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Change of hydrogen stable isotope ratios of *n*-alkanes, pristane, phytane, and aromatic hydrocarbons in Miocene siliceous mudstones with increasing maturity

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Abstract

Variation in the hydrogen stable isotope ratios (D/H ratios) of *n*-alkanes, pristane, phytane, and aromatic hydrocarbons with increasing maturity was investigated using a set of immature to mature Miocene siliceous mudstones. The D/H ratios of aromatic hydrocarbons change at the earliest stage ($R_o=0.4$ to 0.5%), giving higher values in immature rocks. A dramatic increase in D/H values is observed in pristane and phytane during the mature stage ($R_o=0.6$ to 0.7%), attributable to hydrogen exchange with sediment pore water. The decrease in D/H ratios in short-chain *n*-alkanes and the disappearance of carbon number predominance observed in *n*-alkane D/H ratios with increasing maturity is a result of the thermal cracking of aliphatic structures in bitumen and kerogen. The D/H ratios of long-chain *n*-alkanes derived from higher plant wax can maintain their initial values even in the zone of extensive oil generation ($R_o<0.7\%$).

Introduction

Hydrogen stable isotope ratios (D/H ratios) of higher plants vary greatly due to differences in the D/H ratios of water and/or by higher plant type. The D/H ratios of higher plant biomarkers preserved in sediments can be a useful parameter for evaluating paleo-hydrological climate (*e.g.*, Sessions et al., 1999; Sachse et al., 2004, 2006). However, previous studies have shown that the D/H ratios of organic matter change with increasing maturity due to the exchange of hydrogen atoms between organic matter and pore water (Alexander et al., 1984; Session et al., 2004; Schimmelmann et al., 2006). The D/H ratios of oils and sedimentary organic matter also tend to change with increasing maturity (Dawson et al., 2005, 2007; Radke et al., 2005; Pedentchouk et al., 2006; Lis et al., 2006). Such variations of the D/H ratios of sedimentary organic matter have not yet been fully investigated across the whole range from diagenesis to catagenesis. Furthermore, relatively few studies have examined D/H ratios in aromatic hydrocarbons, compared to the more numerous studies of kerogen and saturated hydrocarbons, and reconstructions of paleo-hydrological climate have been based on the D/H ratios of organic matter from relatively young and immature sediments.

Diagenetic changes to hydrogen isotope ratios may also be related to inorganic matrix characteristics, such as the abundance and type of clay minerals as catalysts (Alexander et al., 1982; 1984; Leif and Simoneit, 2000). Immature to mature Middle Miocene diatomaceous

siliceous mudstones are well distributed in northeastern Japan along the Japan Sea. Previously studies of these rocks have focused on the thermal transformation of organic matter with increasing maturation (Taguchi et al., 1986; Amo et al., 2007, 2008). In this paper, we examine the diagenetic changes in the D/H ratios of aliphatic and aromatic hydrocarbons.

Materials and Methods

Sedimentary rocks of the Middle Miocene Yakumo and Kusanagi Formations, both largely siliceous mudstones, are distributed throughout northeast Japan and were originally deposited in similar marine environments (Fig. 1). These siliceous mudstones are a known hydrocarbon source rock in northeast Japan, and a set of samples from Yakumo region (42°23'N, 140°10'E) and Shinjo region (38°51'N, 140°08'E) provided sediment in the opal-A, opal-CT, and quartz zones (Taguchi et al., 1986; Amo et al., 2007, 2008). We used these samples to investigate the effects of diagenetic changes on biomarker D/H ratios.

Samples were extracted three times by ultrasonication for 15 min with dichloromethane/methanol (vol./vol.; 1/3, 1/1, and 1/0). Organic extracts were separated into aliphatic and aromatic hydrocarbon fractions using column chromatography. Branched/cyclic hydrocarbons and *n*-alkanes in aliphatic hydrocarbon fractions were separated by urea adduction prior to D/H ratio analysis. The isolated hydrocarbons were analyzed by gas

chromatography (GC; Shimadzu GC-17A) and a gas chromatograph-mass spectrometer (GC/MS; HP6890/HP5973), equipped with a fused silica capillary column DB-5HT (30 m x 0.25 mm i.d.) and employing helium as the carrier gas at a flow rate of 1.0 ml/min. The oven temperature was programmed to hold initially at 50°C for 2 min and then to increase from 50°C to 120°C at 10°C/min, from 120°C to 300°C at 4°C/min where it was held for a further 15 min. Identification of the different compounds was made using Mass Spectral Library data and data available in the literature.

The D/H ratios of hydrocarbons were measured using a GC-high temperature conversion-isotope ratio mass spectrometer (GC-HTC-IRMS, Thermo Fischer DELTA V Advantage), equipped with a fused silica capillary column DB-5HT (30 m x 0.32 mm i.d.), and helium as the carrier gas at a flow rate of 1.0 ml/min. The oven temperature was programmed to hold initially at 50°C for 2 min. It then increased from 50°C to 120°C at 10°C /min, from 120°C to 300°C at 4°C/min, and then held at 300°C for a further 15 min. Hydrocarbons separated by GC were pyrolyzed in a carbon tube at 1450°C. The H₂ gas obtained by high-temperature pyrolysis was continuously introduced into the mass spectrometer to measure D/H ratios. All isotopic data (δD) are reported in permil (‰) relative to the VSMOW standard. The δD value of hydrogen reference gas was predetermined against *n*-alkane standards with known δD values (*n*-C₂₄ -52.7‰, *n*-C₂₅ -114.7‰, *n*-C₂₈ -232.9‰, *n*-C₃₀ -33.6‰, and *n*-C₃₆

-215.8‰), which were determined by the zinc batch method (Coleman et al., 1982) using Oztech hydrogen reference gas ($\delta D_{VSMOW} = -59.74\text{‰}$) (Shoko Co. Ltd.). The H_3^+ factor of the mass spectrometer was determined once a day using external reference gas injections, and was consistently less than 10 (ppm). Reproducibility and accuracy of the analyses were routinely evaluated using *n*-alkane standards (*n*-C₂₄, *n*-C₂₅, *n*-C₂₈, *n*-C₃₀, and *n*-C₃₆). Measurement errors of the D/H ratios were $\pm 5\text{‰}$.

Result and Discussion

Maturity level of the samples

Organic matter extracted from Kusanagi and Yakumo siliceous mudstones is characterized by abundant marine organic matter such as short-chain C₁₆ to C₂₂ *n*-alkanes, and C₂₆, C₂₇, and C₃₀ steranes. The presence of C₂₆ sterane is significant as it is often found in contemporary diatomaceous mudstones (Suzuki et al., 1993) suggesting that much of the organic matter is derived from diatoms. The maturity levels of these siliceous mudstones based on C₂₉ sterane and C₃₂ hopane isomerizations, the sterane/sterene ratio, and silica mineral transformations are variable, being in both the diagenetic and catagenetic stages (Table 1, Fig. 2). Vitrinite reflectance (R_o) of siliceous mudstones from Shinjo region is in the range from 0.4 to 0.7% (Taguchi et al., 1986). Aoyagi and Kazama (1980), Suzuki (1984, 1990), and Amo et al.

(2007) reported that paleo-maximum temperatures range from 40 to 140°C in these samples. A set of the siliceous mudstone samples characterized by similar lithology and organic composition, but with different maturity levels, is essential in a study of diagenetic change of the D/H ratios of saturated and aromatic hydrocarbons.

D/H ratios of hydrocarbons in Miocene siliceous mudstones

The δD values of *n*-alkanes from immature Yakumo siliceous rocks are in the range of -70 to -210‰ (Table 2, Fig. 3) and tend to increase with decreasing carbon number. This result is related to the different origins of lower and higher molecular weight *n*-alkanes (Sachse et al., 2004, 2006; Smith and Freeman, 2006; Li et al., 2009). However, the inverse relationship, namely that D/H ratios of higher molecular weight *n*-alkanes are lighter than those of lower molecular weight *n*-alkanes, has been observed in samples from high latitudes (Pagani et al., 2006). The relationships between D/H ratios and carbon number observed in *n*-alkanes from immature Yakumo siliceous mudstones are consistent with those of mid-latitude sediments. On the other hand, the D/H ratios of even carbon number *n*-alkanes tend to be larger than those of adjacent odd carbon number *n*-alkanes. Similar D/H ratio distributions with a carbon number predominance have been frequently observed in *n*-alkanes from various organisms (Yang and Huang, 2003; Bi et al., 2005; Xiong et al., 2005; Tuo et al., 2006; Chikaraishi et al., 2007).

The δD values of *n*-alkanes from mature Kusanagi siliceous mudstones are all within a limited range of values regardless of their carbon numbers (Fig. 3). The δD values of lower molecular weight *n*-alkanes are about 50‰ lower than those of immature Yakumo siliceous mudstones. However, the δD values of higher molecular weight *n*-alkanes are only slightly different from those of mature Kusanagi siliceous mudstones, ranging from -110 to -190‰. The difference in D/H ratio distributions between siliceous mudstones from the Yakumo and Kusanagi Formations is thought to result from their different maturity levels. Uniform D/H ratio distributions of *n*-alkanes have often been found in mature sedimentary rocks (Schimmelmann et al., 2004; Dawson et al., 2005, 2007; Radke et al., 2005; Pedentchouk et al., 2006).

The δD values of pristane and phytane, typical acyclic isoprenoid hydrocarbons, in both Yakumo and Kusanagi siliceous mudstones range from -260 to -300‰ and from -200 to -330‰, respectively (Fig. 4). These remarkably low δD values, compared to those of *n*-alkanes, are thought to be due to hydrogen fractionation during biosynthesis of isoprenoid side chains (Sessions et al., 1999; Chikaraishi et al., 2004). In immature Yakumo mudstones, the δD values of phytane are about 10‰ heavier than those of pristane (Fig. 4). The difference between the δD values of pristane and phytane is thought to be due to differences in isotope fractionation in their formation from phytol during early diagenesis (Radke et al., 2005; Pedentchouk et al.,

2006). The δD values of pristane and phytane do not change during the immature stage prior to oil generation but change rapidly through the oil generation zone [$R_o > 0.6\%$, C_{29} sterane $20S/(20S+20R) > 0.35$] as shown in Fig. 4, which is consistent with previous studies (Dawson et al., 2005, 2007; Pedentchouk et al., 2006; Schimmelmann et al., 2006).

The δD values of aromatic hydrocarbons in Miocene siliceous mudstones were also measured in this study. Various types of di-, tri-, tetra-, and penta-aromatic hydrocarbons were detected in Yakumo and Kusanagi siliceous mudstones as shown in Fig. 5. The δD values of tetra- and penta-aromatic hydrocarbons, however, were not measured because of the very low number of hydrogen atoms per molecule. Immature Yakumo siliceous mudstones contain significant amount of di- and tri-aromatic hydrocarbons such as simonellite and retene. The mature Kusanagi siliceous mudstones contain phenanthrene and its alkylated homologues. The δD values of these di- and tri-aromatic hydrocarbons in the Yakumo and Kusanagi siliceous mudstones range from -180 to -250‰ and from -80 to -140‰ , respectively. The δD values of tri-aromatics are lower than those of *n*-alkanes during the immature stage, but are the highest in the oil generation zone (Fig. 4). The increase in the D/H ratios of aromatic hydrocarbons occurs at a comparatively immature stage [$R_o < 0.5\%$, C_{29} sterane $20S/(20S+20R) < 0.2$], which is lower than that of acyclic isoprenoid hydrocarbons. Few studies have reported on diagenetic change in D/H ratios of aromatic hydrocarbons. Tuo et al. (2006) found that the D/H ratios of

simonellite and dehydroabietane in Eocene coal and carbonate rocks ranged from -152 to -198‰ at $R_o = \sim 0.5\%$.

Diagenetic change of D/H ratios of hydrocarbons in sedimentary rocks

Miocene Yakumo and Kusanagi siliceous mudstones are characterized by similar organic type and inorganic mineral matrix. The marked increase in the D/H ratios in aromatic and acyclic isoprenoid hydrocarbons (Fig. 4) is thought to be due to an increase in organic maturation. The hydrogen exchange between sedimentary organic matter and pore water is considered to be responsible for the increase in D/H ratios of sedimentary organic matter with increasing maturity because the D/H ratio of pore water is generally higher than that of sedimentary organic matter (Alexander et al., 1982; Schimmelmann et al., 2006; Pedentchouk et al., 2006). Abrupt and dramatic increases of the D/H ratios of pristane and phytane in the oil generation zone observed in this study are consistent with findings of Schimmelmann et al. (2006), who suggested that significant change in D/H ratios occurred at the paleo-maximum temperature of 120°C. Schimmelmann et al. (2006) also suggested that hydrogen exchange between aromatic hydrocarbons and pore water proceeds in the maturation stage, similar to in pristane and phytane. However, the present study shows that the increase in D/H ratios of aromatic hydrocarbon proceeds before that of acyclic isoprenoid hydrocarbons (Fig. 4).

Alexander et al. (1982) showed that the hydrogen–exchange of naphthalenes on homoionic bentonites proceeded at low temperature less than 70°C. They concluded that acidic site at the clay mineral promote a hydrogen-exchange of aromatic compounds by an electrophilic substitution mechanism which proceeds via an arenium ion intermediate. Hydrogen attached to the benzyl carbon atom can be more easily released to exchange for hydrogen of pore water compared to the hydrogen attached to tertiary, secondary, and primary carbon atoms (Alexander et al., 1984; Hoering, 1984). The benzyl carbon atoms are significantly present in aromatic compounds such as simonellite, retene, and methyl phenanthrenes. The hydrogen-exchange of aromatic compounds by a catalytic electrophilic substitution reaction and abundant benzyl carbon atoms in a molecule, compared to in branched and normal alkanes, can be responsible for the earlier timing of the D/H ratio increase in aromatic hydrocarbons.

The water-derived hydrogen incorporation and isotopic differential fractionation during thermal cracking can also be important processes to alter the D/H ratio of n-alkanes. Lewan (1997) has demonstrated that water reacts chemically with terminal n-alkenes during hydrous pyrolysis, resulting in incorporation of water-derived hydrogen in hydrocarbons. According to Leif and Simoneit (2000), the terminal n-alkenes can undergo acid-catalyzed double bond isomerization under hydrothermal conditions, which results in incorporation of

hydrogen from water into the hydrocarbon skeleton. However, the D/H ratio of long chain terminal *n*-alkenes ($>C_{25}$) generated by thermal cracking is not so much affected by the water hydrogen incorporation because of their abundant original hydrogen atoms.

The thermal cracking of an isotopically lighter long chain *n*-alkane can proceed more easily than that of its isotopically heavier counterpart. Tang et al. (2005) demonstrated the hydrogen isotope fractionation of *n*-alkanes during anhydrous pyrolysis, showing that the thermal cracking of an individual *n*-alkane generates D-depleted shorter chain-length *n*-alkanes and leaves the remaining uncracked *n*-alkane enriched in D. This differential fractionation significantly proceeds at higher maturation stage ($R_o > 1.0\%$) (Tang et al., 2005). The influence of thermal cracking to the D/H ratio of long chain *n*-alkanes is considered to be minor in the present study since the maturity level of the samples is less than $R_o = 0.7\%$.

The δD values of pristane and phytane increase with increasing maturity while the long-chain *n*-alkanes generally remain at a constant isotopic composition (Fig. 4). The similar observations have been reported by Dawson et al. (2005, 2007) and Pedentchouk et al. (2006). The increase of δD values of pristane and phytane is interpreted as mainly due to the hydrogen isotopic exchange with water via carbocation mechanism (Dawson et al., 2005). The stable carbocation center forms preferentially at a tertiary center in pristane and phytane, and hydrogen exchange proceeds at the adjacent methyl and methylene carbon atoms (Alexander et

al., 1984). Compared to pristane and phytane, *n*-alkanes do not have molecular structures favorable for carbocation formation, suggesting that the hydrogen exchange reactions of *n*-alkanes are not significant in the maturity level less than $R_o=0.7\%$.

The δD values of short-chain *n*-alkanes from the siliceous mudstones change to be lower with increasing maturity (Figs 3 and 4). This trend is opposite to those of pristane, phytane, and aromatic hydrocarbons. If the hydrogen exchange with water proceeds with increasing maturity, the δD value of short-chain *n*-alkanes increases as well because of the higher D/H ratio of pore water. The significant input of short-chain *n*-alkanes derived from long aliphatic chains with lower D/H ratio can result in the decrease of δD value of short-chain *n*-alkanes. Thermal cracking of long-chain aliphatic structures in bitumen and kerogen with increasing maturity can be responsible for the changes in the D/H ratios of short-chain *n*-alkanes and the uniform distribution of D/H ratios regardless of the *n*-alkane carbon number. The δD distribution in the mature samples is characterized by the slightly higher δD in long chain *n*-alkanes and slightly lower δD in short chain *n*-alkanes (Fig. 3). This may suggest the differential thermal cracking of long chain *n*-alkanes, although their δD values do not show any significant changes in the maturity level less than $R_o<0.7\%$.

Conclusions

Using a set of immature to mature Miocene siliceous mudstones characterized by similar organic type and mineral matrix, this study investigated the change of D/H ratios of *n*-alkanes, pristane, phytane, and aromatic hydrocarbons during diagenesis to catagenesis. Long-chain *n*-alkanes maintain their initial D/H ratios even during extensive oil generation, in contrast to short-chain *n*-alkanes, branched hydrocarbons, and aromatic hydrocarbons. The earliest diagenetic increase of D/H ratios at an immature stage affects aromatic hydrocarbons. In branched hydrocarbons, change in D/H ratios occurs in the mature stage during extensive oil generation. The increase of D/H ratios of aromatic and acyclic isoprenoid hydrocarbons is thought to result from hydrogen exchange with sediment pore water. On the other hand, the D/H ratios of short-chain *n*-alkanes do not show any significant increase with increasing maturity, but rather exhibit a slight increase, becoming similar to the D/H ratios of long-chain *n*-alkanes. The disappearance of carbon number predominance for the *n*-alkane D/H ratio with increasing maturity results from the extensive thermal cracking of aliphatic structures in bitumen and kerogen. The present study shows that the D/H ratios of long-chain *n*-alkanes derived from higher plant wax can maintain their initial values even in the extensive oil generation zone ($R_o < 0.7\%$). The D/H ratios of long-chain *n*-alkanes in mature sedimentary rocks can still be a potential parameter for evaluating paleo-hydrology/humidity on land.

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Table 1

Maturity levels of Middle Miocene siliceous mudstones.

Sample #	Formation	Silica Mineral Zone	20S/20S+20R	22S/22S+22R	Sterane/Sterene
0013	Yakumo	Opa-A/CT	0.00	0.24	0.75
0012	Yakumo	Opa-A/CT	0.00	0.22	0.42
0011-1	Yakumo	Opa-A/CT	0.00	0.23	0.63
0010	Yakumo	Opal-CT	0.00	0.24	0.68
009	Yakumo	Opal-CT	0.02	0.27	0.62
008	Yakumo	Opal-CT	0.02	0.27	0.74
007	Yakumo	Opal-CT	0.03	0.21	0.93
006-2	Yakumo	Opal-CT	0.03	0.26	0.72
006-1	Yakumo	Opal-CT	0.02	0.27	0.91
005-2	Yakumo	Opal-CT	0.03	0.23	1.00
005-1	Yakumo	Opal-CT	0.03	0.28	1.00
004-6	Yakumo	Opal-CT	0.03	0.24	1.00
004-5	Yakumo	Opal-CT/Quartz	0.03	0.21	1.00
004-3	Yakumo	Opal-CT/Quartz	0.03	0.31	1.00
004-4	Yakumo	Quartz	0.03	0.27	1.00
004-2	Yakumo	Quartz	0.03	0.26	1.00
004-1	Yakumo	Quartz	0.03	0.32	1.00
003-2	Yakumo	Quartz	0.06	0.32	1.00
003-1	Yakumo	Quartz	0.06	0.29	1.00
001-1	Yakumo	Quartz	0.03	0.27	1.00
8111061	Furukuchi	Quartz	0.18	0.39	1.00
83002	Kusanagi	Quartz	0.22	0.45	1.00
83001	Kusanagi	Quartz	0.28	0.48	1.00
90101	Kusanagi	Quartz	0.38	0.54	1.00
8111055	Kusanagi	Quartz	0.43	0.57	1.00
90103	Kusanagi	Quartz	0.44	0.57	1.00
90104	Kusanagi	Quartz	0.44	0.57	1.00
8111056	Kusanagi	Quartz	0.47	0.58	1.00

20S/20S+20R; 5 α -C₂₉ sterane isomer ratio, 22S/22S+22R; C₃₂ hopane isomer ratio, Sterane/Sterene; 5 α -sterane/(5 α -sterane+ster-5-ene) ratio (Amo *et al.*, 2007)

Table2

δD values (‰ vs. VSMOW) of *n*-alkanes, pristane, phytane, and some aromatic hydrocarbons from Middle Miocene siliceous mudstones.

Sample #	<i>n</i> -C16	<i>n</i> -C17	<i>n</i> -C18	<i>n</i> -C19	<i>n</i> -C20	<i>n</i> -C21	<i>n</i> -C22	<i>n</i> -C23	<i>n</i> -C24	<i>n</i> -C25	<i>n</i> -C26	<i>n</i> -C27	<i>n</i> -C28	<i>n</i> -C29	C17,19*1	C27,29	Pr	Ph	Sim	Ret	Phe	C1-Phe
0011-1	-99	-119	-88	-138	-146	-100	-151	-179	-141	-166	-161	-194	-173	-194	-129	-194	n.d.	n.d.	n.d.	-200	n.d.	n.d.
009	-90	-100	-96	-101	-88	-125	-57	-70	-131	-83	n.d.	-131	n.d.	-172	-101	-152	-284	-276	n.d.	n.d.	n.d.	n.d.
007-1	-100	-104	-92	-106	-94	-111	-118	-145	-123	-111	-105	-147	-134	-196	-105	-172	-311	-303	-239	-237	n.d.	n.d.
005-1	-102	-130	-96	-115	-90	-194	-121	-115	-152	-70	-127	-132	-194	-214	-123	-173	-301	-287	n.d.	-208	n.d.	n.d.
003-1	-94	-105	-78	-118	-89	-131	-92	-128	n.d.	-137	-120	-144	-119	-179	-111	-161	n.d.	n.d.	-203	n.d.	n.d.	n.d.
001-1	-113	-140	-108	-172	-127	-169	-153	-169	-112	-105	-147	-166	-205	-209	-156	-188	-288	-281	n.d.	n.d.	n.d.	n.d.
8111061	-140	-170	-169	-182	-175	-185	-184	-174	-172	-173	-172	-181	-167	-186	-176	-184	-310	-329	-141	-107	-137	-137
83002	-156	-182	-184	-176	-177	-181	-181	-180	-180	-181	-182	-178	-175	-165	-179	-172	-289	-296	n.d.	n.d.	n.d.	n.d.
83001	-166	-182	-186	-174	-180	-180	-184	-179	-146	-161	-165	-164	-162	-150	-178	-157	-284	-287	n.d.	-94	-99	-107
90101	-197	-191	-196	-183	-187	-183	-189	-184	-178	-177	-173	-174	-175	-183	-187	-178	-307	-307	n.d.	n.d.	-96	-82
8111055	-131	-131	-131	-135	-134	-136	-138	-131	-131	-128	-123	-124	-112	-112	-133	-118	-235	-232	n.d.	-135	-126	-112
90103	-189	-187	-182	-177	-176	-173	-172	-169	-167	-167	-166	-172	-183	-165	-182	-168	-263	-251	n.d.	n.d.	-136	-142
90104	-185	-188	-180	-189	-185	-186	-180	-175	-175	-170	-165	-166	-165	-169	-188	-167	-267	-264	n.d.	n.d.	n.d.	-77
8111056	-164	-172	-175	-174	-171	-171	-169	-165	-151	-158	-152	-146	-154	-151	-173	-149	-197	-220	n.d.	n.d.	n.d.	n.d.

C17,19 and C27,29 are average hydrogen isotope ratios, Pr; pristane, Ph; phytane, Sim; simonellite, Ret; retene, Phe; phenanthrene, C1-Phe; methylphenanthrenes, n.d.; not determined

Figure Captions

Figure 1. Location map of Yakumo and Shinjo regions, where outcrops of Middle Miocene Yakumo and Kusanagi diatomaceous siliceous mudstones are exposed, respectively.

Figure 2. Generalized lithostratigraphic column and maturity levels shown by silica mineral transformation, C₂₉ sterane and C₃₂ hopane isomer ratios, and sterane to sterene ratios of the Middle Miocene Yakumo and Kusanagi diatomaceous siliceous mudstones. Vitrinite reflectance is from Taguchi et al. (1986). Km F.; Kuromatsunai Formation, Fk F.; Furukuchi Formation, Plio.; Pliocene, Mdst.; Mudstone.

Figure 3. The relationship between the D/H ratios and carbon numbers of *n*-alkanes from immature Yakumo and mature Kusanagi siliceous mudstones.

Figure 4. Change of D/H ratios of saturated and aromatic hydrocarbons with increasing maturity. The relationship between the 20S/(20S+20R) ratio of C₂₉ steranes and vitrinite reflectance is from Taguchi et al. (1986) and Suzuki et al. (1987).

Figure 5. Representative total ion chromatograms (TICs) showing distribution of aromatic hydrocarbons in Middle Miocene Yakumo and Kusanagi siliceous mudstones. A. Phenanthrene, B. Methylphenanthrenes, C. Simonellite, D. Retene, E. 2-Methylretene, F. 3, 3, 7-Trimethyl-1, 2, 3, 4-tetrahydrochrysene, G. Perylene, H. 7-Methyl-3'-ethyl-1, 2-cyclopenteno-chrysene, I. Tetraaromatic lupine, J. 2, 2, 9-Trimethyl-1, 2, 3, 4-tetrahydropicene, K. 2, 9-Dimethylpicene.

Fig. 1



Fig. 2

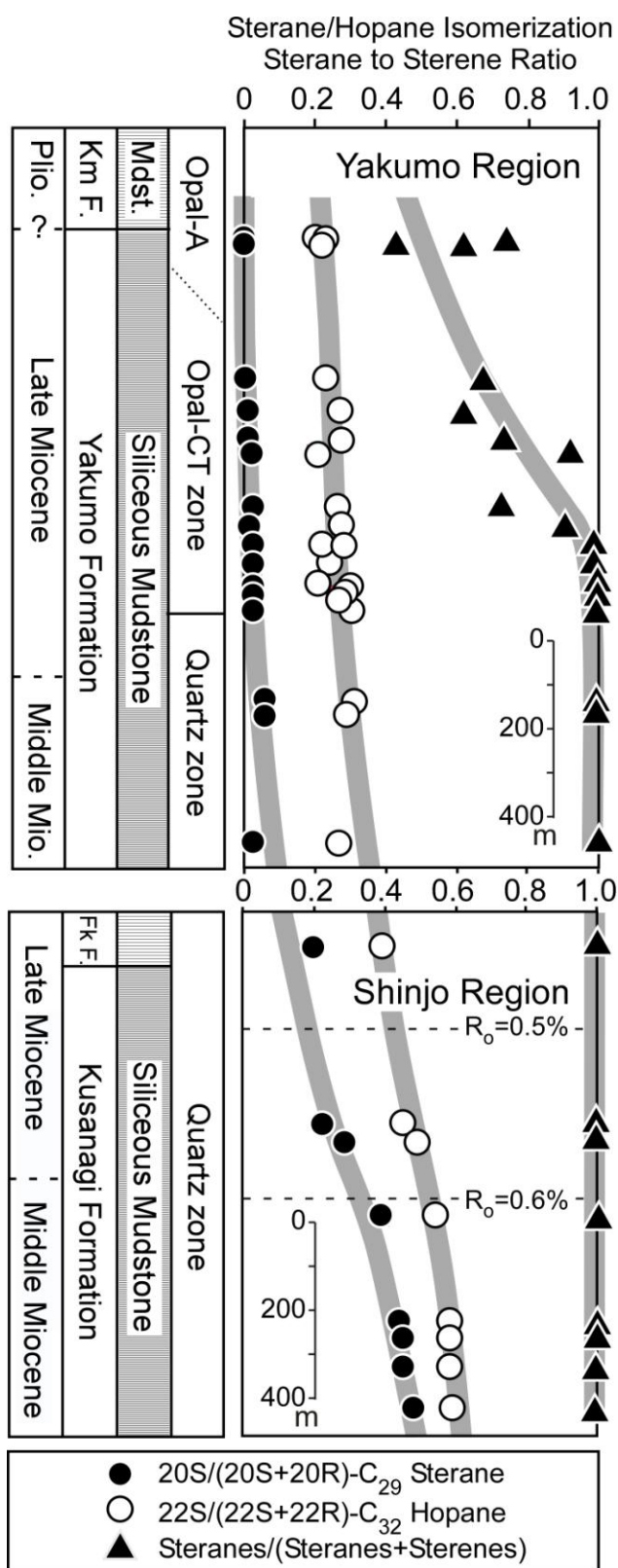


Fig. 3

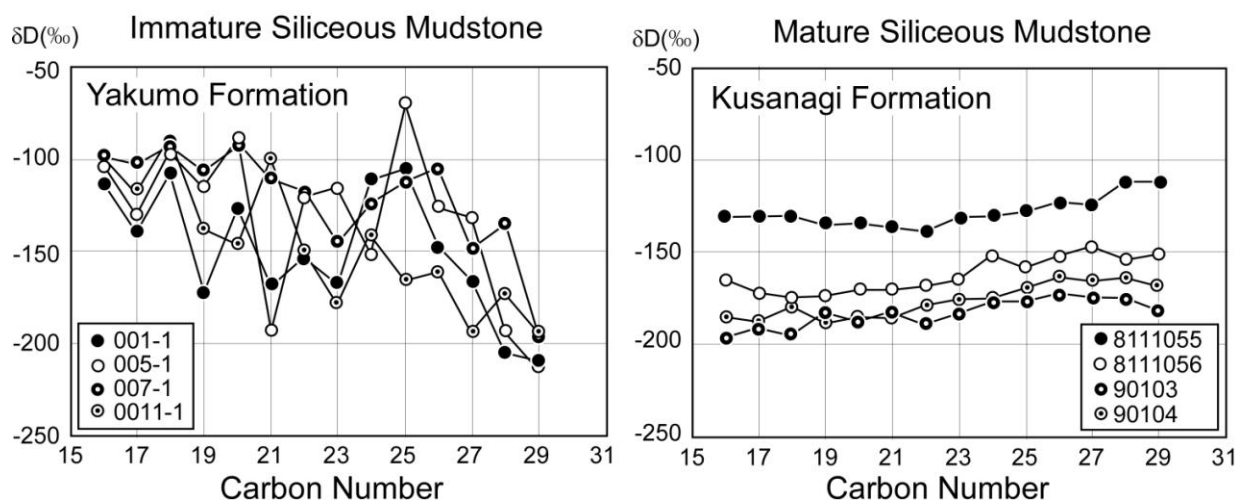


Fig. 4

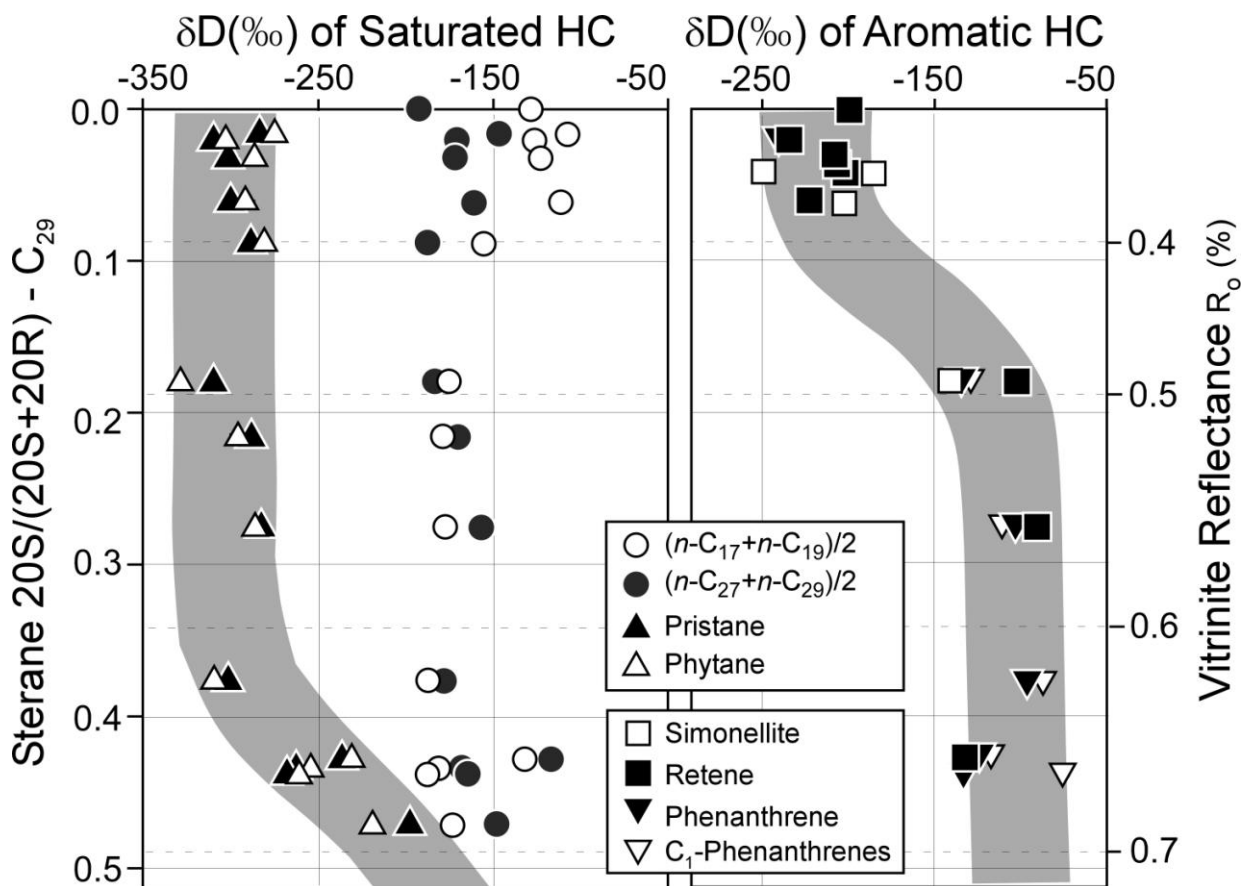


Fig. 5

