

Chapter 3

Thiophenes in the Cretaceous/Tertiary Boundary Sediments at Kawaruppu, Hokkaido, Japan

ABSTRACT – One kind for each of C₂₅ highly branched isoprenoid (HBI) thiophenes and C₂₅ HBI alkanes, and five kinds of polynuclear aromatic thiophenes were detected in the Cretaceous/Tertiary (K/T) boundary sediments at Kawaruppu, Hokkaido, Japan. The C₂₅ HBI thiophene was found only in the sediments below the boundary claystone but not in the claystone and sediments above it. On the other hand, the C₂₅ HBI alkane was present in all the sediments. However, its concentration decreased drastically at the bottom of the claystone, stayed in low over the bottom two third portion of the claystone, and started increasing upwards from the two third horizon. This distribution pattern resembles that of the longer chain *n*-alkanes (Mita and Shimoyama, 1999a). The depth profiles of the thiophene and alkane concentrations possibly reflect the massive extinction of organisms. Among the polynuclear aromatic thiophenes dibenzothiophene and benzo[b]naphto[1,2-d]thiophene are relatively abundant. Their concentrations were roughly constant in the sediments below the horizon at the upper one third of the boundary claystone. Their increase began at the one third horizon towards the 40 cm horizon (26 cm above the top horizon of the claystone) and then they steeply decreased in the sediment above the horizon. A nearly constant ratio of 4- to 1-methyldibenzothiophene found in the sediments above, within and below the boundary claystone indicates that the 65 million year diagenesis has influenced evenly over the sediments. The depth profile of the dibenzothiophene concentrations resembles that of the reported sulfide contents (Kajiwara and Kaiho, 1992) and suggests that the polynuclear aromatic thiophene formation largely related to the sulfide content at deposition.

INTRODUCTION

The massive extinction of organisms ranging from dinosaurs to marine plankton at the end of Cretaceous (approximately 65 million years ago) is one of the most significant biological events in earth history. An interesting postulate for the cause of the extinction is a global fallout of debris and dust due to an impact of an extraterrestrial body or bolide (Alvarez *et al.*, 1980; Smit and Hertogen, 1980) or extensive volcanism (Officer and Drake, 1983; McLean, 1985). In this connection, some organic geochemical studies on the Cretaceous/Tertiary (K/T) boundary sediments have investigated evidences for extraterrestrial organic compounds (Zhao and Bada, 1989) and wildfires triggered by the bolide impact (Wolbach *et al.*, 1985, 1988; Venkatesan and Dahl, 1989; Heymann *et al.*, 1994, 1996, 1998; Arinobu *et al.*, 1999). Other studies of organic compounds in the K/T boundary sediments examined microbial hydrocarbons and fatty acids in the K/T boundary claystone (Simoneit and Bellar, 1985, 1987) and microbial fatty acids and additional terrestrial resin acids in the sediments above and below the claystone at Stevns Klint, Denmark (Meyers and Simoneit, 1990).

The K/T boundary sediments at Kowaruppu, Hokkaido, Japan provide a good sedimentary sequence for organic geochemical studies. The claystone at Kowaruppu is thicker (nearly 14 cm) than those at other sites (*e.g.*, Stevns Klint in Denmark, Gubbio in Italy and Woodside Creek in New Zealand) and can be analyzed for organic compounds in detail along the depth. Previously, organic geochemical studies of amino acids (Mita *et al.*, 1996) and dicarboxylic acids (Mita *et al.*, 1998) in the sediments discussed on the possibility of the presence of extraterrestrial organic compounds as well as terrestrial ones. Characteristic distributions of aliphatic hydrocarbons (Mita and Shimoyama, 1999a), and

polycyclic aromatic hydrocarbons (PAHs) (Mita and Shimoyama, 1999b) in the sediments were reported in relation to the massive extinction and wildfires, respectively. Other published studies of the sediments dealt with planktonic foraminifera (Kaiho and Saito, 1986; Kaiho, 1992), palynomorphs (Saito *et al.*, 1986), sulfur isotopes (Kajiwara and Kaiho, 1992) and Ir accumulation and clay minerals (Tasaki *et al.*, 1992). In this chapter, the author detected a C₂₅ highly branched isoprenoid (HBI) thiophene in the sediments below the boundary claystone, and polynuclear aromatic thiophenes below, within and above the claystone. The depth distributions of these thiophenes are compared with those of the C₂₅ HBI alkane detected together and the longer chain *n*-alkanes (Mita and Shimoyama, 1999a) besides that of sulfide concentration (Kajiwara and Kaiho, 1992). Furthermore, the results of the C₂₅ HBI thiophene are discussed in relation to the massive extinction of diatoms, and the polynuclear aromatic ones to the redox conditions during the deposition and the diagenesis of the K/T boundary sediments at Kawaruppu.

EXPERIMENTAL

Samples

The K/T boundary sediments occur near Kawaruppu Town, Tokachi District, Hokkaido, and its location and lithology were reported by Saito *et al.* (1986), and Kaiho and Saito (1986). Briefly, the sedimentary sequence at Kawaruppu consists predominantly of a marine, dark gray siltstone, bearing occasional calcareous concretions. The boundary claystone is grayish black and nearly 14 cm thick. The locality and stratigraphic sequence of the samples are shown in Fig. 3-1. A total of 20 sediment samples whose horizons were reported by Mita *et al.* (1996, 1998) were analyzed for this study. They included 9 samples within the boundary claystone (0.8 – 13.2 cm), 5 samples above (40 – 495 cm) and 6 samples below (–395 – 0 cm) the boundary claystone. Concentrations of total organic carbon (TOC), *n*-alkanes and PAHs are shown in Fig. 3-2 (Mita *et al.*, 1986; Mita and Shimoyama, 1999a and b).

Analyses

Analytical procedure for thiophenes in the K/T boundary sediments is basically same as described in Chapter 2.

For each analysis, 3 g of a powdered sample were extracted six times with 5 ml of a mixture of dichloromethane and methanol (4:1 by vol.) by sonication for 30 min. The extracted solutions were combined, 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). C₂₅ HBI thiophenes and alkanes were recovered in F1, and polynuclear

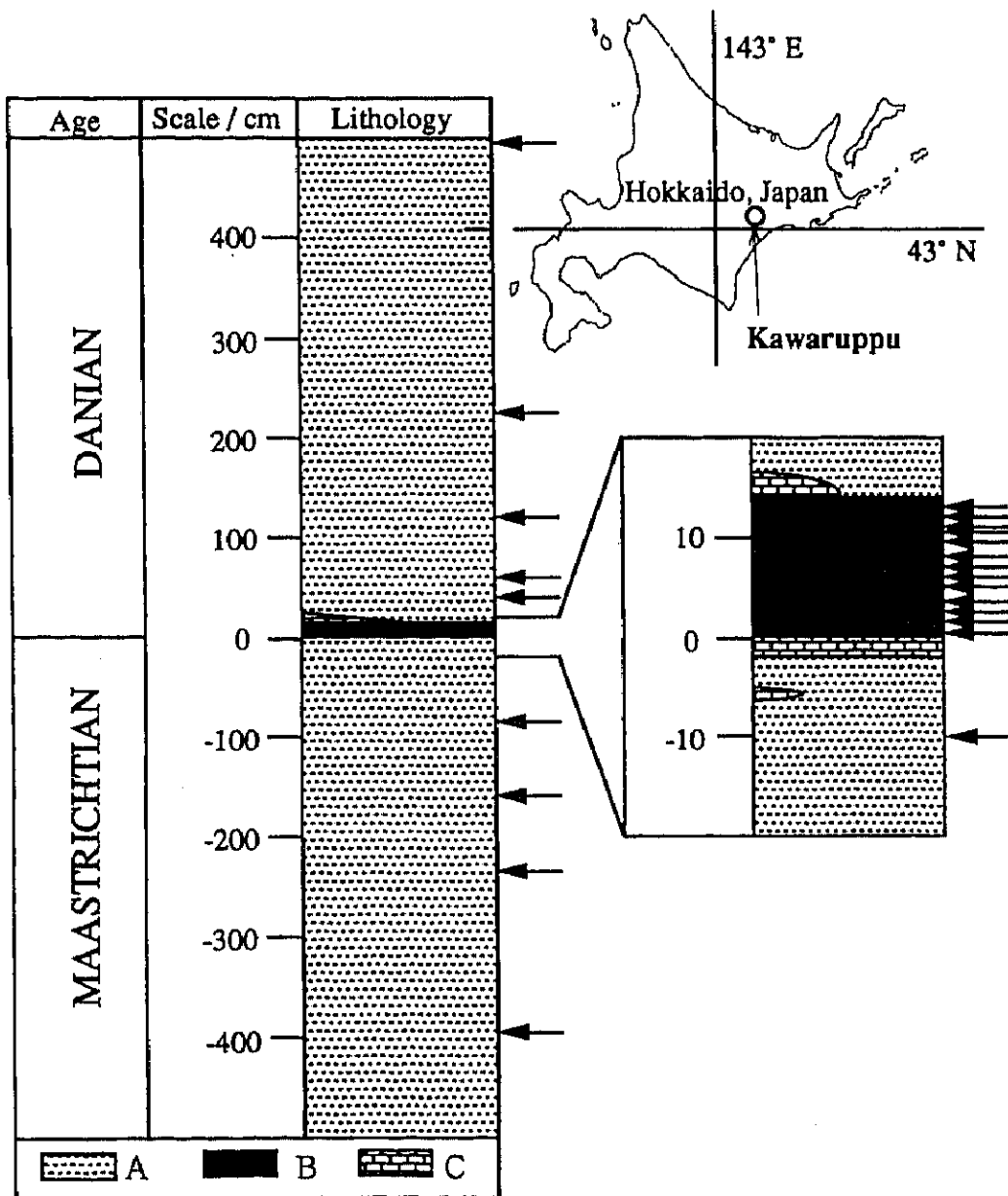


Fig. 3-1. Location of the Kawaruppu section, and the lithology and sampling points of the K/T boundary in the Kawaruppu. Lithologies are A: siltstone, B: claystone, C: limestone. Arrows show the sampling points. Scale is measured from the base of the K/T boundary claystone, plus is for Danian and minus is for Maastrichtian. Lithology diagram is based on Saito *et al.* (1986).

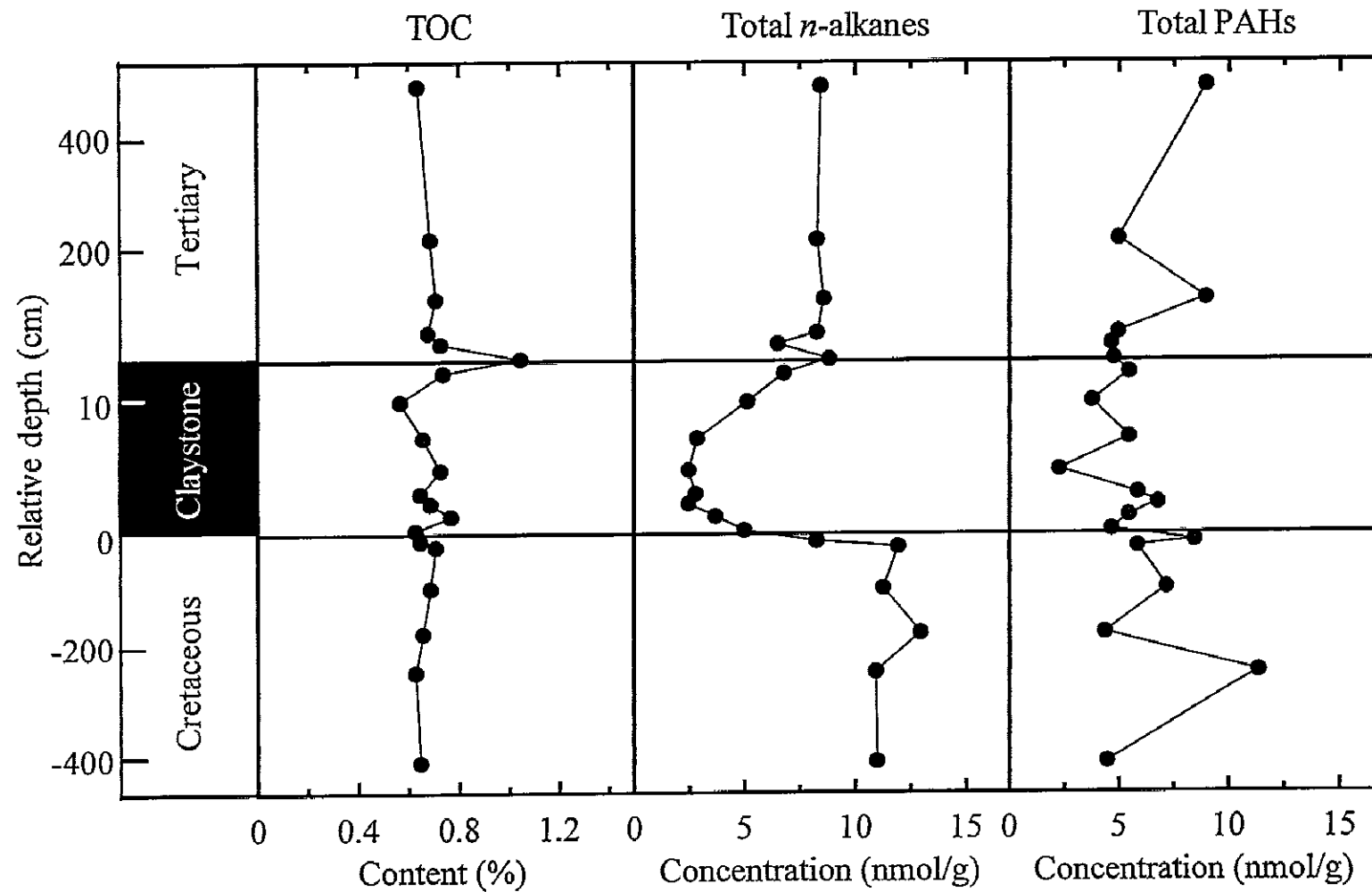


Fig. 3-2. Depth profiles of total organic carbon (TOC) contents, and total *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) concentrations in the K/T boundary sediments at Kawaruppu. Data are from Mita *et al.* (1996), and Mita and Shimoyama (1999a and b).

aromatic thiophenes in F2. Free sulfur in F1 was removed with reduced copper (Wako Pure Chemicals). F1 and F2 were carefully concentrated to 50 μl under a nitrogen flow for the analysis of individual thiophenes by a gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 6890 instrument combined with a Hewlett-Packard 5973 mass spectrometer. The GC was equipped with a splitless injection system and a DB-5ht capillary column (30 m \times 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 $^{\circ}\text{C}$ for initial 5 min, to increase from 50 to 120 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$ and from 120 to 310 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C min}^{-1}$, and to hold at 310 $^{\circ}\text{C}$ for 10 min. Mass spectra were obtained by an electron impact mode at 70 eV scanning from m/z 50 to 600 at every 1.4 s. Identification of a C_{25} HBI thiophene and a C_{25} HBI alkane was described in the section of *C₂₅ HBI thiophene*. Relative abundances of the thiophene and the alkane were estimated by their peak areas on mass fragmentograms of m/z 293 and 238, respectively. Identification and quantification of polynuclear aromatic thiophenes were generally performed by comparison of peak retention times and areas, respectively, on mass fragmentograms for selected ions with those of standard compounds. These compounds used were dibenzothiophene (DBT) and benzo[b]naphto[1,2-d]thiophene (BNT).

All glassware was heated at 500 $^{\circ}\text{C}$ for at least 3 h prior to use in order to remove organic contaminants. Organic solvents were doubly distilled and then used. A procedural blank was carried out with 0.5 g pre-ignited sand powder and it was found that there was no significant contamination during the analysis.

RESULTS AND DISCUSSION

C₂₅ HBI thiophene

Figure 3-3 shows mass fragmentograms of a compound recovered from the sediment at the -395 cm horizon. Mass spectrum of this compound (Fig. 3-4a) showed fragment ions at m/z 378 (corresponds the molecular ion of alkyl thiophene with 25 carbons), and 321 and 293 (due to β -cleavages). This compound numbered 1 was identified as a C₂₅ HBI thiophene (compound name in Table 3-1) considering its relative retention time on GC and the mass spectrum reported by Sinninghe Damsté *et al.* (1989b). Other alkyl and isoprenoid thiophenes were not detected in the K/T boundary sediments at Kwaruppu. The author also analyzed thiophenes in Neogene sediments by the same procedure (Katsumata and Shimoyama, 2000), and detected three C₂₅ HBI and three C₂₀ isoprenoid thiophene isomers. Therefore, this analytical method could have detected other alkyl thiophenes if they had existed in the Kwaruppu sediments. Three kinds of C₂₅ HBI thiophenes including the one we detected were found in Cretaceous sediments from the Jurf ed Darawish Oil Shale (Sinninghe Damsté *et al.*, 1989b). Furthermore, a C₂₅ HBI alkane was detected on the mass fragmentogram of m/z 57 (not shown) eluting just after the *n*-C₂₁ alkane. A mass spectrum of the C₂₅ HBI alkane (Fig. 3-4b) showed characteristic ions at m/z 210, 238 and 266 which were interpreted due to the cleavages of the C-C bonds at C-7 and C-8, C-6 and C-7, and C-7 and C-1' positions, respectively. The mass spectrum is very similar to that reported by Rowland and Robson (1990), and therefore, the alkane was assigned as 2, 6, 10, 14-tetramethyl-7-(3-methylpentyl)pentadecane. These thiophene and alkane could not be quantified because of the lack of these standard compounds. However, they are likely

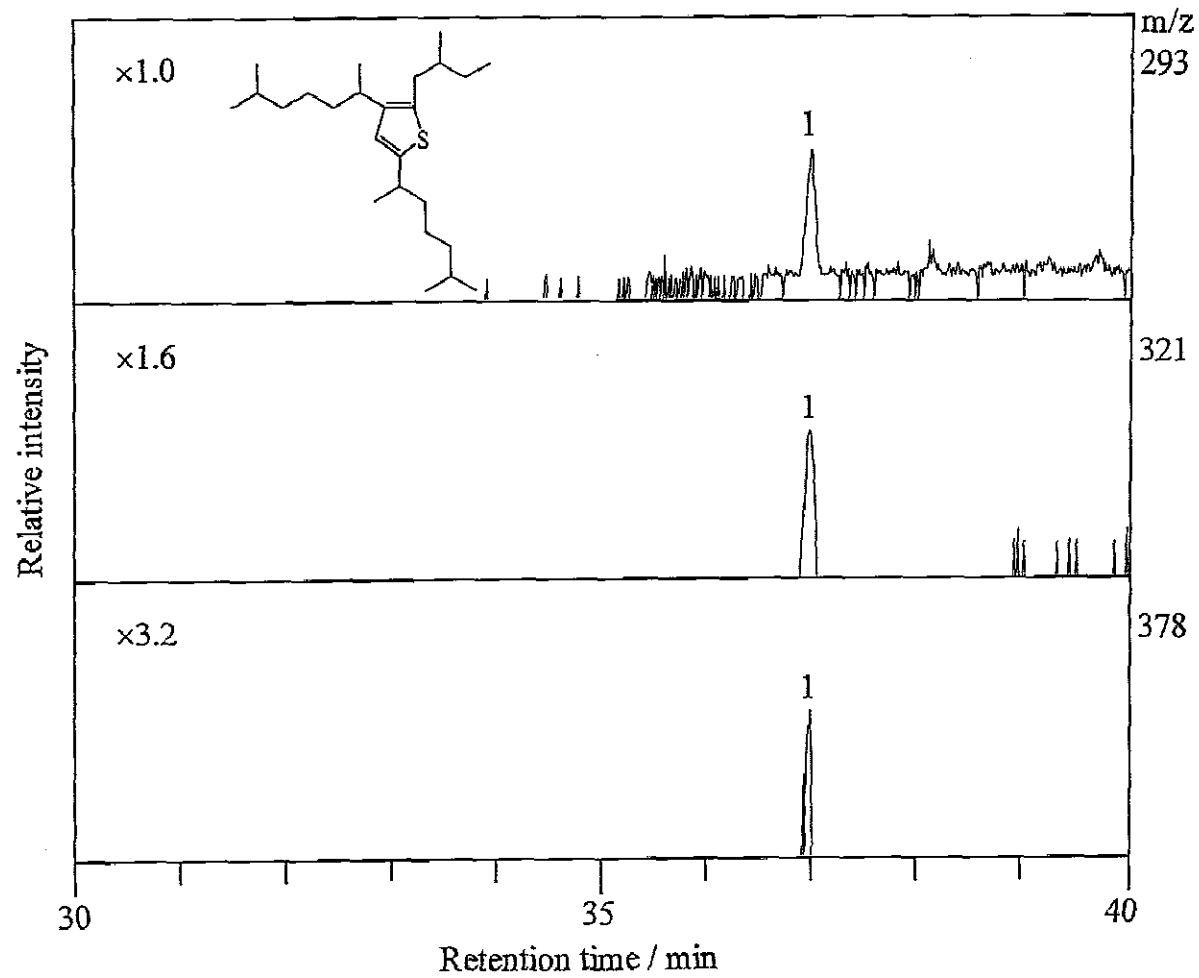


Fig. 3-3. Mass fragmentograms of C₂₅ HBI thiophene recovered from the sediment at the -395 cm horizon of the K/T boundary sediments at Kawaruppu. The peak number 1 corresponds that in Table 3-1.

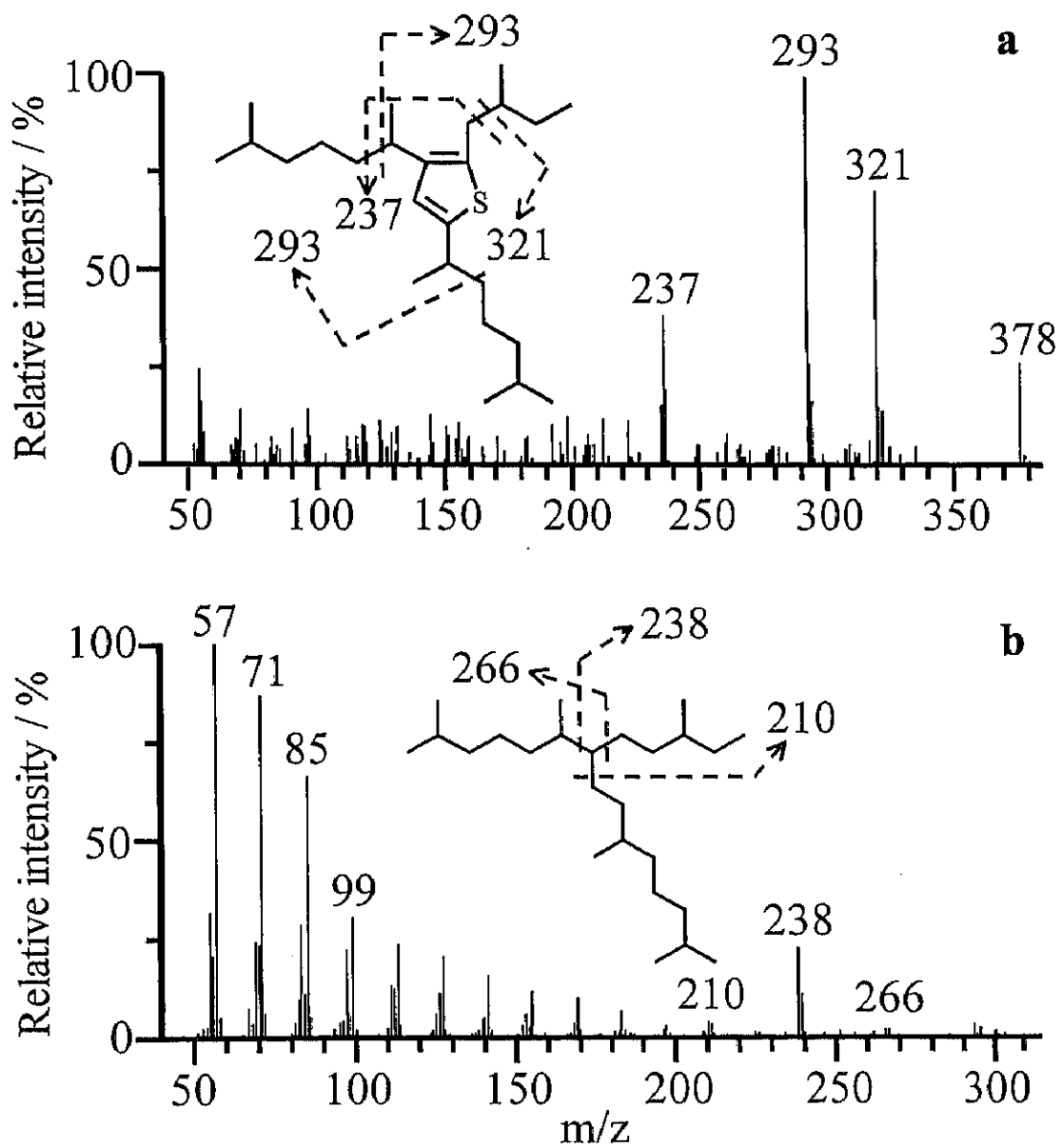


Fig. 3-4. Mass spectra of (a) C₂₅ HBI thiophene and (b) C₂₅ HBI alkane from the sediment at the -395 cm horizon of the K/T boundary sediments at Kwaruppu.

Table 3-1. Thiophenes in the K/T boundary sediments at Kowaruppu and their major mass numbers (*m/z*)

Peak No.	Compound	Major mass numbers (<i>m/z</i>)
C ₂₅ HBI thiophene		
1	2-(2'-methylbutyl)-3,5-di-(2'-(6'- methylheptyl)) thiophene	237, 293, 321, 378
Polynuclear aromatic thiophenes		
2	dibenzothiophene	184
3	4-methyldibenzothiophene	198
4	2- and 3-methyldibenzothiophene	198
5	1-methyldibenzothiophene	198
6	benzo[b]naphto[1,2-d]thiophene	234

present at most at the levels of one (thiophene) and ten-pmol⁻¹ (alkane) judging from the MS detection levels. Their relative abundances are listed in Table 3-2.

Four kinds of C₂₅ HBI thiophenes were found in various immature sedimentary rocks (Sinninghe Damsté *et al.*, 1989a and b; Sinninghe Damsté and Rijpstra, 1993; de las Heras *et al.*, 1997). In addition, it has been suggested that those C₂₅ HBI thiophenes were formed from C₂₅ HBI alkadienes derived from specific diatoms by the incorporation of reduced sulfur species in the early stage of diagenesis (Kohnen *et al.*, 1992). The structures of C₂₅ HBI thiophenes produced depend on the double bond positions in the structures of the alkadienes. Therefore, the C₂₅ HBI alkadienes as precursor of the C₂₅ HBI thiophene found in the K/T sediments were likely 7(1'),8-, 7(1'),9-, 1',8- and 1',9-dienes.

Relative abundances of the C₂₅ HBI thiophene and the C₂₅ HBI alkane at each sample horizon are shown in Fig. 3-5, together with the concentrations of the longer chain *n*-alkanes from C₂₇ to C₂₉ (Mita and Shimoyama, 1999a). The depth profile of the C₂₅ HBI thiophene is different from those of the C₂₅ HBI alkane and the *n*-alkanes. The C₂₅ HBI thiophene was detected only in the sediments below the boundary claystone (Fig. 3-5a). It was reported that each C₂₅ HBI thiophene isomer is derived from each specific kind of diatoms (Schouten *et al.*, 1997). As shown in Fig. 3-9, the depth profile of the total sulfide contents (Kajiwara and Kaiho, 1992) indicates that more than enough sulfur species must have been present to react with the C₂₅ HBI alkadienes on the formation of the C₂₅ HBI thiophene in the early diagenesis. Therefore, it is likely that specific diatoms which produced the C₂₅ HBI alkadienes existed until the end of Cretaceous at Kawaruppu. Since this thiophene was detected over a stratigraphic sequence of Neogene sediments at difference place (Katsumata and Shimoyama, 2000), it is likely that the absence of the thiophene in the boundary claystone and the sediments above it is not due to the extinction of those diatoms but their drastical decrease in population at the K/T boundary.

Table 3-2. Relative abundances of C₂₅ HBI thiophene and C₂₅ HBI alkane in the K/T boundary sediments at Kawaruppu

Relative depth (cm)	C ₂₅ HBI thiophene	C ₂₅ HBI alkane
495	0	62.1
225	0	42.4
120	0	43.1
60	0	34.8
40	0	55.6
13.2	0	29.9
12.2	0	18.8
10.6	0	17.2
7.4	0	6.9
5.1	0	7.8
3.4	0	7.7
2.7	0	7.9
1.8	0	8.9
0.8	0	10.9
0	0	12.6
-10	100	74.5
-85	78.8	77.1
-165	83.5	94.5
-235	68.2	72.1
-395	83.6	100

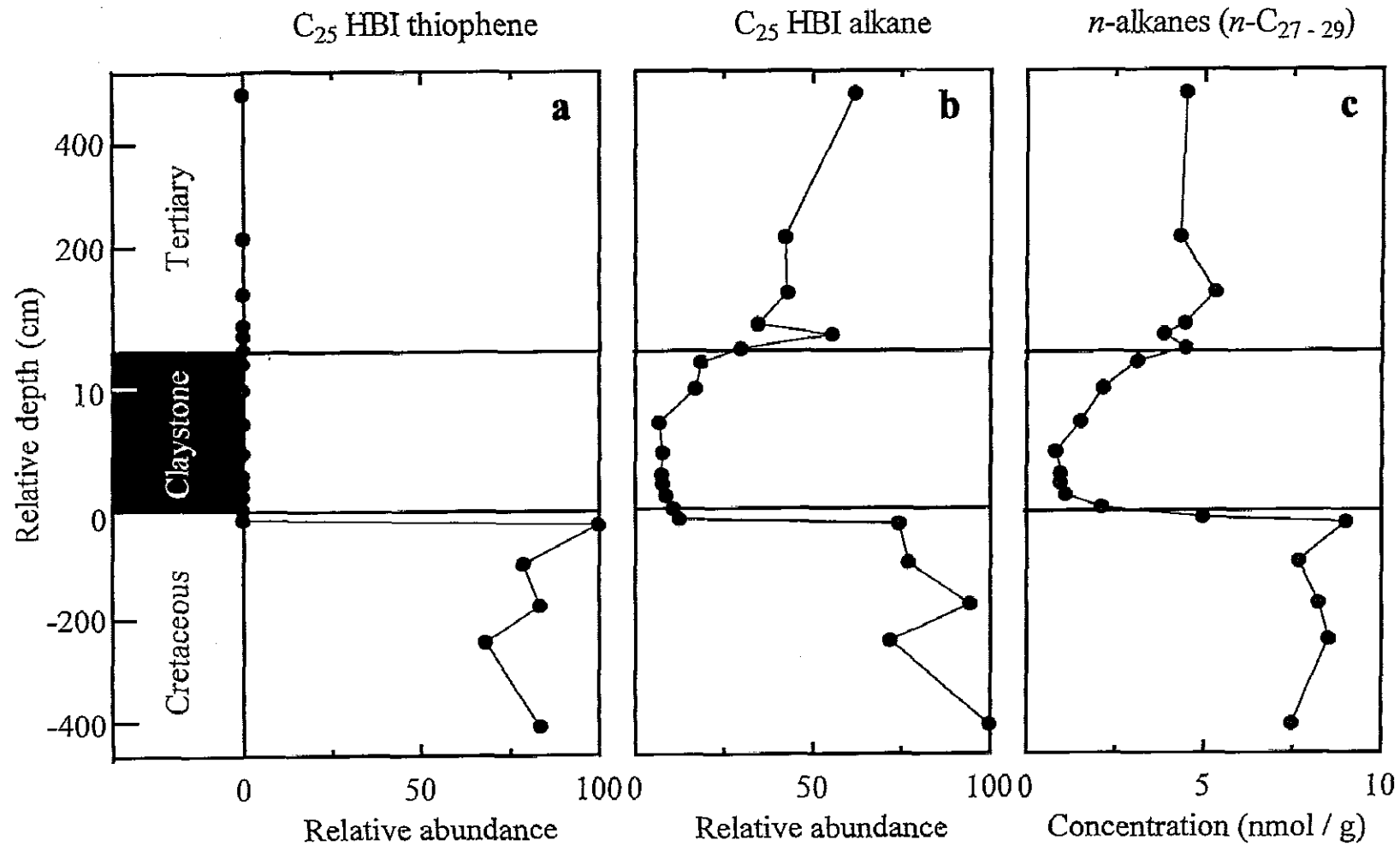


Fig. 3-5. Depth profiles of C_{25} HBI thiophene, C_{25} HBI alkane and n -alkanes (C_{27} to C_{29}) in the K/T boundary sediments at Kawaruppu. The names of the C_{25} HBI thiophene and alkane are in Table 3-1 and the section of C_{25} HBI thiophene in the text, respectively. n -Alkanes data are from Mita and Shimoyama (1999a).

Abundance of the C₂₅ HBI alkane decreased significantly at the lowest horizon in the boundary claystone from those in the sediments below the boundary claystone (Fig. 3-5b). The abundance continued to be small over the lower two third portion (0.8 to 10.6 cm) of the claystone and then gradually increased from the horizon at the upper one third (10.6 cm) of the claystone to the sediments above the boundary claystone. The concentration of the *n*-alkanes also decreased at the lowest horizon in the boundary claystone from those in the sediments below the boundary claystone (Mita and Shimoyama, 1999a). They suggested that smaller concentration of the *n*-alkanes within the boundary claystone was related to smaller inputs of terrestrial organic matter than into the sediments above and below it. It is considered that the C₂₅ HBI alkane is a reduced product from C₂₅ HBI polyenes (Kohnen *et al.*, 1992) derived from non-specific diatoms (Kening *et al.*, 1995). Therefore, the decrease in concentration of the C₂₅ HBI alkane within the boundary claystone also indicates a smaller input of those diatoms into the claystone than the sediments above and below it. These results indicate that abundances of the C₂₅ HBI thiophene and the C₂₅ HBI alkane can be useful parameters to examine the population changes of the specific and non-specific diatoms, respectively, during the deposition.

Polynuclear aromatic thiophenes

Figure 3-6 shows mass fragmentograms for molecular ions of polynuclear aromatic thiophenes in the sediment at the 40 cm horizon. Specific mass numbers of *m/z* 184, 198 and 234 for the polynuclear aromatic thiophenes gave 5 compounds numbered from 2 to 6 in Table 3-1. Their concentrations or relative ones are listed in Table 3-3. The position of a methyl group in C₁-alkylDBTs was determined based on the previous studies (Chakhmakhchev and Suzuki, 1995; Santamaría *et al.*, 1998). Concentrations of C₂-alkylDBTs were at a trace level, and longer alkylDBTs and alkylBNTs were not detected. The depth profiles of the polynuclear aromatic thiophenes over the sediments

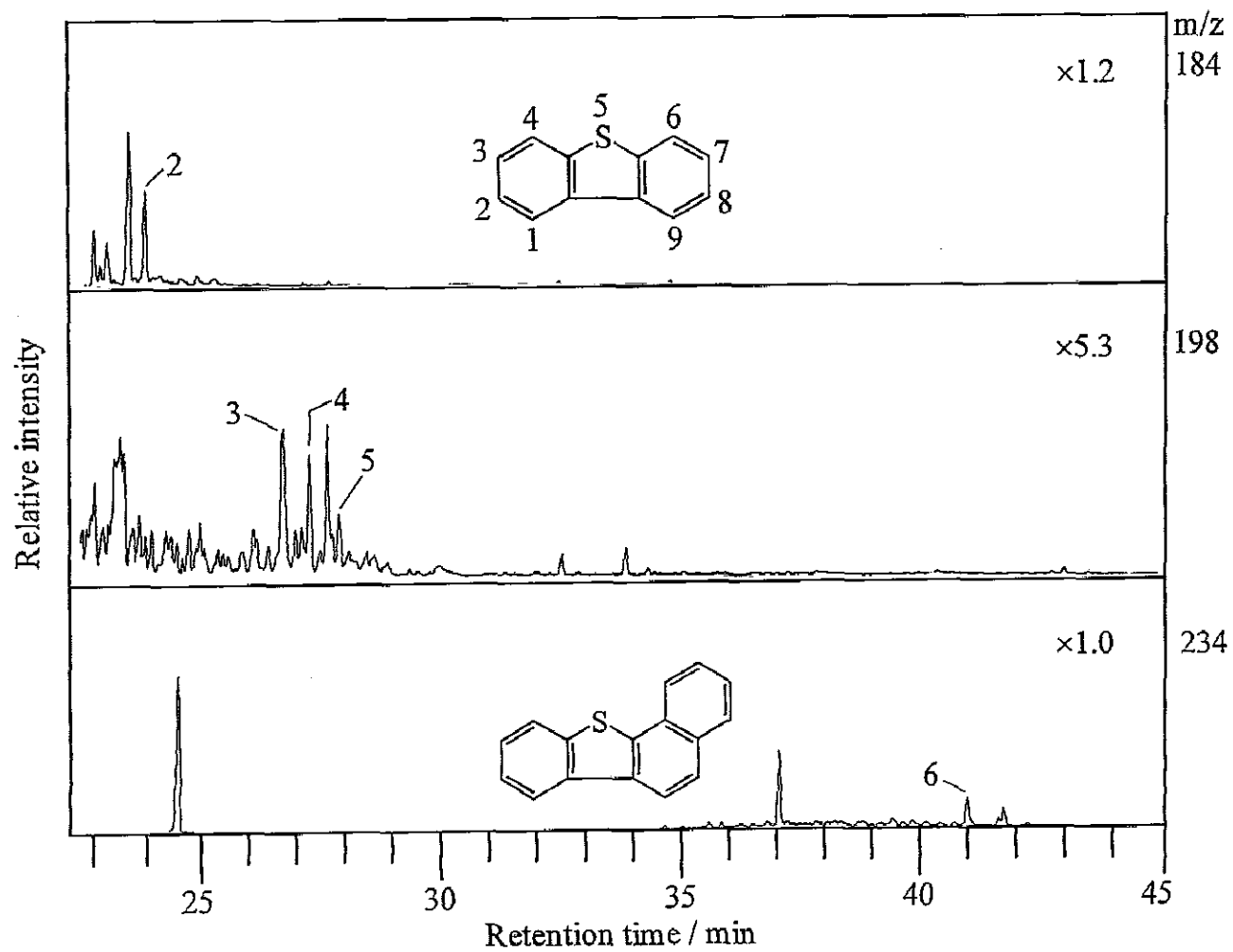


Fig. 3-6. Mass fragmentograms of polynuclear aromatic thiophenes recovered from the sediment at the 40 cm horizon of the K/T boundary sediments at Kawaruppu. The peak numbers correspond those in Table 3-1.

Table 3-3. Concentrations and relative ones of polynuclear aromatic thiophenes in the K/T boundary sediments at Kawaruppu

Relative depth (cm)	Peak No.				
	2	3*	4*	5*	6
	pmol g ⁻¹		pmol g ⁻¹		
495	27	18	10	5	36
225	45	33	15	9	54
120	97	88	46	22	82
60	140	95	39	21	85
40	170	110	64	27	110
13.2	100	100	49	29	93
12.2	84	64	40	18	93
10.6	60	49	34	13	94
7.4	27	17	13	5	63
5.1	28	17	13	4	63
3.4	13	9	7	3	29
2.7	16	12	8	4	52
1.8	29	21	14	5	72
0.8	16	12	6	2	61
0	25	15	10	4	50
-10	18	11	5	2	49
-85	22	16	10	3	68
-165	17	13	9	3	50
-235	12	9	6	2	40
-395	14	11	7	2	36

Peak numbers of compounds correspond those in Table 3-1.

* Relative concentrations of compounds numbered 3 to 5 were determined by the dibenzothiophene standard.

are shown in Fig. 3-7. The mean values in the concentration of DBT and BNT were 41 and 69 within the boundary claystone, 18 and 49 in the sediments below, and 96 and 73 pmol g⁻¹ in those above the boundary claystone, respectively. The depth profile of the DBT as well as BNT showed the maximum abundance at the 40 cm horizon (Fig. 3-7a). Concentrations of DBT at the K/T boundaries at Stevns Klint and Woodside Creek are also at ten-pmol g⁻¹ level or less and the compound was not detected at Gubbio (Venkatesan and Dahl, 1989). However, BNT was not found in the three K/T boundaries.

The DBT concentrations were roughly constant in the sediments below the boundary claystone (Fig. 3-7a). The concentration continued over the lower two third portion (0.8 to 10.6 cm) of the boundary claystone and then sharply increased at the upper one third horizon (10.6 cm) of the boundary claystone. The concentration increase ceased at the 40 cm horizon and sharply decreased in the sediments above the horizon. The depth profiles of the BNT and the methylDBTs (MDBTs) concentrations roughly resemble that of the DBT (Fig 3-7). The depth profiles of these polynuclear aromatic thiophenes are quite different from that of the C₂₅ HBI thiophene and do not show an event related to the massive extinction. Furthermore, the distributions of the polynuclear aromatic thiophenes are not consistent with those of total and individual PAHs (Mita and Shimoyama, 1999b), indicating that the formation pathways of those thiophenes were likely different from those of the PAHs in the sediments. A portion of the PAHs within the boundary claystone is considered to be a combustion origin (Mita and Shimoyama, 1999b).

It has been reported that 4- MDBT is more stable than 1-MDBT during diagenesis, increasing the ratio of 4- to 1-MDBT with increasing temperature (Radke *et al.*, 1986; Chakhmakhchev and Suzuki, 1995). The ratios in the Kawaruppu sediments fall in a range from 4 to 6 (Fig. 3-8). A similar type of results was reported from the Kawaruppu sediments that the ratios of β- to α-alkylated PAHs such as 2- to 1-methylnaphthalene, 2- to 1-methylphenanthrene and 3- to 1-methylphenanthrene were roughly constant over the

sediments (Mita and Shimoyama, 1999b). Therefore, it is likely that the 65 million year diagenesis has taken place evenly over the sediments above, within and below the boundary claystone for the DBTs as well as the PAHs.

As seen in Fig. 3-9, the depth profiles of the polynuclear aromatic thiophene concentrations showed a similar pattern to that of the reported sulfide one (Kajiwara and Kaiho, 1992). It is likely that polynuclear thiophenes were derived from sulfur-containing aromatic moieties of macromolecules and were released from them during diagenesis of sediments (Katsumata and Shimoyama, 2000). Although the concentrations of the polynuclear aromatic thiophenes strongly depend on the degree of diagenesis (Sinninghe Damsté *et al.*, 1989a), the degree is similar over the sediments above, within and below the boundary claystone as seen in Fig. 3-8. The atomic ratios of sulfur in DBT to the sulfur in the K/T boundary and Neogene sediments (Katsumata and Shimoyama, 2000) were in the range of 3.0×10^{-7} to 1.7×10^{-6} and 1.7×10^{-7} to 1.2×10^{-6} , respectively, and showed similar average values (8.6×10^{-7} and 6.6×10^{-7} , respectively) in spite of their difference in place and geological age. Therefore, the concentration of DBT as well as other polynuclear aromatic thiophenes was likely related to that of sulfide which could react with precursor compounds of these thiophenes to form sulfur-containing aromatic moieties in the macromolecules. The sulfide profile indicates that Kawaruppu had been a reducing condition for sediments from the 10.6 to 120 cm horizon and the rests were deposited under an oxidizing condition. The DBT at 60 pmol g^{-1} corresponds a boundary level of reducing (higher) and oxidizing (lower) conditions. However, a sulfur isotopic study (Kajiwara and Kaiho, 1992) suggested a reducing condition for sediments from the 0 to 60 cm horizon. Although the concentration changes of the polynuclear aromatic thiophenes are in accordance with that of the sulfide (Kajiwara and Kaiho, 1992), further studies are necessary to elucidate the polynuclear aromatic thiophene formation and the sulfide concentration.

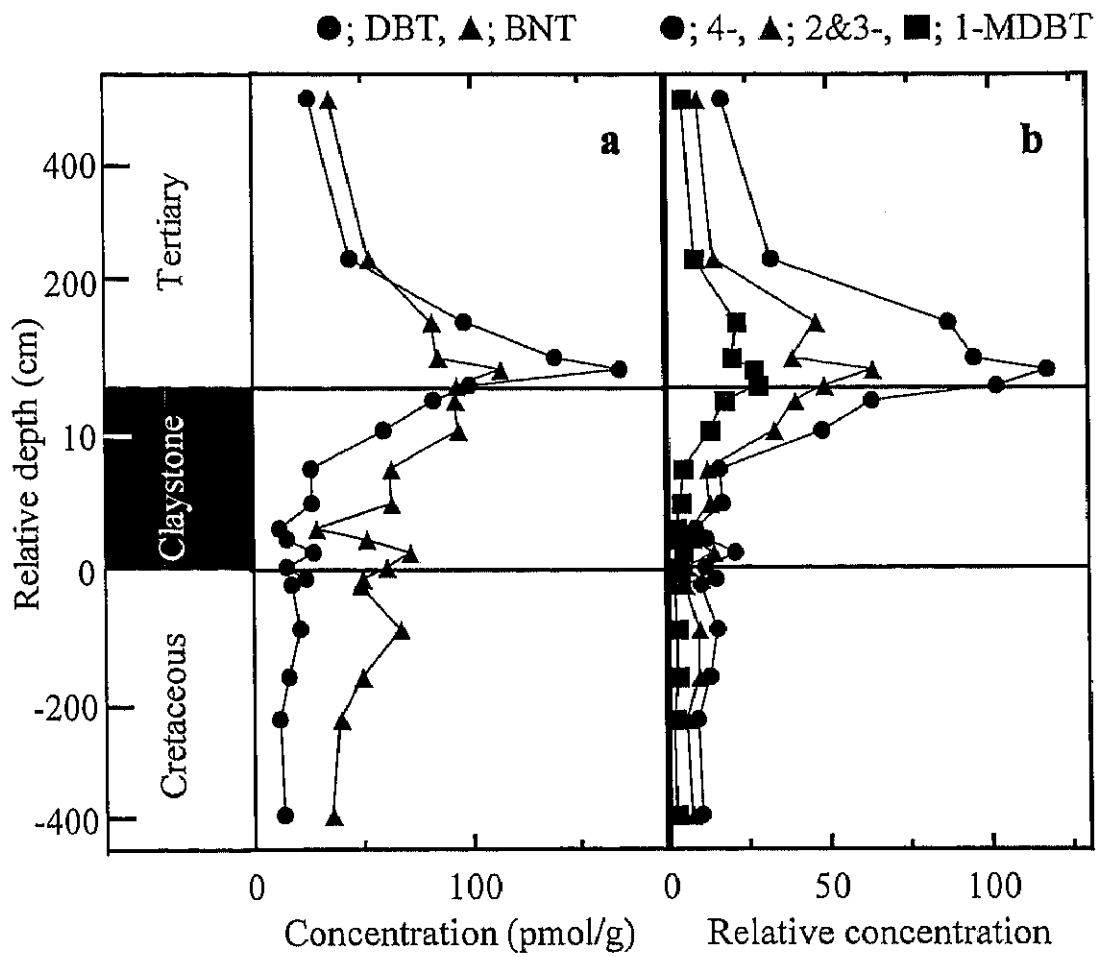


Fig. 3-7. Depth profiles of polynuclear aromatic thiophenes in the K/T boundary sediments at Kawaruppu.

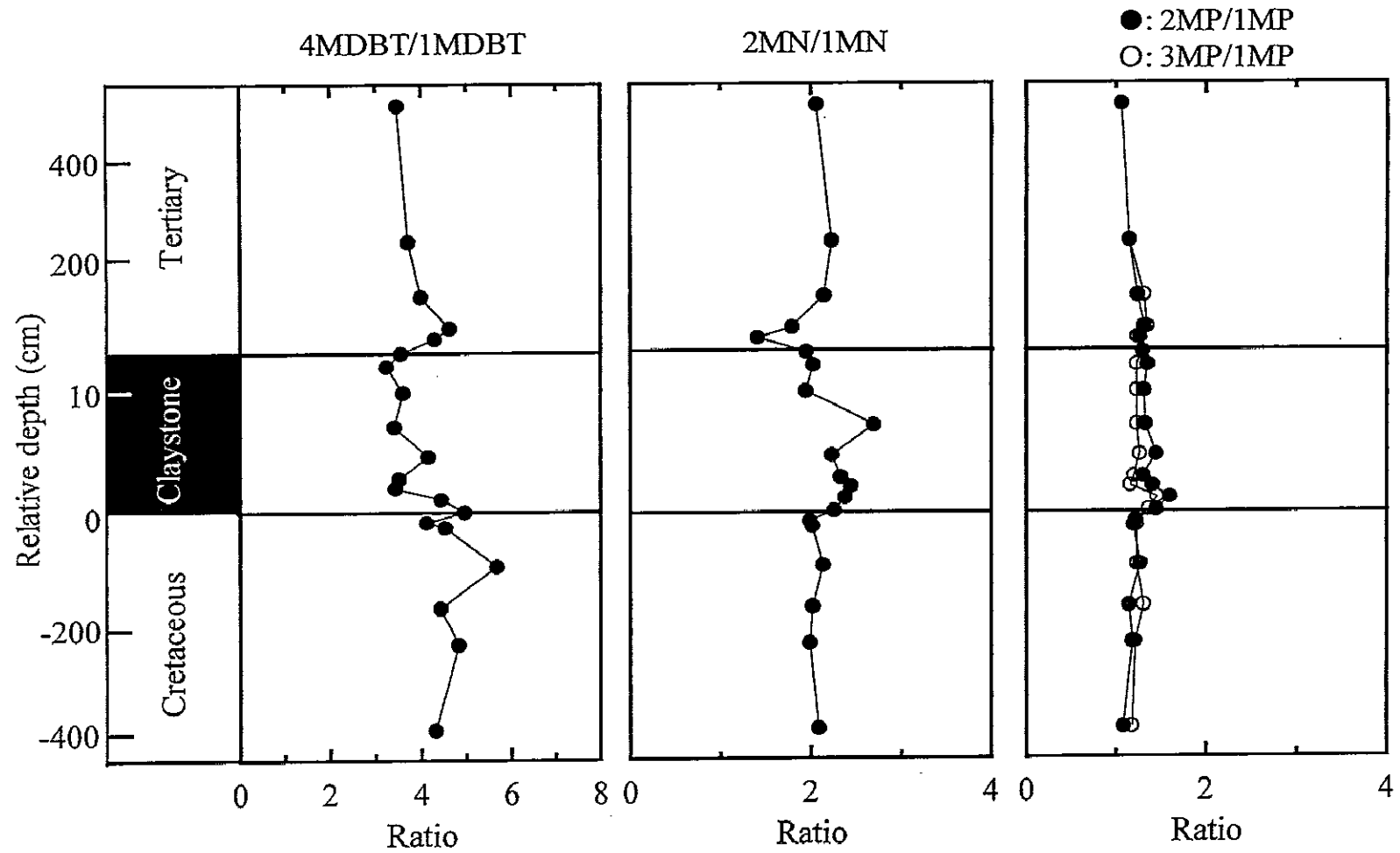


Fig. 3-8. Depth profiles of ratios of β - to α -alkylated dibenzothiophene, naphthalene and phenanthrene for the K/T boundary sediments at Kawaruppu. Methyl naphthalene and methylphenanthrene data are from Mita and Shimoyama (1999b).

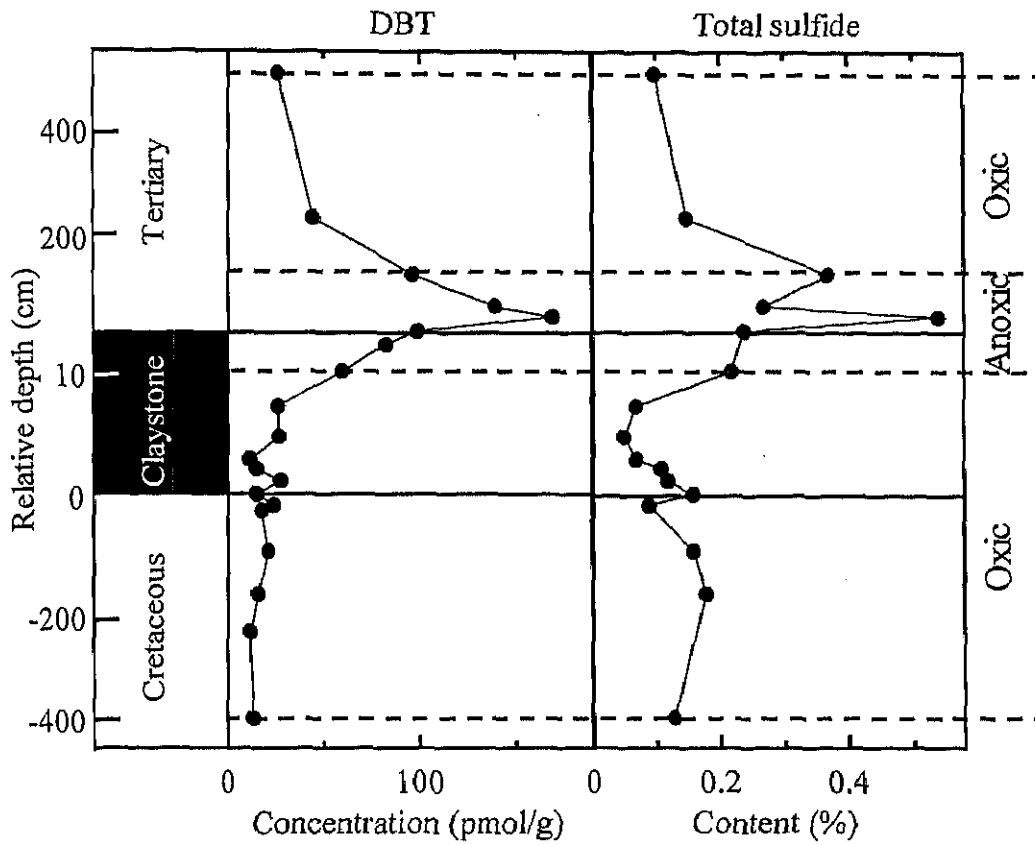


Fig. 3-9. Depth profiles of dibenzothiophene and total sulfide concentrations in the K/T boundary sediments at Kawaruppu. Total sulfide data are from Kajiwara and Kaiho (1992).

CONCLUSIONS

The K/T boundary claystone and the sediments above and below it at Kowaruppu were analyzed for thiophenes. Examination of the result led the following conclusions.

1. Only one kind each for the C₂₅ HBI thiophenes and the C₂₅ HBI alkanes, and five kinds of polynuclear aromatic thiophenes were detected in the sediments. Concentrations of DBT and BNT were at a level of ten to hundred-pmol g⁻¹ (mean value was 50 pmol g⁻¹ for each).
2. The C₂₅ HBI thiophene was found in the sediments below the boundary claystone, and was absent in the claystone and sediments above it. The compound was likely derived from specific diatoms through four kinds of C₂₅HBI alkadienes. If so, the population of the specific diatoms extremely decreased at the end of Cretaceous.
3. The C₂₅ HBI alkane was present in all sediments being less concentrated in the boundary claystone than sediments above and below it. The compound was likely derived from non-specific diatoms. If so, they decreased intensely at the lowest horizon of the boundary claystone. However, those non-specific diatoms started recovering their population around the upper one third horizon of the claystone.
4. The concentrations of the DBT and the BNT were roughly constant over the sediments below the boundary claystone to the lower two third of it. Increase of their concentrations began at the upper one third horizon of the boundary claystone (10.6 cm). The increase ceased at the 40 cm horizon and then changed to decrease in the sediments above the horizon. The depth profiles of the polynuclear aromatic thiophenes were different from that of the C₂₅ HBI thiophene, indicating that the polynuclear aromatic thiophenes had not been related to the biomass extinction event.

5. The ratio of 4- to 1-MDBT is roughly constant over the sediments above, within and below the boundary claystone, indicating that the 65 million year diagenesis had taken place evenly over the K/T sediment horizons.
6. The depth profiles of the polynuclear aromatic thiophene concentrations showed a similar pattern to that of the sulfide one (Kajiwara and Kaiho, 1992). Therefore, the concentrations of these thiophenes were likely related to that of the sulfide. The DBT at 60 pmol g^{-1} corresponds a boundary level of reducing (higher) and oxidizing (lower) conditions for the Kawaruppu K/T sediments.

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