

Chapter 2

Thiophenes in Neogene Sediments of the Shinjo Basin, Japan

ABSTRACT – Alkyl and polynuclear aromatic thiophenes were detected in sedimentary rocks of a stratigraphic sequence from Miocene to Pliocene in Shinjo basin, Japan. C₂₅ Highly branched isoprenoid (HBI) thiophenes, dibenzothiophene, C₁- and C₂-alkyldibenzothiophenes, and benzo[b]naphto[1,2-d]thiophene were rather predominantly present. The C₂₅ HBI thiophenes consist of three isomers including a pair of diastereomers. They were present in sediments from the Nakawatari to the upper part of the Kusanagi Formations and absent at the middle and lower parts of the formation. The depth profiles of their concentrations do not coincide with those of the C₂₅ HBI alkane concentration and bulk sulfur content in the same sediment samples. It is postulated that the C₂₅ HBI thiophenes and the C₂₅ HBI alkane were produced by the reaction of C₂₅ HBI alkadiene and C₂₅ HBI polyene, respectively, with reduced sulfur during early diagenesis. The variation in composition of the C₂₅ HBI thiophene isomers was observed in the sediments, suggesting that they were derived from different kinds of C₂₅ HBI alkadienes. The concentrations of the polynuclear aromatic thiophenes showed an increasing trend downwards the upper to middle Kusanagi Formation. Among these thiophenes dibenzothiophene and benzo[b]naphto[1,2-d]thiophene concentrations varied from 10 to 730 and 14 to 210 pmol g⁻¹, respectively. The depth profiles of their concentrations were different from that of the C₂₅ HBI thiophenes. It is likely that the polynuclear aromatic thiophene formation started from different precursors followed by different processes from those of the C₂₅ HBI thiophenes.

INTRODUCTION

Thiophenes have been widely found in sedimentary rocks and crude oils (Brassell *et al.*, 1986; Sinninghe Damsté *et al.*, 1987, 1989a and b; Fukushima *et al.*, 1992). Among these thiophenes alkyl thiophenes provide information for palaeobiota and depositional environment (Kohnen *et al.*, 1990; Sinninghe Damsté *et al.*, 1990; Fukushima *et al.*, 1992; de las Heras *et al.*, 1997). C₂₀ Isoprenoid and C₂₅ highly branched isoprenoid (HBI) thiophenes were possibly produced by the reaction of H₂S to phytol or phytadiene derived from chlorophyll (Brassell *et al.*, 1986) and C₂₅ HBI alkenes derived from the phytoplankton such as diatoms (Sinninghe Damsté *et al.*, 1989c), respectively, during early diagenesis. Recently, several studies of C₂₅ HBI thiophenes pointed out that incorporation of reduced sulfur species depends on double bond positions in C₂₅ HBI alkadienes and C₂₅ HBI polyenes (Sinninghe Damsté *et al.*, 1989a; Kohnen *et al.*, 1992; de las Heras *et al.*, 1997).

Polynuclear aromatic thiophenes are a useful indicator for the evaluation of source rocks and diagenetic maturation (Chakhmakhchev and Suzuki, 1995a and b). Dibenzothiophenes were more abundant in marine crude oils than in non-marine ones (Fan *et al.*, 1990). Radke *et al.* (1982a and b) reported that dibenzothiophene and 4-methyldibenzothiophene were the most abundant di-nuclear aromatic thiophenes found in the type III kerogen. Furthermore, the ratio of 4- /1-methyldibenzothiophene was proposed as a maturity parameter for both marine and terrestrial organic matter (Radke *et al.*, 1986). However, little is known about the precursors and formation pathways of polynuclear aromatic thiophenes, although some studies suggested that these thiophenes were formed by cyclization and aromatization of alkyl thiophenes (Sinninghe Damsté *et*

al., 1987, 1989a).

The purpose of this chapter is to uncover the occurrence and distribution of thiophenes in sediments from a stratigraphic sequence from Miocene to Pliocene in the Shinjo basin in Yamagata Prefecture, northern Japan. The sequence is suitable for a geochemical study of thiophenes during late diagenesis and early catagenesis because the maturity of the sequence ranges from about 0.4 to 0.6 % R_o (Taguchi *et al.*, 1986). The author presents result of detection of C_{20} isoprenoid and C_{25} HBI thiophenes as well as C_{25} HBI alkane, and polynuclear aromatic thiophenes in the sediments and describes the depth profiles of the concentrations of these thiophenes together with those of C_{25} HBI alkane, bulk sulfur and the reported *n*-alkanes (Ishiwatari and Shioya, 1986). Furthermore, the formation pathways of the isoprenoid and polynuclear aromatic thiophenes in the sediments based on their distributions are discussed.

EXPERIMENTAL

Samples

Sediment samples analyzed were aliquots of common samples collected at outcrops along the Oashizawa route in the Shinjo basin in 1980 for the joint study on the diagenesis of organic and inorganic constituents, and the results were summarized by Taguchi *et al.* (1986). The samples are mainly marine shales and mudstones of the Nakawatari, Noguchi, Furukuchi and Kusanagi Formations, ranging from Pliocene to Middle Miocene. Their horizons are shown in the stratigraphic and lithologic sections in Fig. 2-1 (Taguchi *et al.*, 1986). The samples were discontinuously numbered from 83110 (top) to 90105 (bottom) of the 1600 m thick sedimentary sequence.

Approximately 100 g each of freshly powdered samples had been prepared from hand-sized specimens of the common samples after removal of apparent surface contaminants. A portion of each powdered sample had already been used in the previous studies of several kinds of organic compounds (Shimoyama and Matsubaya, 1985; Shimoyama *et al.*, 1988, 1991, 2000; Mita *et al.*, 1996; Nomoto *et al.*, 2000; Hagiwara *et al.*, 2000). In this chapter, the author analyzed thiophenes in the 18 samples over the sedimentary sequence. Concentrations of total organic carbon (TOC) and extractable organic compounds (EOC), and stable carbon isotopic compositions of these samples are shown in Fig. 2-2 (Shimoyama and Matsubaya, 1985).

Analyses

Analytical procedure for thiophenes is schematically shown in Fig. 2-3. For each analysis, 3 g of powdered sample were extracted six times with 5 ml of a mixture of

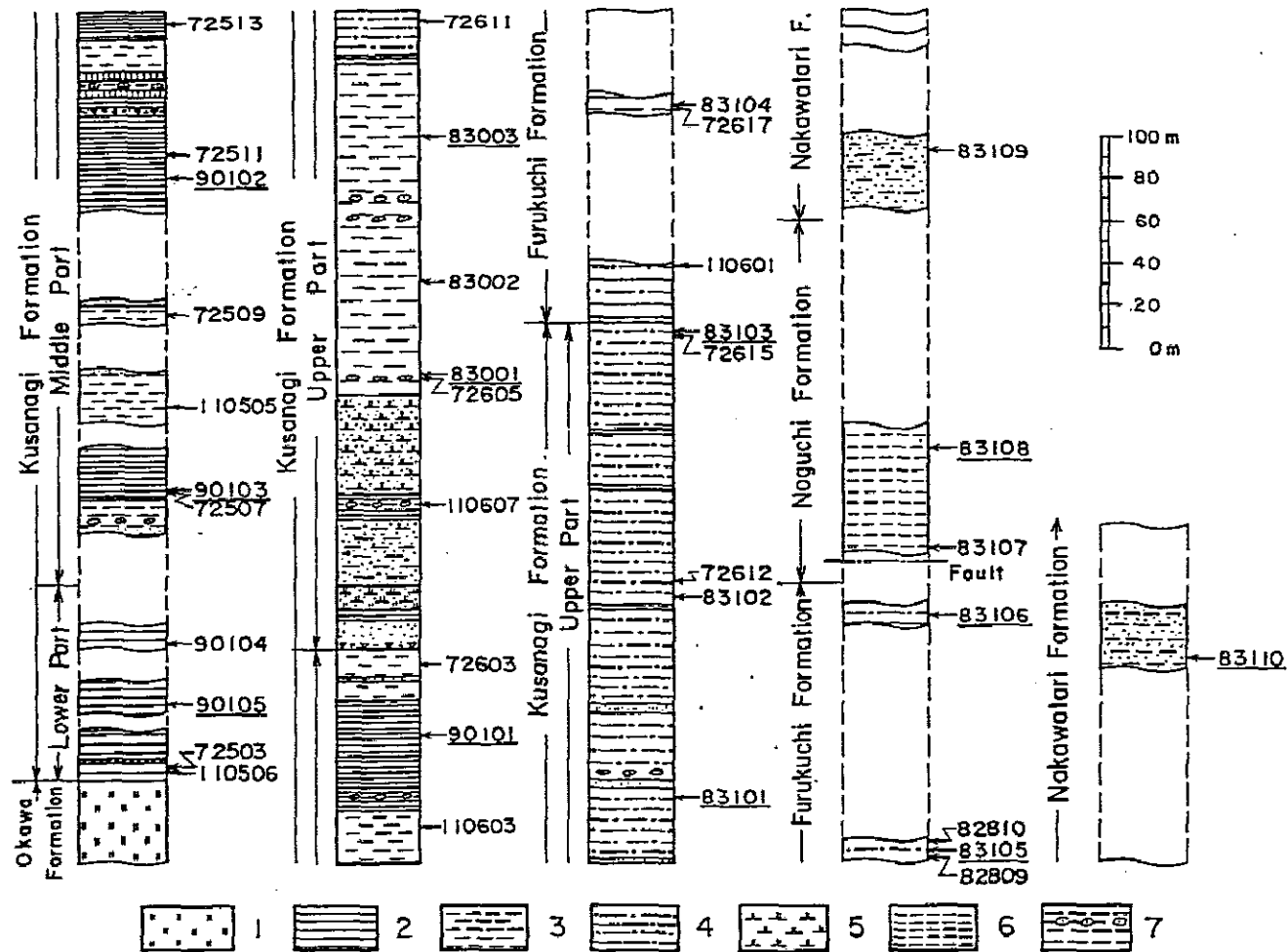


Fig. 2-1. Stratigraphic and lithologic sections of the Shinjo sedimentary rocks (Taguchi *et al.*, 1986).

Numbers in the column indicate sampling points.

Major rock facies: 1. Dark brown andesinic tuff breccia, 2. Very hard siliceous shale, 3. Grey hard siltstone, 4. Dark gray hard siltstone, 5. Sandy tuff, 6. Gray sandy siltstone, 7. Calcareous concretion.

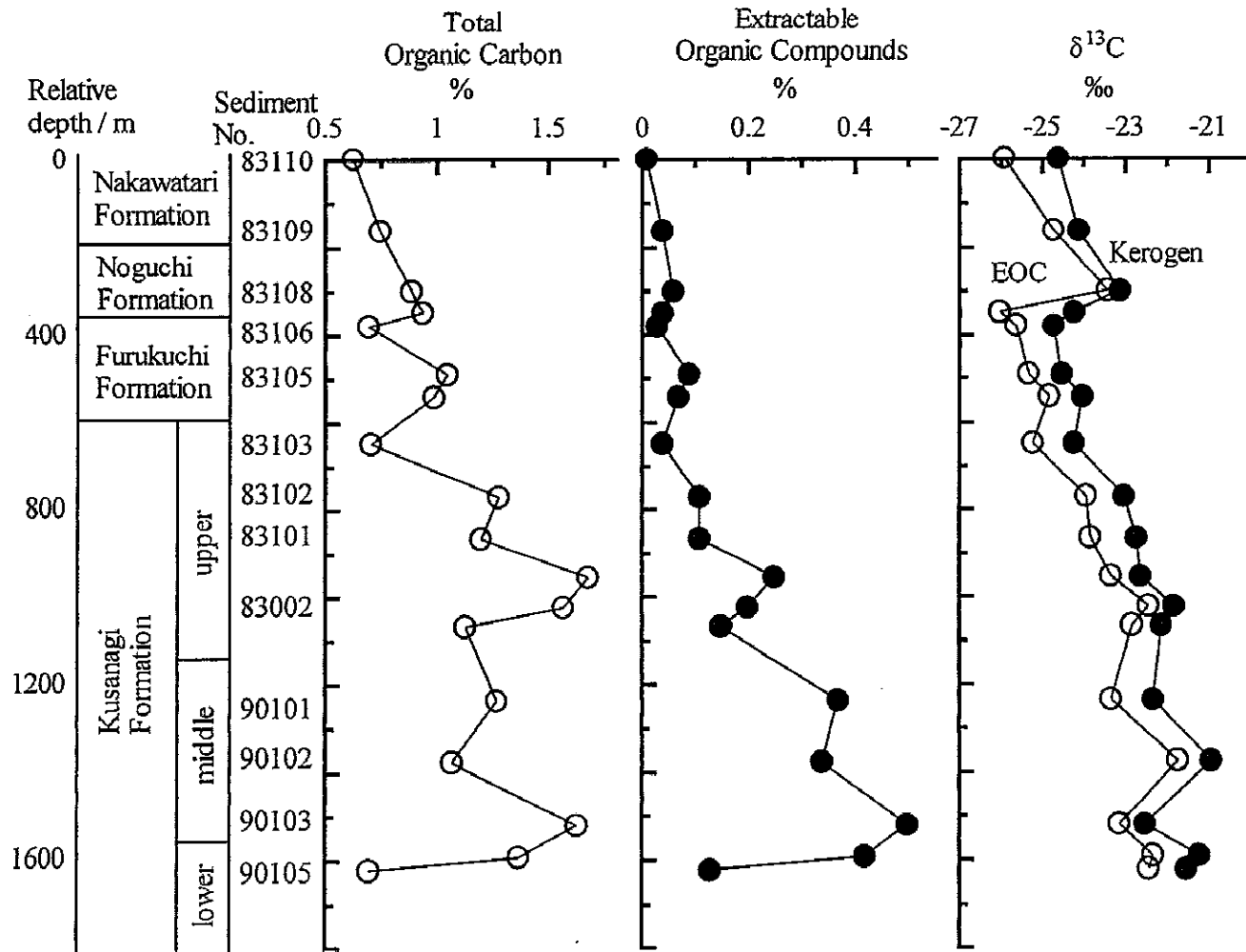


Fig. 2-2. Depth profiles of total organic carbon, extractable organic compounds and stable carbon isotopic compositions in Neogene sediments of the Shinjo basin. Data are from Shimoyama and Matsubaya (1985).

dichloromethane and methanol (4:1 by vol.) by sonication for 30 min. The extracted solutions were combined together, concentrated under reduced pressure, and applied to a silica gel column (130 mm × 10 mm i.d.; Kieselgel-60, Merck). The column was washed with 10 ml of hexane (F1) and then 10 ml of a mixture of hexane and ethyl acetate (9:1 by vol.) (F2). Alkyl thiophenes and C₂₅ HBI alkane were recovered in F1 and polynuclear aromatic thiophenes in F2. Free sulfur in F1 was removed with reduced copper (Wako Pure Chemicals). F1 and F2 were concentrated carefully to 50 µl under a nitrogen flow.

The condensed F1 and F2 were analyzed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 6890 instrument coupled with a Hewlett-Packard 5973 mass spectrometer. The GC was equipped with a splitless injection system and a DB-5ht capillary column (30 m × 0.25 mm i.d.). Helium was used as a carrier gas with a flow rate of 1 ml min⁻¹. Oven temperature was programmed to hold 50 °C for initial 5 min, to increase from 50 to 120 °C at a rate of 10 °C min⁻¹ and from 120 to 310 °C at 3 °C min⁻¹, and to hold 310 °C for 10 min. Mass spectra were obtained by scanning *m/z* from 50 to 600 every 1.4 s in the electron impact mode at 70 eV. Identification of alkyl thiophenes was described in the section of *Alkyl thiophenes*. Relative abundances of these thiophenes were estimated by measuring peak areas on mass fragmentograms of *m/z* 293 and/or 265 for C₂₅ HBI thiophene isomers. Identification of C₂₅ HBI alkane was performed by comparison of the mass spectrum reported by Rowland and Robson (1990). Relative abundance of the alkane was determined by peak area on mass fragmentogram of *m/z* 238. Identification and quantification of polynuclear aromatic thiophenes were chiefly carried out by comparison of peak retention times and areas, respectively, on mass fragmentograms of selected ions with those of standard compounds. The standard compounds were dibenzothiophene (DBT) and benzo[b]naphtho[1,2-d]thiophene (BNT).

The bulk sulfur contents were measured according to the silver absorption method

using a Sulfur and Halogen Determination Apparatus (Mitamura Riken Kogyo Inc.) at Chemical Analysis Center, University of Tsukuba.

Water, analytical grade hexane, methanol, dichloromethane and ethyl acetate were twice distilled and used. All glassware was heated at 500 °C for at least 3 h prior to use to remove organic contaminants. A procedural blank was carried out with 0.5 g pre-ignited sand powder and no significant contamination was found during the analysis. A recovery test of alkyl and polynuclear aromatic thiophenes was performed. The compounds used were 3-*n*-octylthiophene, 3-*n*-decylthiophene, 3-*n*-dodecylthiophene, benzo[b]thiophene (BT), DBT and BNT. The recoveries are shown in Table 2-1. Although some compounds did not show sufficient recoveries in quality, the results were acceptable for the purpose of this study.

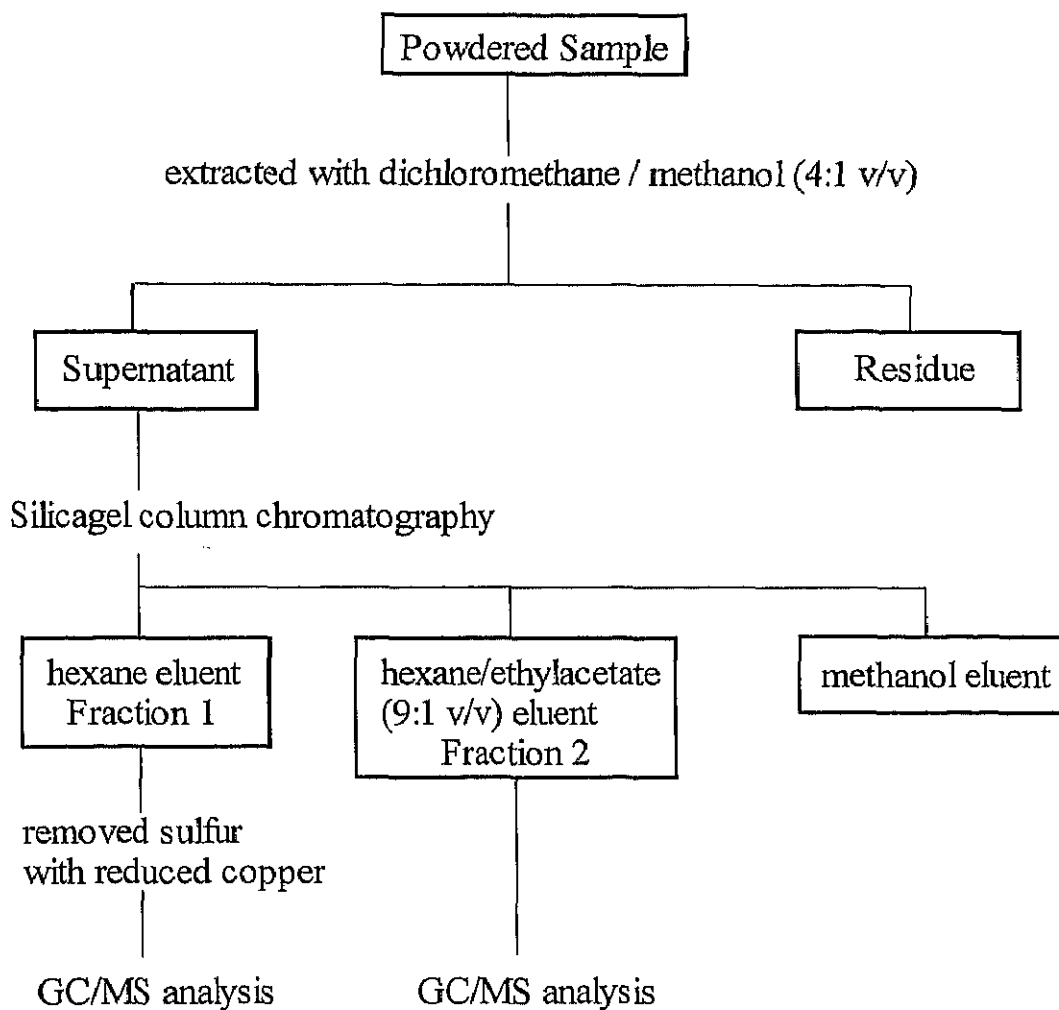


Fig. 2-3. Analytical procedure for thiophenes in Neogene sediments of the Shinjo basin.

Table 2-1. Recovery test of thiophenes by the analytical method

Compound	Added nmol/ μ L	Found nmol/ μ L	Recovery %
3-Octylthiophene	0.16	0.11	68
3-Decylthiophene	0.15	0.12	80
3-Dodecylthiophene	0.20	0.20	100
Benzo[b]thiophene	0.23	0.12	52
Dibenzothiophene	0.18	0.16	89
Benzo[b]naphto[1,2-d]thiophene	0.13	0.13	100

RESULTS AND DISCUSSION

Alkyl thiophenes

Figure 2-4 shows mass fragmentograms for alkyl thiophenes in the Shinjo 83109 sample. The three peaks numbered from 1 to 3 (Fig. 2-4) showed an ion at m/z 308 which can be considered as molecular ions in their mass spectra (Figs. 2-5a to c). The diagnostic fragment ions, m/z 125 for peak no. 1, 111 for no. 2 and 98 for no. 3, indicated the presence of a thiophene ring with two, one and zero methyl groups, respectively. These compounds were identified as isoprenoid thiophenes with 20 carbons ($C_{20}H_{36}S$) by comparing their relative retention times and the mass spectra with those reported by Brassell *et al.* (1986) and Fukushima *et al.* (1992), and are listed in Table 2-2. Furthermore, three C_{25} alkyl thiophenes were detected on the mass fragmentogram of m/z 378 (Fig. 2-4) which was found to be their molecular ions from their mass spectra (Figs. 2-5d to f). The first eluting isomer (peak no. 4 in Fig. 2-4) showed fragment ions in its mass spectrum (Fig. 2-5d) at m/z 321 and 293. Therefore, the peak no. 4 is one of C_{25} HBI thiophene isomers. The peak nos. 5 and 6 showed identical mass spectra (Figs. 2-5e and f). The ion at m/z 265 was formed by β -cleavage and the ion at m/z 125 was most likely a secondary ion, indicating a trialkylthiophene. They were identified as a pair of diastereomers. The three mass spectra of the C_{25} HBI thiophenes (Figs. 2-5d to f) enabled the structural identification with the help of the literature data (Sinninghe Damsté *et al.*, 1989c) and these thiophenes are listed in Table 2-2. Other alkyl and isoprenoid thiophenes were not detected. The mass spectrum of C_{25} HBI alkane showed a characteristic ion at m/z 238. The most prominent fragment ion was formed by the cleavage of the bond between two tertiary carbons at C-6 and C-7 positions, and therefore, the alkane was

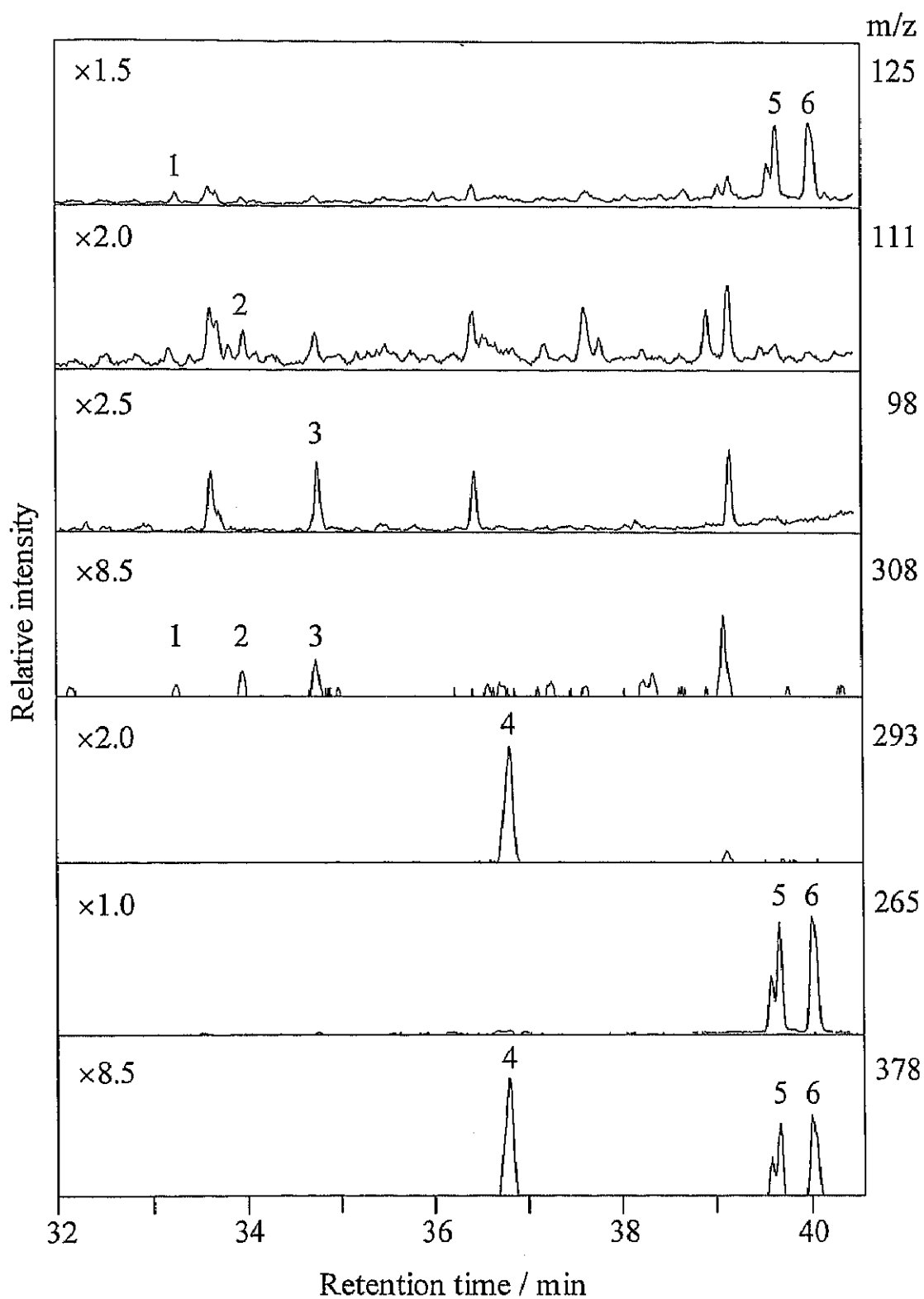


Fig. 2-4. Mass fragmentograms of alkyl thiophenes in the Shinjo 83109 sample. Peak numbers correspond those in Table 2-2.

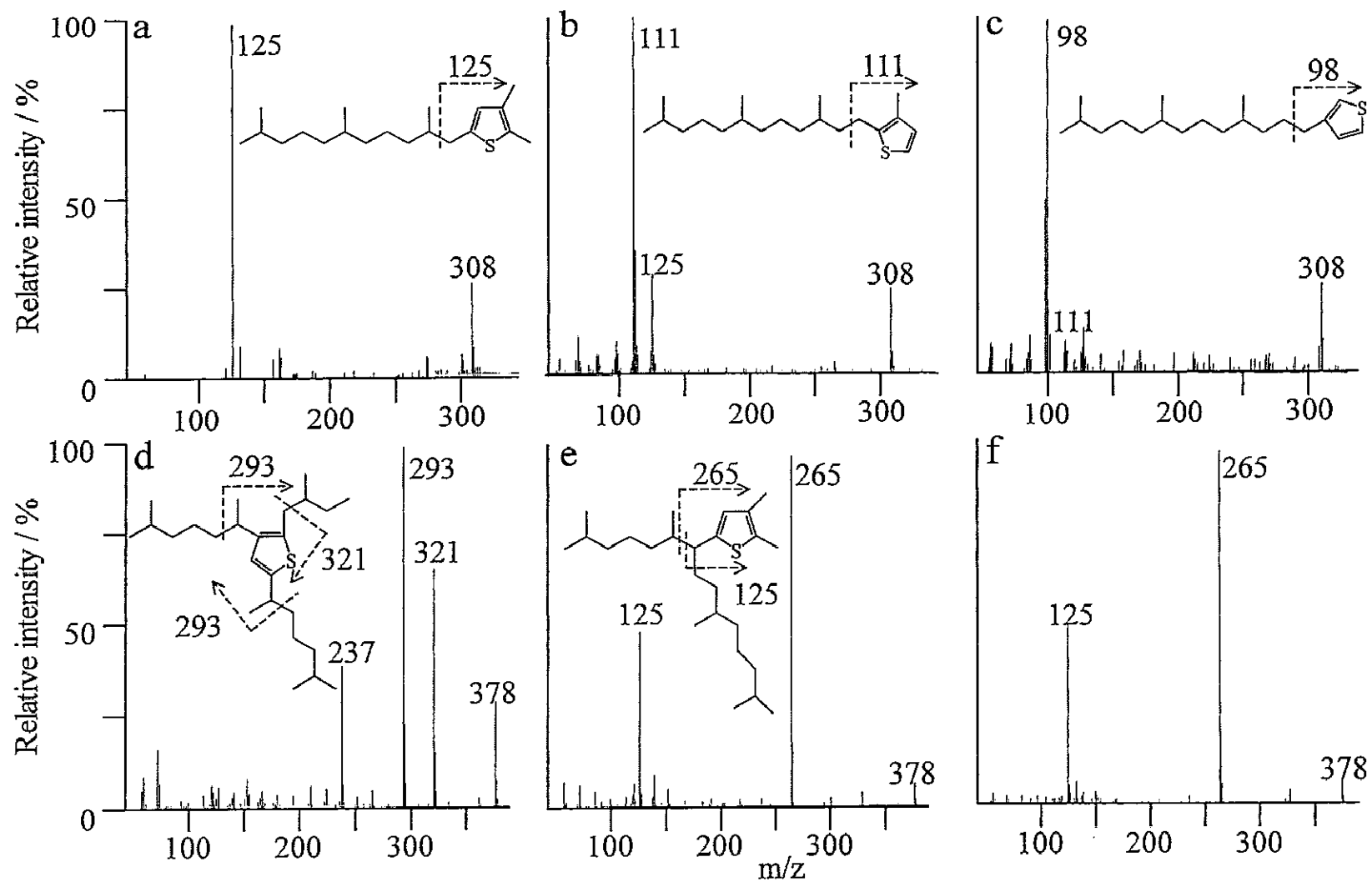


Fig. 2-5. Mass spectra of C₂₀ isoprenoid (a-c) and C₂₅ HBI (d-f) thiophenes from the Shinjo 83109 sample.

Table 2-2. Thiophenes in Neogene sediments of the Shinjo basin and their major mass numbers (*m/z*)

Peak No.	Compound	Major mass numbers (<i>m/z</i>)
Alkyl thiophenes		
1	2,3-dimethyl-5-(2,6,10-trimethyl undecyl) thiophene	125, 308
2	3-methyl-2-(3,7,11-trimethyldodecyl)thiophene	111, 308
3	3-(4,8,12-trimethyltridecyl)thiophene	98, 308
4	2-(2'-methylbutyl)-3,5-di-(2'-(6'- methylheptyl)) thiophene	237, 293, 321, 378
5	2,3-dimethyl-5-[7'-(2',6',10',14'-tetramethyl pentadecyl)]thiophene	125, 265, 378
6	2,3-dimethyl-5-[7'-(2',6',10',14'-tetramethyl pentadecyl)]thiophene	125, 265, 378
Polynuclear aromatic thiophenes		
7	dibenzothiophene	184
8	4-methyldibenzothiophene	198
9	2- and 3-methyldibenzothiophene	198
10	1-methyldibenzothiophene	198
11	ethyl dibenzothiophene	212
12	4,6-dimethyldibenzothiophene	212
13	C ₂ -alkyldibenzothiophene isomers	212
14	benzo[b]naphto[1,2-d]thiophene	234

assigned as 2, 6, 10, 14-tetramethyl-7-(3-methylpentyl)pentadecane. These alkyl thiophenes and alkane could not be quantified because of the lack of these standard compounds. However, they are likely present at most at the levels of ten-pmol g⁻¹ (thiophene) and sub-nmol g⁻¹ (alkane) judging from the MS detection levels.

Relative abundances of the C₂₅ HBI thiophene and the C₂₅ HBI alkane together with the bulk sulfur contents are listed in Table 2-3, and their depth profiles are shown in Fig. 2-6. The depth profiles showed quite different each other. The C₂₅ HBI thiophenes were generally present in the Nakawatari to the upper Kusanagi Formations with relatively high abundance at the Shinjo 83105 and 83002 samples. However, they were absent in the middle to lower Kusanagi Formation. The absence may be due to their degradation by more intense diagenesis at the middle and lower parts than the upper part of the Kusanagi Formation. Koopmans *et al.* (1995) reported that thiophenes with phytanic carbon skeleton could be converted to free phytane by hydrous pyrolysis of the Gessoso-solfifera Formation (Messinian) in the Vena del Gesso basin (northern Italy). On the other hand, relative abundance of the C₂₅ HBI alkane increased drastically at the Shinjo 90102 sample (middle of the Kusanagi Formation). It is possible to suggest that a part of the C₂₅ HBI alkane detected in the middle to lower Kusanagi Formation might have been formed by the degradation of the C₂₅ HBI thiophenes. However, since depth profiles of these thiophenes and the alkane were not related each other, it is likely that those compounds had different precursors and formation pathways from each other. It was reported that the stable carbon isotopic composition of C₂₅ HBI thiophenes was different from that of sulfur-bound C₂₅ HBI alkane, indicating that the thiophenes and the alkane had been derived from different precursors (Kohnen *et al.*, 1992).

The C₂₅ HBI thiophenes could be produced by the reaction of C₂₅ HBI alkadienes and inorganic reduced sulfur species. C₂₅ HBI alkadienes occur widely in Recent sediments (Dunlop and Jefferies, 1985; Robson and Rowland, 1986; Rowland and

Table 2-3. Relative abundances of C₂₅ HBI thiophenes and C₂₅ HBI alkane, and bulk sulfur contents in Neogene sediments of the Shinjo basin

Sediment No.	C ₂₅ HBI thiophene			C ₂₅ HBI alkane	Sulfur content / %
	Peak No.				
	4	5	6		
83110	0	0	0	0.5	0.35
83109	1.0	2.3	2.4	0.4	0.75
83108	2.7	17.0	18.3	1.3	1.00
83107	2.4	2.8	2.1	0.6	0.38
83106	4.7	4.5	4.7	1.6	0.85
83105	100	59.9	66.8	7.5	0.57
83104	8.2	9.4	10.2	1.7	0.86
83103	4.4	20.1	22.3	2.3	1.02
83102	1.3	2.1	2.7	3.1	1.05
83101	13.8	28.1	31.9	4.4	1.27
83003	15.3	15.8	18.2	8.6	0.99
83002	82.6	73.3	86.3	14.3	1.47
83001	15.8	29.9	34.5	14.6	0.83
90101	0	0	0	39.0	1.51
90102	0	0	0	100	1.72
90103	0	0	0	50.0	1.21
90104	0	0	0	25.9	1.04
90105	0	0	0	22.1	0

Peak numbers of compounds correspond those in Table 2-2.

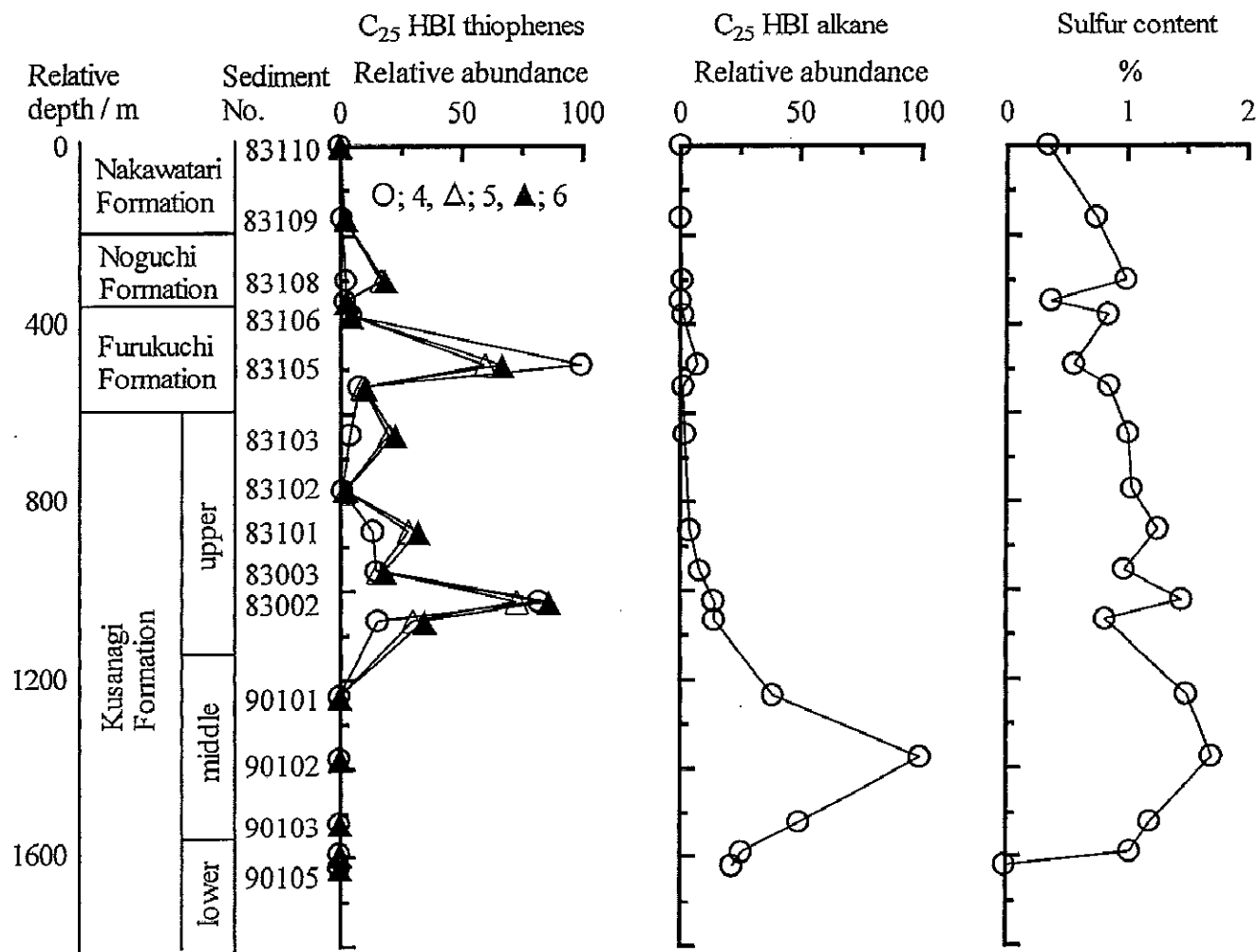


Fig. 2-6. Depth profiles of C₂₅ HBI thiophenes, C₂₅ HBI alkane and bulk sulfur contents in Neogene sediments of the Shinjo basin. Numbers of compounds in the C₂₅ HBI thiophene profile correspond those in Table 2-2. The name of the C₂₅ HBI alkane is in section of *Alkyl thiophenes*.

Robson, 1990). Bacterial sulfate reduction leading to the formation of hydrogen sulfide is a common phenomenon in Recent marine organic-rich sediments. Reactive iron easily reacts with hydrogen sulfide to form iron sulfide. Therefore, concentrations of hydrogen sulfide and reactive iron were thought to be a limiting factor in the production of thiophenes in sediments (Sinninghe Damsté *et al.*, 1989a). Iron contents in clay-poor sediments are small and, therefore, excess free sulfur species left after the iron sulfide formation can react with organic compounds. It is known that the Kusanagi Formation is relatively clay-poor than the upper parts of the sequence (Taguchi *et al.*, 1986). In addition, hydrogen sulfide might have been abundant at the deposition of the Kusanagi Formation because of an anoxic depositional environment judging from its low pristane to phytane ratio (Suzuki and Taguchi, 1982). This is probably why the C₂₅ HBI thiophenes were rather abundant in the Shinjo 83002 sample (the Kusanagi Formation). However, similar concentrations of these thiophenes were also found in the Shinjo 83105 sample (the Furukuchi Formation) which was probably deposited under more oxic condition than the Kusanagi Formation (Suzuki and Taguchi, 1982). Therefore, it seems that the major limiting factor for the formation of the C₂₅ HBI thiophenes was the concentration of the C₂₅ HBI alkadienes (Fig. 2-7) which possessed double bonds at suitable positions rather than that of inorganic reduced sulfur. This interpretation is supported by the marked difference between the depth profiles of the C₂₅ HBI thiophene concentrations and the bulk sulfur content over the sedimentary sequence as seen in Fig. 2-6. The bulk sulfur content indicates that there must have been more than enough amount of sulfur species present to react with the C₂₅ HBI alkadienes on the formation of the C₂₅ HBI thiophenes. This is why the two depth profiles are not related each other, although the presence of hydrogen sulfide is necessary for the formation. It is obvious that the precursors of the C₂₅ HBI thiophenes must have been relatively abundant at the two maxima (the Shinjo 83105 and 83002 samples) of the depth profile. The detection of the two C₂₅ HBI thiophenes

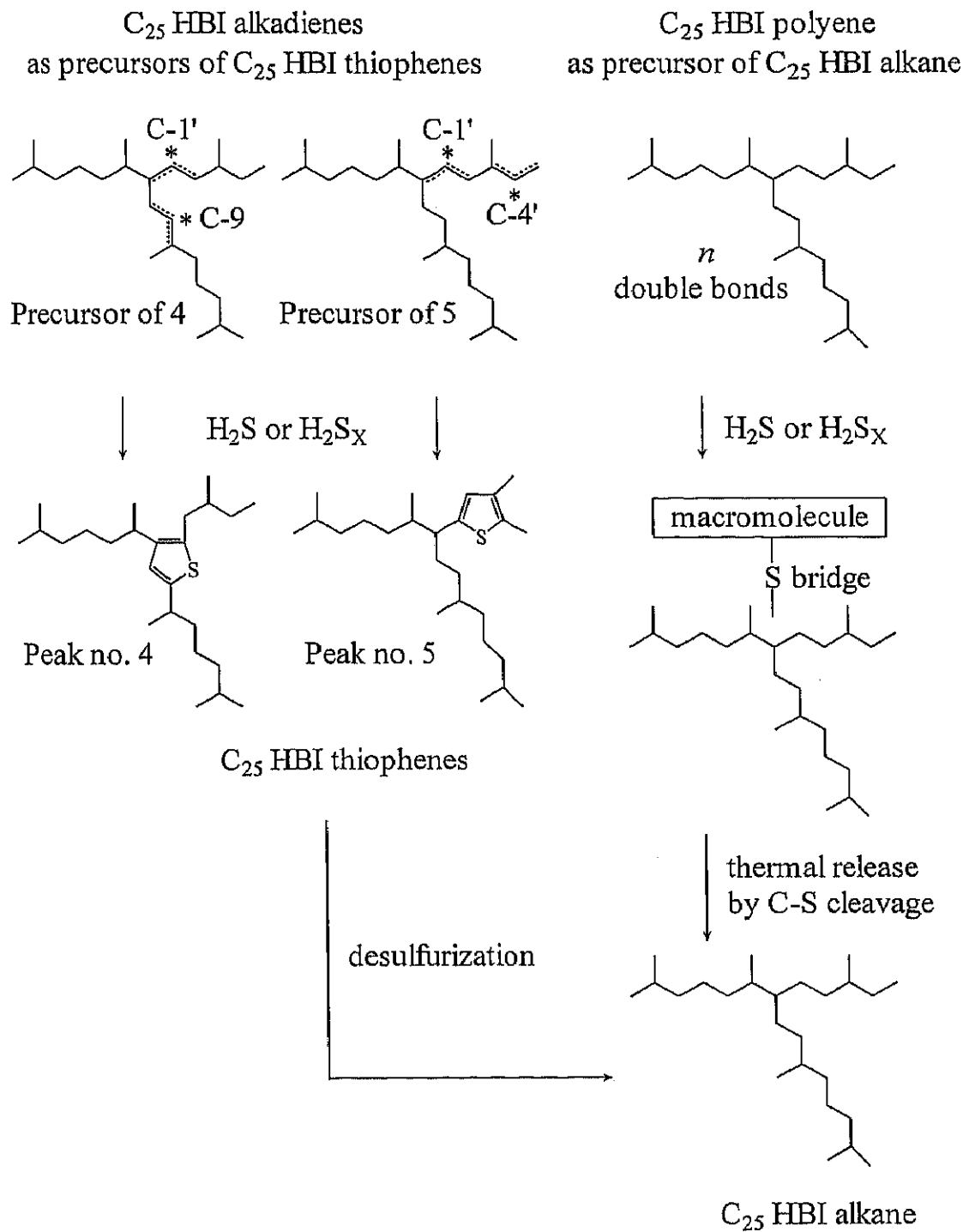


Fig. 2-7. Postulated diagenetic pathways of C_{25} HBI carbon skeletons (modified from Kohnen *et al.*, 1992). Numbers of compounds in the C_{25} HBI thiophenes correspond those in Table 2-2. The name of the C_{25} HBI alkane and double bond positions of the C_{25} HBI alkadienes are in the section of *Alkyl thiophenes*.

(nos. 4 and 5) specifies the double bond positions of the C₂₅ HBI alkadienes as shown in Fig. 2-7. The positions in the C₂₅ HBI alkadienes as precursors of 4 and 5 were likely 7(1'),8-, 7(1'),9-, 1',8- and 1',9-dienes, and 7(1'),3'-, 7(1'),4'-, 1'3'- and 1',4'-dienes, respectively.

The C₂₅ HBI alkane was probably produced from C₂₅ HBI polyene (Fig. 2-7). Kohnen *et al.* (1990) suggested that this compound could incorporate into macromolecular compounds such as kerogen and asphaltene in the presence of inorganic reduced sulfur forming sulfur bridged bonds between carbons at double bonds and the macromolecular compounds. At the same time the sulfur species can contribute to reduce the double bonds. The sulfur bridged bonds cleave rather easily with a further progress of sediment diagenesis, releasing the C₂₅ HBI alkane from the macromolecular compounds. In the Kusanagi Formation, sufficient hydrogen sulfide to form the sulfur bridged bonds was likely present at deposition as stated in the proceeding part of C₂₅ HBI thiophenes.

The compositions of the C₂₅ HBI thiophene isomers over the sedimentary sequence are shown in Fig. 2-8. The composition of the compound 4 varied in the range from 7.1 to 44.1 % and therefore, those of the compounds 5 and 6 (a pair of diastereomers) varied. Nevertheless, ratios of the compound 5 to 6 were similar at various depths. The difference in composition between the compound 4 and the pair (5 and 6) indicates that the C₂₅ HBI alkadiene isomers in Fig. 2-7 were likely derived from different sources. Schouten *et al.* (1997) reported that the stable carbon isotopic composition of the isomer 4 showed a different value from those of the pair indicating two different sources for the isomers.

Polynuclear aromatic thiophenes

Figure 2-9 shows mass fragmentograms for molecular ions of polynuclear aromatic thiophenes in the Shinjo 90102 sample. Characteristic mass numbers of *m/z* 184, 198, 212 and 234 for the polynuclear aromatic thiophenes gave 8 compounds numbered from 7 to

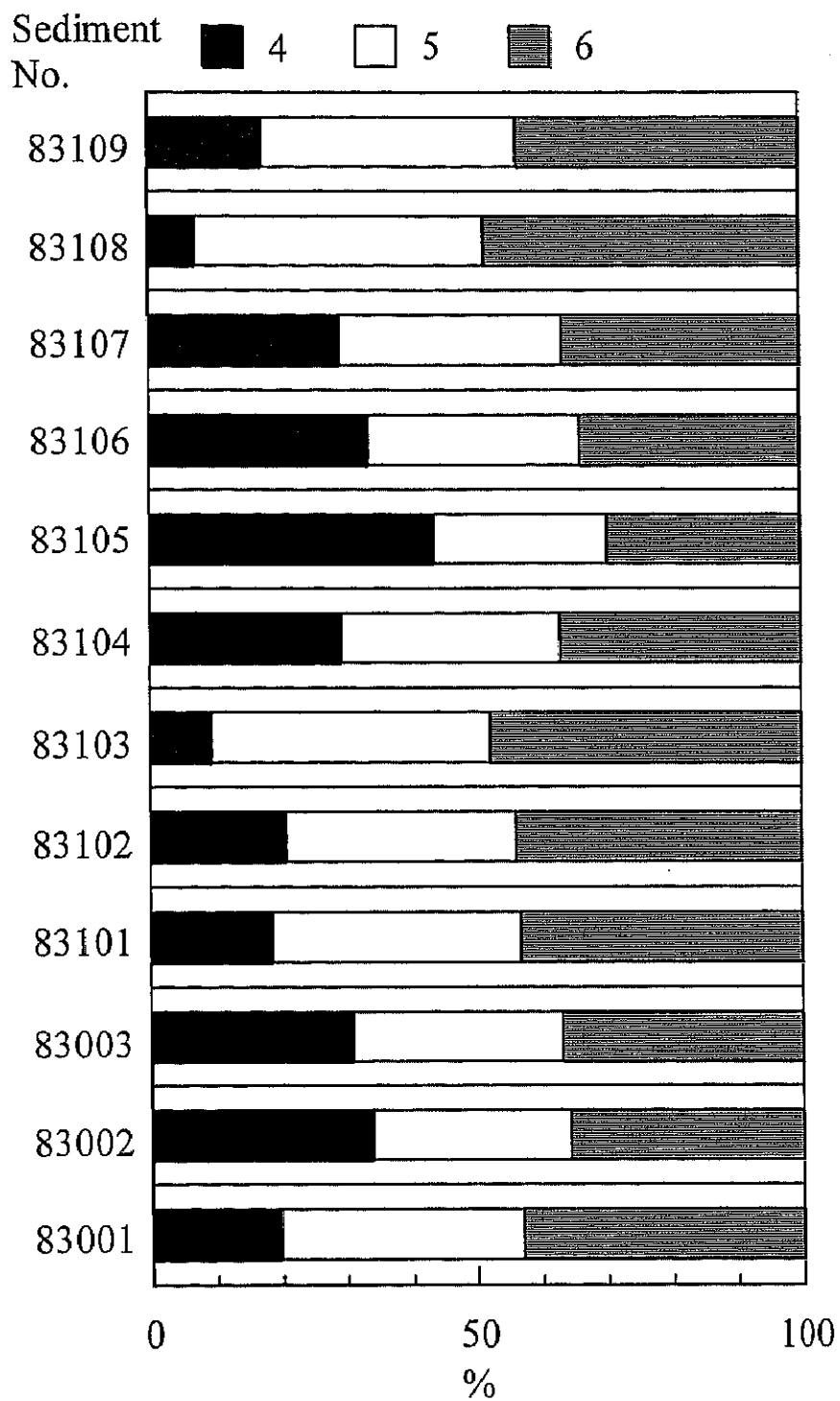


Fig. 2-8. Compositions of C₂₅ HBI thiophene isomers in Neogene sediments of the Shinjo basin. Numbers of compounds correspond those in Table 2-2.

14 (Fig. 2-9) which are listed in Table 2-2. Their concentrations or relative ones are listed in Table 2-4. Positions of methyl groups in C₁- and C₂-alkylDBTs were determined based on the previous studies (Chakhmakhchev and Suzuki, 1995b; Santamaría *et al.*, 1998). Concentrations of C₃-alkylDBTs and C₁-alkylBNTs were at a trace level and longer alkyl derivatives were not detected.

The concentrations of DBT and BNT varied from 10 to 730 and 14 to 210 pmol g⁻¹, respectively (Table 2-4), and are shown in Fig. 2-10, with those of TOC (Shimoyama and Matsubaya, 1985) and total *n*-alkanes (Ishiwatari and Shioya, 1986). The depth profiles of the DBT and the BNT showed the most abundant concentrations at the Shinjo 83003 and 90103 samples, respectively. The concentrations of all polynuclear aromatic thiophenes increased over the depth from the upper to middle parts of the Kusanagi Formation and decreased at the lower part of the Formation. These depth profiles showed a similar pattern to that of the total *n*-alkanes (Ishiwatari and Shioya, 1986) and were different from those of the C₂₅ HBI thiophenes. It is likely that the polynuclear aromatic thiophene formation caused by a diagenetic process similar to that of *n*-alkane generation and followed by different processes from those of the C₂₅ HBI thiophenes. If so, these polynuclear aromatic thiophenes were possibly derived from sulfur-containing aromatic moieties of macromolecules and were released from them during later diagenesis of the sediments.

The above interpretation agrees with previous reports (Suzuki and Taguchi, 1982; Ishiwatari and Shioya, 1986; Taguchi *et al.*, 1986). As described in the earlier section, hydrogen sulfide to incorporate into the macromolecules might have been abundant at the deposition of the Kusanagi Formation. Furthermore, kerogen in the Kusanagi Formation is a type II which is different from those in the upper parts of the sequence (Taguchi *et al.*, 1986). Therefore, it is likely that the Kusanagi Formation at its deposition had contained more than enough free sulfur species and a sufficient amount of precursor compounds

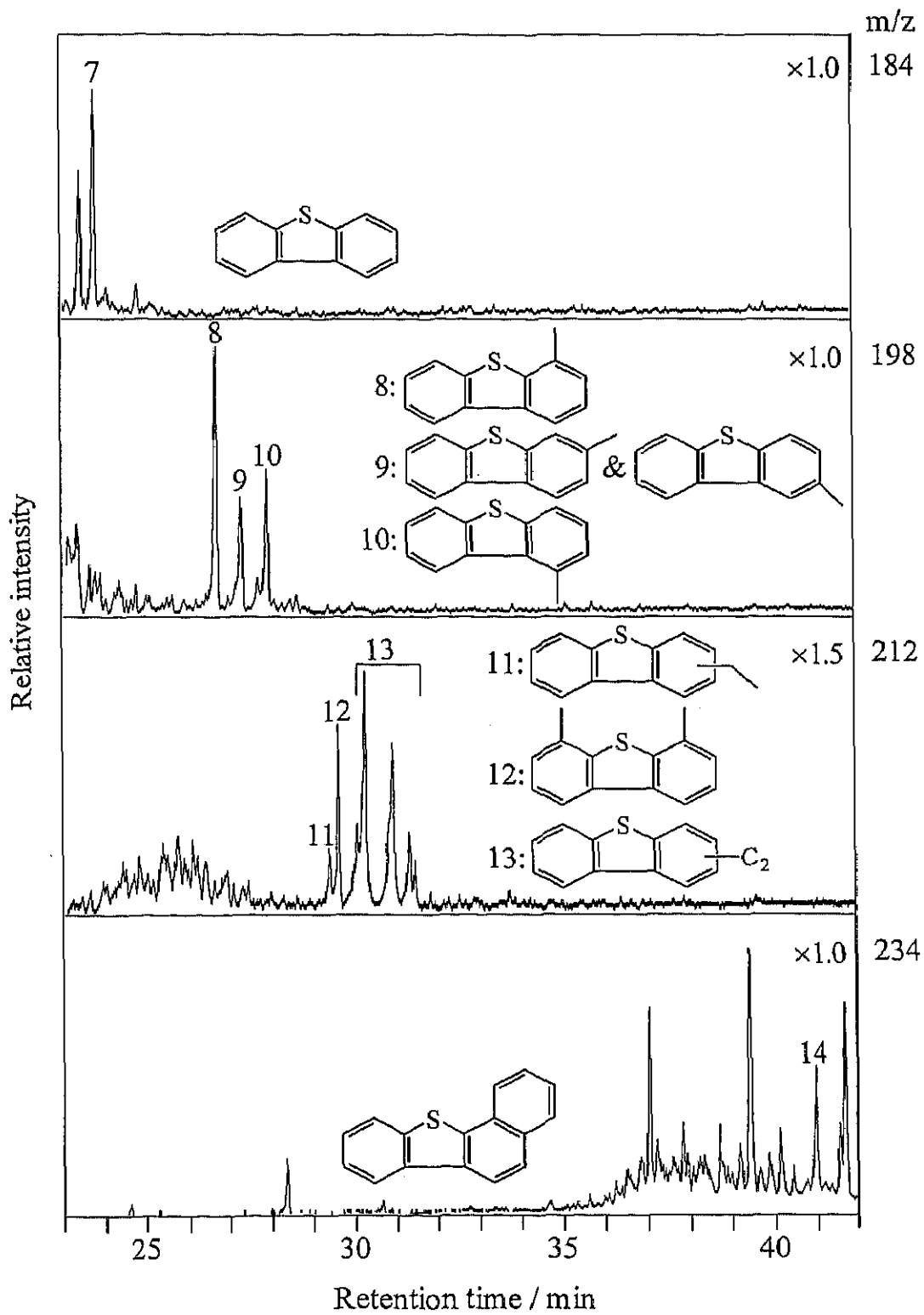


Fig. 2-9. Mass fragmentograms of polynuclear aromatic thiophenes in the Shinjo 90102 sample. Peak numbers correspond those in Table 2-2.

Table 2-4. Concentrations and relative ones of polynuclear aromatic thiophenes in Neogene sediments of the Shinjo basin

Sediment No.	Peak No.						
	7	8*	9*	10*	11*	12*	14
	pmol g ⁻¹						pmol g ⁻¹
83110	28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
83109	n.d.	5	10	4	n.d.	3	n.d.
83108	54	37	11	14	3	25	trace
83107	10	13	8	8	n.d.	6	14
83106	90	76	35	28	14	68	20
83105	110	71	42	33	13	58	23
83104	47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
83103	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
83102	140	91	50	39	13	53	28
83101	230	220	99	60	19	49	34
83003	730	520	280	320	78	98	130
83002	470	250	220	230	84	210	89
83001	250	320	150	99	21	71	44
90101	590	530	310	370	61	120	62
90102	270	330	170	170	41	110	190
90103	360	650	320	360	98	410	210
90104	58	230	96	140	37	52	154
90105	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	35

Peak numbers of compounds correspond those in Table 2-2.

* Relative concentrations of compounds numbered from 8 to 12 are determined by the dibenzothiophene standard.

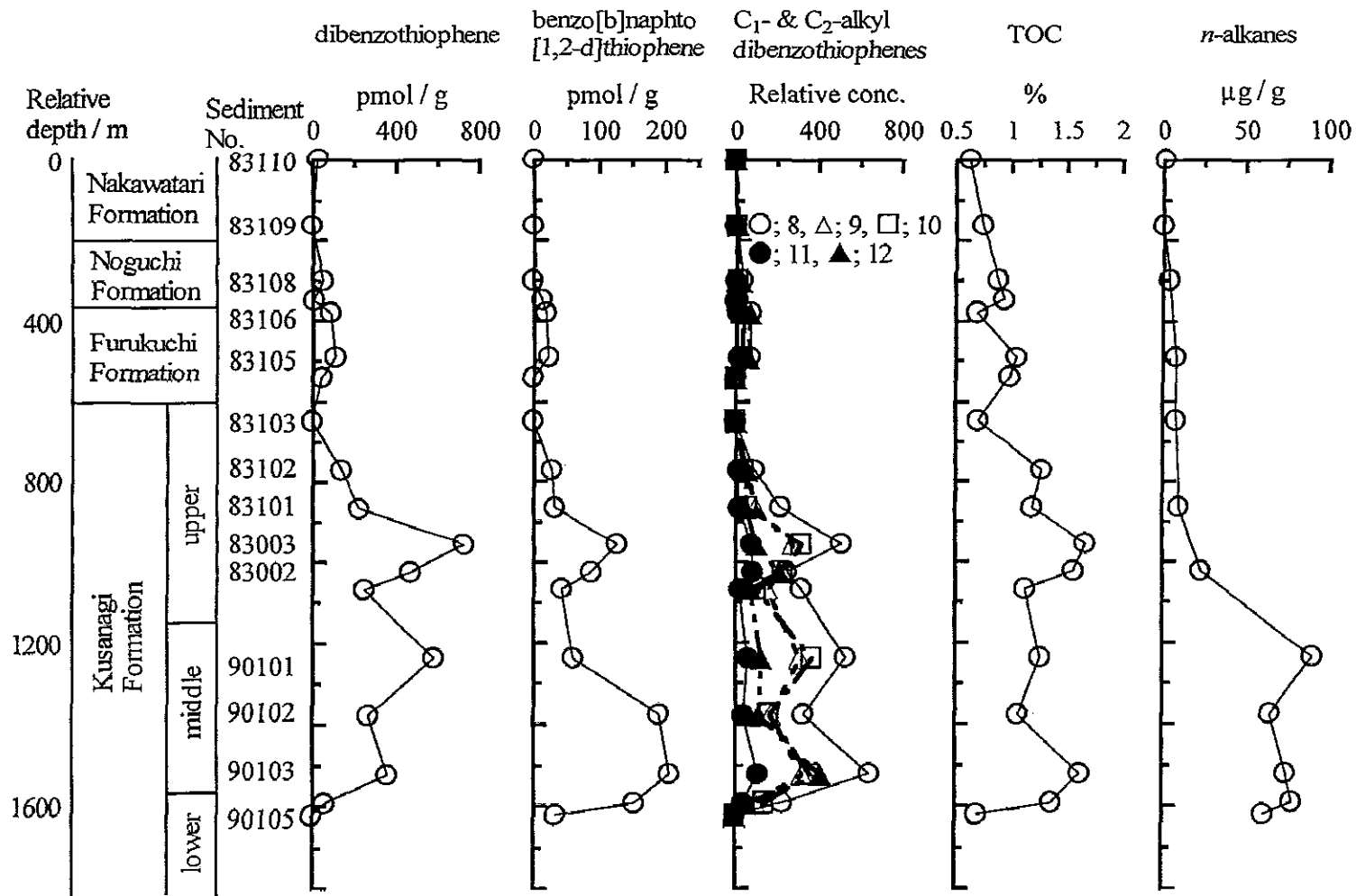


Fig. 2-10. Depth profiles of polynuclear aromatic thiophenes, total organic carbon (TOC) and total n -alkanes contents in Neogene sediments of the Shinjo basin. Numbers of compounds in C_1 - and C_2 -alkyldibenzothiophene profile correspond those in Table 2-2. TOC and n -alkane data are from Shimoyama and Matsubaya (1985), and Ishiwatari and Shioya (1986), respectively.

with functional groups to form macromolecules with sulfur-containing aromatic moieties.

Simple organic sulfur compounds such as alkyl thiophenes including isoprenoid thiophenes have been found only in immature sediments and petroleum (Sinninghe Damsté *et al.*, 1987, 1989a and b; Kohnen *et al.*, 1990; de las Heras *et al.*, 1997). However, mature petroleum contains organic sulfur compounds which have thiophene rings as a part of more complex ring systems such as BTs, DBTs and BNTs with much shorter alkyl side-chains (Arpino *et al.*, 1987; Radke and Willsch, 1994; Chakhmakhchev and Suzuki, 1995a and b). Polynuclear aromatic thiophene formation was explained by cyclization and aromatization of alkyl thiophenes (Sinninghe Damsté *et al.*, 1987, 1989a; Kohnen *et al.*, 1990). The typical formation process is shown in Fig. 2-11a (Sinninghe Damsté *et al.*, 1987). A part of the polynuclear aromatic thiophenes in the Kusanagi Formation might have been produced by the process. This process is favorable reaction for BT formation. However, this compound was not found in the Neogene sediments. If the polynuclear aromatic thiophene formation is only explained by that reaction pathway, BTs should have been detected in the sediments. Therefore, the explanation of polynuclear aromatic thiophene formation should not be limited to the pathway because little has been known about their precursors and diagenetic pathways leading to the formation of those thiophenes. In a separate experiment, DBT was generated by a heating experiment of 2-2'-biphenol with FeS or elemental sulfur in the presence or absence of water and clay at 200 °C. Time-course plots of DBT produced by the experiment are shown in Fig. 2-12. This result may indicate a plausible diagenetic reaction of DBT formation in addition to the formation by cyclization and aromatization of alkyl thiophenes (Sinninghe Damsté *et al.*, 1987, 1989a). The formation process is that aromatic compounds having hydroxyl groups are incorporated into macromolecules followed by the substitution of the groups by sulfur species, producing bound-DBTs (Fig. 2-11b). Later, these thiophenes are released from the macromolecules by a further

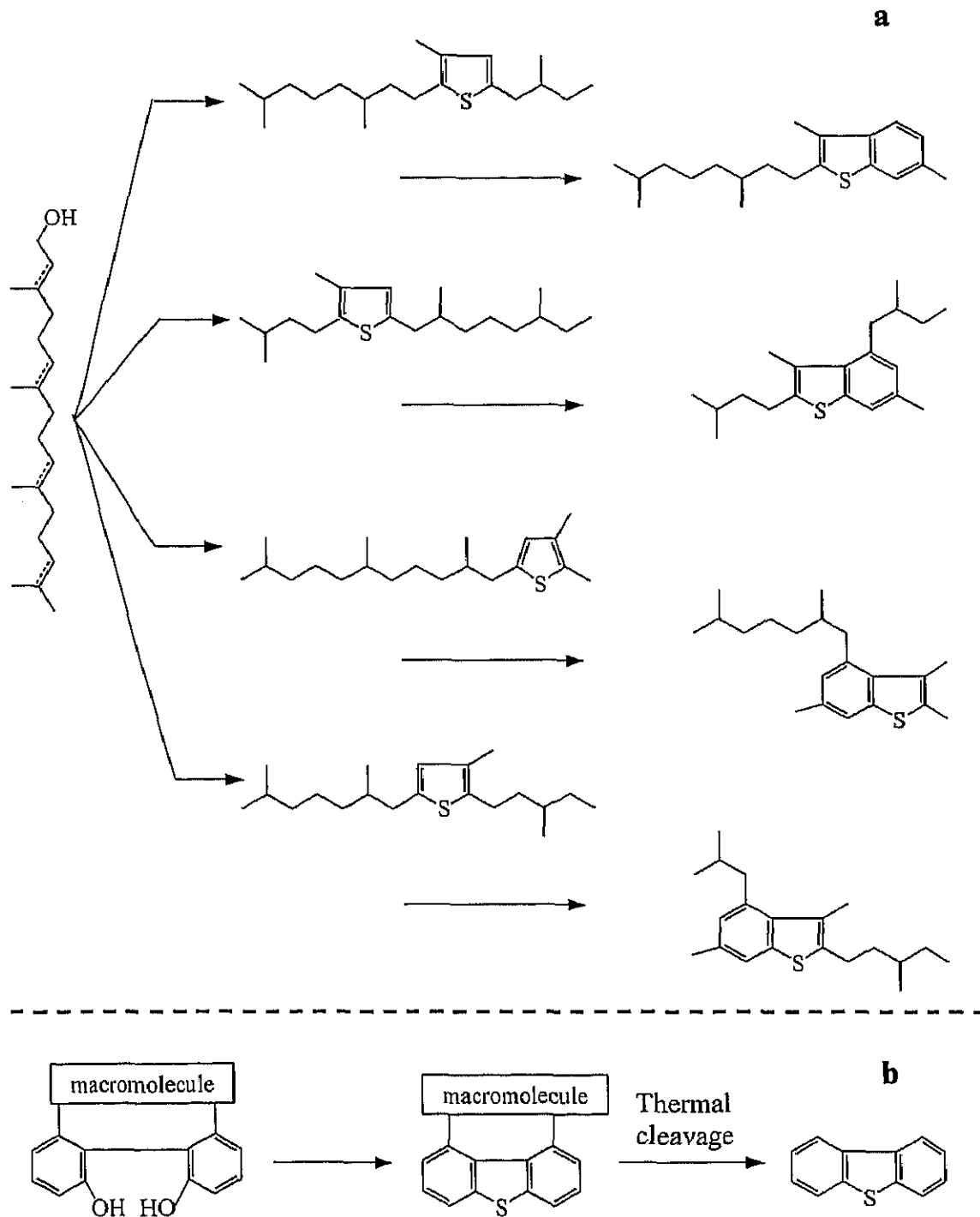


Fig. 2-11. Postulated diagenetic pathways of (a) alkyl to benzothiophenes starting from unsaturated phytanols (modified from Sinnighe Damsté *et al.*, 1987) and of (b) 2-2'-biphenol to dibenzothiophene based on the heating experiment.

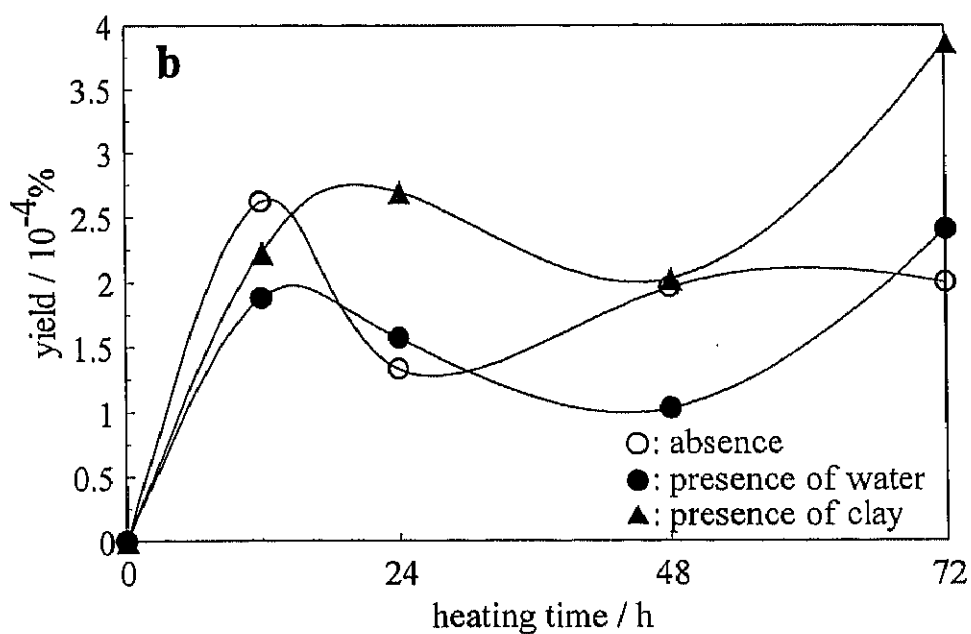
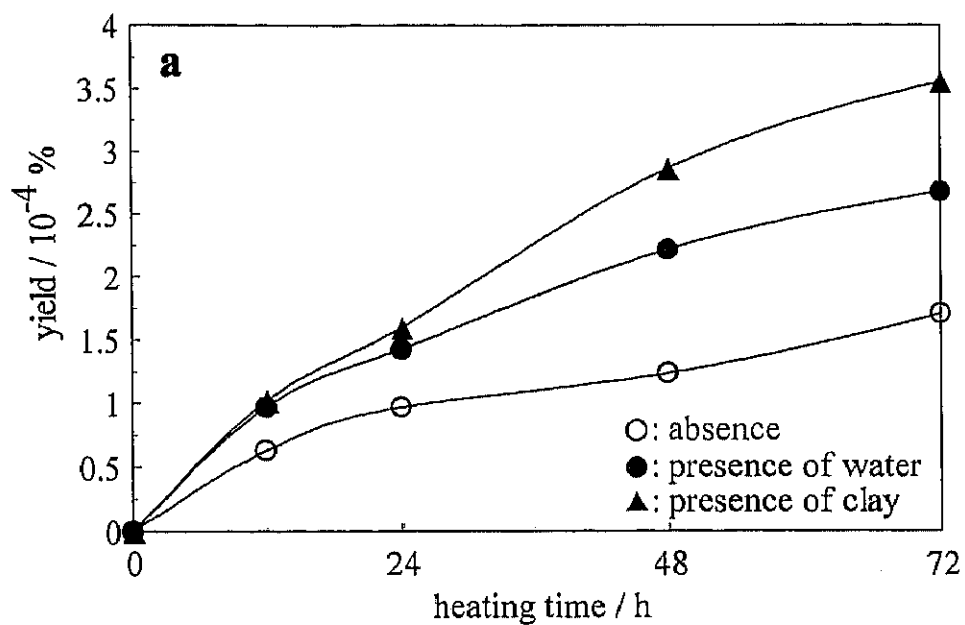


Fig. 2-12. Time-course plots of dibenzothiophene produced by the heating experiment using 2-2'-biphenol with (a) FeS and (b) elemental sulfur at 200 °C.

progress of diagenesis. However, further studies are necessary for the polynuclear aromatic thiophene formation in the sedimentary rocks.

CONCLUSIONS

Eighteen Neogene sediments from the Shinjo basin were analyzed for alkyl and polynuclear aromatic thiophenes, and the following conclusions were drawn to characterize the thiophenes in the sediments.

1. Three kinds for each of C₂₀ isoprenoid and C₂₅ HBI thiophenes, and eight kinds of polynuclear aromatic thiophenes were detected. The concentrations of DBT and BNT ranged from 10 to 730 and 14 to 210 pmol g⁻¹, respectively.
2. The C₂₅ HBI thiophenes showed a unique depth profile, *i.e.*, they existed from the Nakawatari to the upper part of the Kusanagi Formations. However, they were absent at the middle and lower Kusanagi Formation. It was postulated that the number and position of the double bonds in C₂₅ HBI alkadienes were primary important for the formation of the C₂₅ HBI thiophenes during early diagenesis. The variation in composition of the C₂₅ HBI thiophene isomers was observed in the sediments indicating that they were derived from different kinds of C₂₅ HBI alkadienes.
3. The depth profiles of polynuclear aromatic thiophenes were different from those of the C₂₅ HBI thiophenes and similar to that of the reported total *n*-alkanes (Ishiwatari and Shioya, 1986). The concentrations of all polynuclear aromatic thiophenes increased in the range from the upper to middle Kusanagi Formation and decreased at deeper depth. This result possibly indicates that the polynuclear aromatic thiophene formation followed a similar process to *n*-alkane generation and caused by different processes from those of the C₂₅ HBI thiophenes. In this connection, a possibility was postulated that the polynuclear aromatic thiophenes were formed from sulfur-containing aromatic moieties of macromolecules and were released during later stage of diagenesis.

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