	-27.5	-26.7	-28.3	-26.7
3200	Unit B	-24.5				-23.2	-25.2	-25.0		
3260	Unit B	-24.2	-24.8							
3360	Unit B						-26.4	-26.9	-27.3	
3420	Unit B	-23.7		-26.1	-25.6	-26.9	-25.1	-25.4		-27.2
3680	Unit A	-23.5								-25.6
average		-23.1	-24.6	-26.0	-26.3	-25.3	-26.6	-27.0	-26.8	-26.3

D. Retene, E. Trimethyltetrahydrochrysene, F. Perylene, G. 8, 14-Seco-oleanoid, H. 2, 2, 4a, 6a, 9-Pentamethyl-1, 3, 4, 5, 6, 13, 14, 14a, 14b-nonahydropicene, I. 1, 2, 4a, 9-Tetramethyl-1, 2, 3, 4, 4a, 5, 6, 14b-octahydropicene, J. Tetraaromatic lupine, K. 1, 2, 9-Trimethyl-1,2,3,4-tetrahydropicene, L. 2, 2, 9-Trimethyl-1,2,3,4-tetrahydropicene.

Figure 1 (Image)

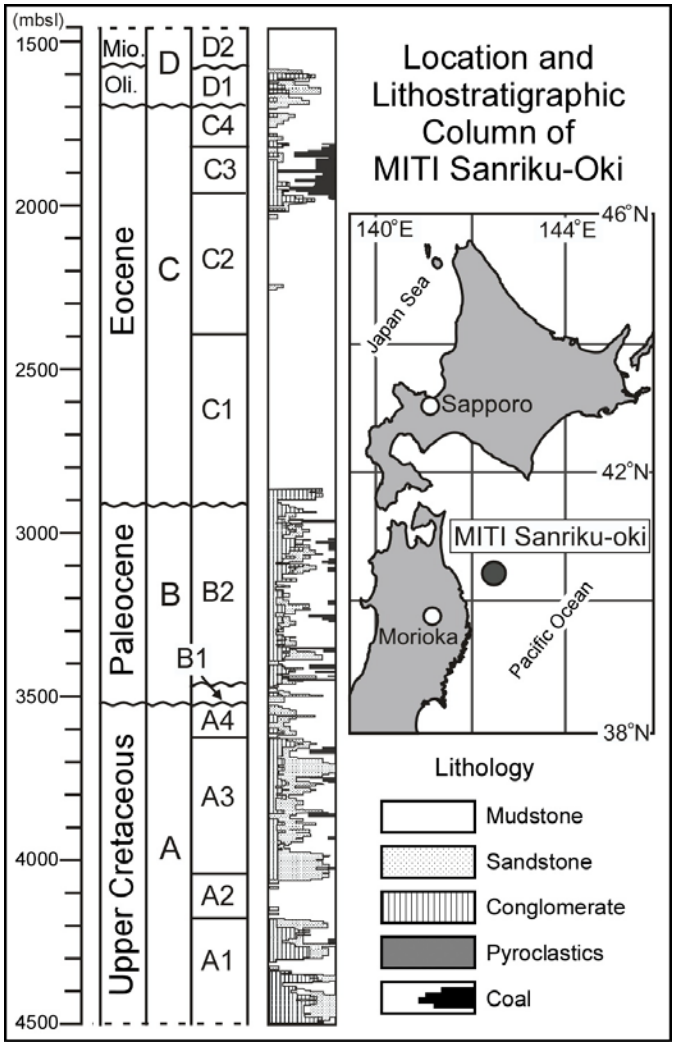

Figure 2 (Image)

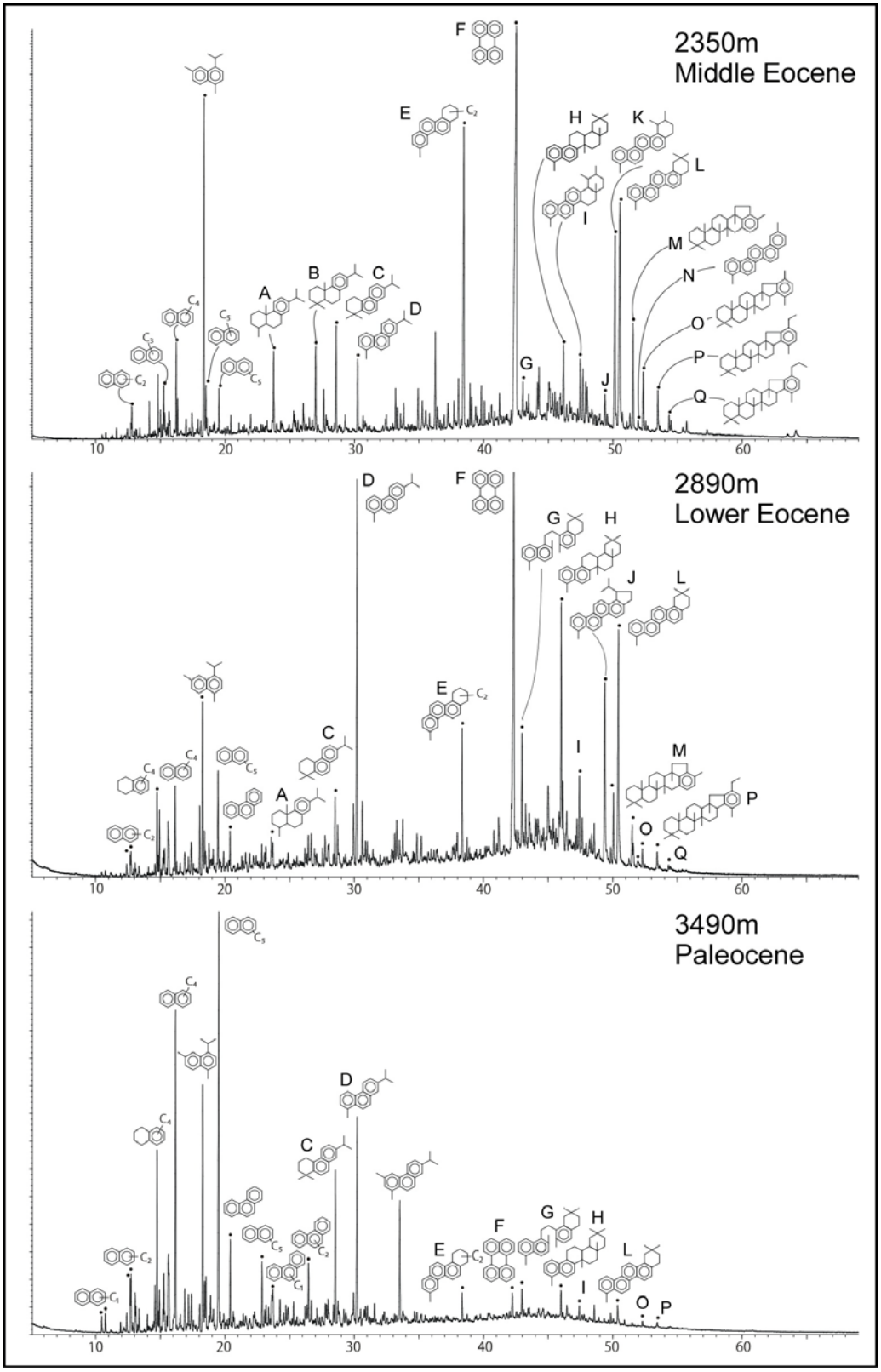

Figure 3 (Image)