

1 - 3 . 芳香族炭化水素

1 - 3 - 1 . 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 events in earth history. A postulated cause for the extinction is a global fallout of debris and dust due to an impact of an extraterrestrial body or bolide^{6, 7)} or to extensive volcanism^{8, 9)}. Organic geochemical studies on the K/T boundary sediments have found evidence for extraterrestrial organic compounds²⁶⁾ and wild fires triggered by the bolide impact¹⁷⁻²²⁾.

The K/T boundary sediments at Kawaruppu, Hokkaido, Japan, provide a good sedimentary sequence to study the environmental changes at the K/T boundary. The reported PAH analyses in the K/T boundary sediments at Stevns Klint, Denmark, Gubbio, Italy and Woodside Creek, New Zealand dealt with the boundaries and one horizon above and one below it (Venkatesan and Dahl, 1989). The claystone at Kawaruppu is thicker (nearly 14 cm) than those at the other three sites and can be analyzed in detail along the depth. Therefore, PAHs were analyzed in the K/T boundary sediments at Kawaruppu. Results of the total and individual PAH concentrations were described along the depth of the sediments, and the concentrations and ratios in sediments within the boundary claystone were compared with those above and below it. The results are discussed in relation to the wild fires at the K/T boundary time and the diagenesis of the sediments.

1 - 3 - 2 . Experiments

1-3-2-1 . Samples

The K/T boundary sediments occur near Kawaruppu Town, Tokachi District, Hokkaido, and its location and lithology were shown in Fig. 1-1. 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 sediment samples used in this section and their horizons were shown in Section 1-1. A total of 23 sediment samples were analyzed for PAHs. They included 12 samples from different horizons within the boundary claystone (0 - 13.7 cm), 5 samples above (40 - 495 cm) and 6 samples below (-395 - 0 cm) the boundary claystone.

1-3-2-2. Analyses

For each analysis, 1 g of powdered sediment was extracted three times with 5 ml of a mixture of benzene 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 x 10 mm i.d.; Kieselgel-60, Merck). The column was eluted with 10 ml hexane and then 10 ml benzene. PAHs were recovered in the benzene elute. This benzene solution was concentrated to 50 ? l under nitrogen flow for the analysis of individual PAHs.

A GC-MS (Shimadzu GC-MS QP-5000) was used for separation and detection of the PAHs. The GC was equipped with a DB-5ht capillary column (30 m x 0.25 mm i.d.). Oven temperature was programmed to give 60 °C for initial 1 min, from 60 to 100 °C at a rate of 10 °C min⁻¹, from 100 to 130 °C at a rate of 3 °C min⁻¹, and from 130 to 300 °C at a rate of 4 °C min⁻¹. Helium was used as carrier gas with a flow rate of 1.5 ml min⁻¹. The mass spectra were acquired every 0.5 s over m/z 40 to 510 in the electron impact ionization mode and mass fragmentograms every 0.2 s. Identification and quantification were generally made by

comparison of peak retention time and area, respectively, on mass fragmentograms for selected ions with those of standard compounds.

Analytical grade hexane (Wako Pure Chemicals), and twice distilled methanol and benzene were used. All glassware was heated at 500 °C for at least 3 h prior to use in order to eliminate organic contaminants. 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.

1 - 3 - 3 . Results and discussion

1-3-3-1. PAHs and their depth dsistributions

Figure 1-3-1 shows a total ion chromatogram of PAHs recovered from the lowest horizon of the claystone (0 - 0.8 cm). Analysis of a composite chromatogram of specific mass numbers of m/z 128, 142, 154, 156, 166, 178, 192, 202, 216, 228, 252, 276 and 300 for PAHs gave 26 compounds shown in Fig. 1-3-1 and listed in Table 1-3-1. These compounds consist of 13 parent (i.e., non-alkylated) PAHs and 13 alkylated PAHs. Their concentrations were quantified for all the sediment samples and listed in Table 1-3-2. Although concentrations of naphthalene were estimated, they are not listed in Table 1-3-2, because it is likely that this compound has been lost to a certain degree during burial in sediments and analysis in laboratory due to its rather high volatility. Examination of the total ion chromatogram showed another 28 compounds (Fig. 1-3-1). These 28 were identified or assigned by comparisons of mass spectra with the library data of the National Institute of Standards and Technology, USA (1992). They include isomers of alkylated PAHs and are listed in Table 1-3-3.

Depth dsistributions of the total concentrations of the 25 PAHs are shown in Fig. 1-3-2. The dsistribution does not coincide with that of the total organic carbon contents, probably indicating that various classes of organic compounds are present in different proportions with depth of the sediments. The total PAH concentration at each horizon is in the range of 2.3 to 11.4 nmol g^{-1} with average 5.9 nmol g^{-1} . They vary irregularly with depth and do not show a feature of higher concentration in the sediments within the boundary claystone than above and below it. On the other hand, the total PAH concentrations at the K/T boundaries at Gubbio and Woodside Creek are clearly higher than those in the sediments above and below their boundaries (comparative data at Stevns Klint are not available in the reference)¹⁹.

Individual concentrations of parent PAHs are sub- nmol g^{-1} or less (Table 1-3-2) and their depth dsistributions are shown in Fig. 1-3-3. Phenanthrene shows only irregular distribution with depth, so does anthracene in much smaller concentration than phenanthrene. However, unlike the tricyclic PAHs, the concentrations of tetracyclic PAHs, fluoranthene, pyrene, 2,3-benzofluorene and chrysene (probably with a small portion of triphenylene) show higher concentrations in sediments within the boundary claystone, particularly over the lower two thirds of the claystone, than above and below it. Somewhat similar dsistributions to those of the tetracyclic PAHs are observed in sediments within the boundary claystone for larger PAHs than the tetracyclic ones, such as benzo[*a*]pyrene, perylene, benzo[*g,h,i*]perylene and coronene. However, concentrations of perylene, benzo[*g,h,i*]perylene and coronene are not significantly different with those in sediments above and below the claystone.

Relative abundances of parent PAHs and their C_1 (methyl) and C_2 (dimethyl and/or ethyl) alkylated PAHs were estimated separately for a group of tricyclic ones; phenanthrene, anthracene and their alkylated ones, and for that of tetracyclic ones; pyrene, fluoranthene and their alkylated ones using their relative peak areas on mass fragmentograms for selected ions. Depth dsistributions of these abundances in percentage are shown in Fig. 1-3-4. It seems that the depth dsistributions of the parent tricyclic PAHs and their C_1 and C_2 alkylated ones are

roughly constant. However, in case of the tetracyclic PAHs, the percentage of parent PAHs drastically increases from 23 to 46% at the base of the boundary claystone, and those of the C₁ and C₂ alkylated ones decrease accordingly. The increased percentage of the parent PAHs gradually decreases from there upwards.

1-3-3-2. Effect of diagenesis

The various PAHs found in the K/T sediments at Kawaruppu have experienced 65 million years of diagenesis. It is generally understood that β -alkylated PAHs are more stable than α -alkylated ones during diagenesis, increasing ratios of β - to α -alkylated PAHs with increasing temperature and/or time due to chemical rearrangement of alkyl groups from α - to β -positions of parent PAH structures^{49, 50}). In Fig. 1-3-5 are shown the depth distributions of the ratios of β - to α -isomers of bicyclic and tricyclic PAHs in the Kawaruppu K/T sediments using the values listed in Table 1-3-2. The ratios of 2-methylnaphthalene (2MN) to 1-methylnaphthalene (1MN) are mostly around 2 over the sediments above, within and below the boundary claystone, showing a predominance of the β -isomer over the α -one. Similarly, the β - to α -isomer ratios of dimethylnaphthalenes, such as 2,6- + 2,7-dimethylnaphthalenes to 1,5-dimethylnaphthalene, and 2,6- + 2,7-dimethylnaphthalenes to 1,5- + 1,8-dimethylnaphthalenes are around 5 to 6 and their depth distributions are nearly in parallel each other over the whole sediment horizons. Thus, these dimethylnaphthalene isomers exhibit also a predominance of β - over α - isomers. Monomethylphenanthrene isomers also show a predominance of β - over α - isomers. The ratios of 2-methyl- to 1-methylphenanthrene and 3-methyl- to 1-methylphenanthrene fall within a narrow range of 1.0 to 1.5 and show very similar depth distributions to each other over the whole sediment horizons.

A characteristic feature of these mono- and dimethyl PAHs is that their ratios of β - to α -isomers are roughly constant individually over the sediments above, within and below the boundary claystone, although the ratios are different from each other. Peri-condensed PAHs are chemically more stable than linear-condensed PAHs during sediment diagenesis⁵¹). The higher concentrations of phenanthrene over anthracene and pyrene over chrysene are clearly observed for all of the K/T sediments at Kawaruppu (Table 1-3-2). This finding probably relates to their relative stabilities during diagenesis, although a possibility that their precursor compounds might have been present in different concentrations can not be excluded. It is likely that the 65 million year diagenesis has taken place evenly over sediments above, within, and below the claystone as far as the parent PAHs, and those β - and α -isomers are concerned.

1-3-3-3. PAHs and wild fires

The predominance of parent PAHs over their alkylated ones in soils and recent sediments was attributed to a result of wild fires^{52, 53}). PAHs of combustion origin were characterized by parent PAHs, particularly highly peri-condensed compounds, and their dominant presence over alkylated ones was related to Jurassic vegetation fires⁵¹). An unusually high occurrence of β -aminoisobutyric acid and isovaline in sediments around the K/T boundary at Stevns Klint was attributed to a bolide²⁶). Enrichments of soot and charcoal^{17, 18}), PAHs¹⁹), and fullerenes^{21, 22}) in the K/T boundary sediments have been suggested as results of the global wild fires triggered by the bolide impact. Clear dominances of fluoranthene and pyrene over their alkylated ones in the K/T boundaries at Stevns Klint, Gubbio and Woodside Creek, and a similar type of predominances for phenanthrene and

anthracene at Woodside Creek and Gubbio (but not at Stevns Klint) were observed¹⁹). However, the highly peri-condensed compounds, such as pyrene, benzo[*a*]pyrene, benzo[*g,h,i*]perylene and coronene were failed to find at Woodside Creek. From these findings, Venkatesan and Dahl concluded that the dominance of parent PAHs at the three locations is an organic geochemical evidence for the global fires at the time of the K/T boundary¹⁹).

Some findings which might relate to the wild fires are the following. Fluoranthene, pyrene, 2,3-benzofluorene, chrysene and benzo[*a*]pyrene are more abundant over the lower two thirds of the boundary claystone than above and below it (Fig. 1-3-3). The relative abundances of parent PAHs among the tetracyclic PAHs increases drastically at the base of the boundary claystone and decreases gradually from there upwards (Fig. 1-3-4). The enrichment of these PAHs is likely due to their input of at the time of deposition and can not be explained by organic diagenesis and/or an effect of the claystone (discussed previously). On the other hand, following results do not support the wild fires at the end of Cretaceous. Perylene, benzo[*g,h,i*]perylene and coronene which are known to be strong indicators of combustion origin^{51, 53}) are also present in the sediments above and below the boundary claystone as similar concentrations with in the claystone. The relative abundance of parent PAHs among the tricyclic PAHs are roughly constant. Therefore, no clear evidence of wild fires is found by the present study of PAHs in the sediments above, within, and below the K/T boundary claystone at Kawaruppu.

It was failed to find evidence of extraterrestrial amino acids and dicarboxylic acids in the K/T boundary sediments at Kawaruppu. One of the plausible explanations for their absence is the longer distance between Kawaruppu and the impact crater, possibly the Chicxulub crater, Mexico^{14, 15}) than between Stevns Klint and the crater. If so, the influence of the impact might have been smaller at Kawaruppu than Stevns Klint. Likewise, it is possible that the wild fires occurring around Kawaruppu were not intense enough to deliver PAHs of characteristic combustion origin to the Kawaruppu sediments. A similar possibility was discussed for the absence of peri-condensed PAHs at Woodside Creek¹⁹).

1 - 3 - 4 . Conclusions

Twenty-six PAHs consisting of 13 parent and 13 alkylated ones were found in the sediments above, within and below the K/T boundary claystone at Kawaruppu, and their concentrations (except for naphthalene) were estimated. In addition, another 28 PAHs were identified or assigned. Characteristics of these compounds and their concentrations in the K/T sediments are as follows.

6. The total PAH concentrations varied from 2.3 to 11.4 nmol g⁻¹ (average of 5.9 nmol g⁻¹) and their depth dsistribution was not different in the boundary claystone compared to sediments above and below it.
7. Individual PAH concentrations were sub-nmol g⁻¹ or less. Of these, the parent tetracyclic PAHs and, to a certain extent, tetracyclic peri-condensed parent PAHs and benzo[*a*]pyrene were more abundant over the lower two thirds of the boundary claystone than above and below it.
8. The percentage of parent PAHs among the tetracyclic PAHs increased drastically at the base of the boundary claystone and decreased gradually from there upwards.
9. Mono- and dimethyl PAHs showed ? - to ? -isomer ratios roughly constant individually over the sediments above, within, and below the boundary claystone.

10. Higher concentrations of phenanthrene than anthracene and pyrene than chrysene were clearly observed for all of the sediments.

The findings 2 and 3 are not likely due to the 65 million year diagenesis at Kawaruppu because of 4 and 5, and may indicate global wild fires at the K/T boundary time as reported for the K/T boundaries at Stevns Klint, Gubbio and Woodside Creek. However, the evidence of the wild fires at Kawaruppu in this study is not so strong as those at the other three sites. Twenty-three sediment samples were analyzed over the K/T boundary for Kawaruppu against only a few for the other three sites.

Table 1-3-1. Polycyclic aromatic hydrocarbons in the K/T boundary sediments at Kawaruppu, and their abbreviations and mass numbers (m/z) for quantification.

Compound	Abbreviation	Mass number (m/z)
naphthalene	NAP	128
2-methylnaphthalene	2MN	142
1-methylnaphthalene	1MN	142
2,6- and 2,7-dimethylnaphthalene*	2,6&2,7DMN	156
1,3-dimethylnaphthalene	1,3DMN	156
1,6-dimethylnaphthalene	1,6DMN	156
1,4- and 2,3-dimethylnaphthalene*	1,4&2,3DMN	156
1,5-dimethylnaphthalene	1,5DMN	156
1,2-dimethylnaphthalene	1,2DMN	156
1,8-dimethylnaphthalene	1,8DMN	156
acenaphthene	ACN	154
fluorene	FLU	166
phenanthrene	PHN	178
anthracene	ANT	178
3-methylphenanthrene	3MP	192
2-methylphenanthrene	2MP	192
4- and 9-methylphenanthrene	4&9MP	192
1-methylphenanthrene	1MP	192
fluoranthene	FLA	202
pyrene	PYR	202
2,3-benzofluorene	BFLU	216
chrysene and triphenylene**	CHR	228
benzo[a]pyrene	BAP	252
perylene	PER	252
benzo[g,h,i]perylene	BPER	276
coronene	COR	300

Compounds are identified and quantified by standard compounds.

* Compound peaks overlap each other and probably both compounds are present.

** Compound peaks overlap each other and probably triphenylene is in minor.

Table 1-3-2. Concentrations of polycyclic aromatic hydrocarbons in the K/T boundary sediments at Kavaruppu.

Relative depth / cm	Concentration / pmol g ⁻¹										
	2MN	1MN	2,6&2,7DMN	1,3DMN	1,6DMN	1,4&2,3DMN	1,5DMN	1,2DMN	1,8DMN	ACN	FLU
495	1800	870	710	720	540	470	120	210	14	6	38
225	850	380	290	290	150	200	48	93	6	1	31
120	1400	650	870	820	610	530	140	240	19	18	88
60	180	100	220	250	170	170	51	79	9	22	55
40	170	120	230	250	180	170	52	75	9	16	48
12.7 - 13.7	490	250	280	330	240	190	60	90	5	4	22
11.7 - 12.7	610	300	380	380	290	210	70	98	6	9	31
10.6 - 11.7	170	87	140	140	110	87	29	39	2	2	16
8.7 - 10.6	300	130	180	180	130	110	33	51	15	3	17
7.5 - 8.7	870	370	410	390	300	220	64	100	6	7	22
6.3 - 7.5	1000	370	370	350	260	200	58	97	4	9	33
5.5 - 6.3	87	47	140	140	110	97	26	49	0	5	33
4.3 - 5.5	150	67	90	82	63	53	14	24	7	0	6
2.8 - 4.3	630	270	310	300	210	170	36	62	4	10	31
1.8 - 2.8	930	380	460	410	310	240	69	110	6	11	34
0.8 - 1.8	310	130	210	210	150	120	33	60	4	4	24
0 - 0.8	340	150	200	210	160	130	35	64	3	11	30
-3 - 0	1600	800	790	740	550	470	120	210	16	12	74
-10	810	400	360	390	270	250	62	120	6	10	47
-85	900	420	380	400	290	240	63	110	6	5	19
-165	690	340	290	310	230	210	49	97	5	6	38
-235	2600	1300	1100	1100	810	680	160	300	19	15	93
-395	650	310	310	310	230	220	47	97	6	6	28

Abbreviations of compounds are in Table 1-3-1.

Table 1-3-2. (continued)

Relative depth / cm	Concentration / pmol g ⁻¹													
	PHN	ANT	3MP	2MP	4&9MP	1MP	FLA	PYR	BFLU	CHR	BAP	PER	BPER	COR
495	870	54	310	310	320	290	150	230	190	140	50	230	220	120
225	470	33	220	220	230	190	100	160	170	120	48	240	210	200
120	890	48	370	350	340	280	150	250	210	190	65	140	230	100
60	840	57	380	370	330	280	130	220	230	140	52	310	230	160
40	870	57	360	370	310	290	120	210	180	120	44	190	150	86
12.7 - 13.7	650	32	300	300	260	230	160	230	160	130	50	110	120	62
11.7 - 12.7	790	110	310	340	270	250	200	280	170	130	37	82	86	30
10.6 - 11.7	560	33	310	330	270	250	210	320	200	160	79	86	110	55
8.7 - 10.6	430	36	230	240	190	180	170	280	150	140	65	52	84	20
7.5 - 8.7	1000	72	450	460	320	320	390	610	350	290	130	160	230	58
6.3 - 7.5	480	47	260	280	210	210	260	400	200	200	91	46	82	27
5.5 - 6.3	610	30	270	290	210	220	310	500	230	290	170	65	220	69
4.3 - 5.5	220	22	140	160	110	110	150	270	120	150	100	37	120	50
2.8 - 4.3	730	56	350	380	260	290	360	550	250	250	90	72	170	34
1.8 - 2.8	850	69	340	410	240	290	320	500	200	230	130	52	140	38
0.8 - 1.8	760	59	410	450	290	280	360	570	290	250	88	98	250	84
0 - 0.8	520	46	330	350	270	240	250	430	230	200	160	69	160	87
-3 - 0	820	60	320	320	310	260	120	200	180	120	56	130	160	48
-10	790	42	360	350	310	290	120	190	160	130	52	130	150	130
-85	760	40	360	370	320	290	130	220	210	130	64	260	220	990
-165	440	29	250	220	210	190	80	130	130	110	44	110	150	62
-235	880	51	380	370	370	310	130	200	190	160	47	50	84	45
-395	470	31	250	230	230	210	92	140	140	120	54	91	160	110

Table 1-3-3. Polycyclic aromatic hydrocarbons in the K/T boundary sediments at Kawaruppu and their major mass numbers (m/z).

Peak number	Compound	Major mass numbers (m/z)
1	ethylnaphthlene isomers	141 , 156
2	methylbiphenyl isomers	168 , 152
3	dibenzofurne	168 , 139
4	C ₃ -naphthalene isomers	170 , 155
5	C ₂ -biphenyl isomers	182 , 167
6	methyldibenzofurane isomers	182 , 152
7	C ₄ -naphthalene isomers	169 , 184
8	methylfluorene isomers	165 , 180
9	C ₂ -fluorene isomers	179 , 194
10	carbazole	167 , 139
11	methylcarbazole isomers	181 , 152
12	phthalate	149 , 204
13	C ₂ -phenanthrene isomers	206 , 191
14	benzonaphtofurane isomers	218 , 189
15	methylpyrene isomers	216 , 189
16	C ₂ -pyrene isomers	230 , 215
17	chrysene isomers	228
18	benzocarbazole isomers	217
19	benzocarbazole isomers	217
20	methylchrysene isomers	242 , 226
21	binaphthylene isomers	254 , 126
22	benzofluorancene isomers	252
23	benzofluorancene isomers	252
24	methylbenzopyrene isomers	266 , 239
25	benzoperyrene isomers	276
26	dibenzoanthracene isomers	278
27	phenylterphenyl	306 , 289
28	dibenzopyrene isomers	302 , 150

Compounds are identified or assigned by the mass spectra database of NIST, USA.

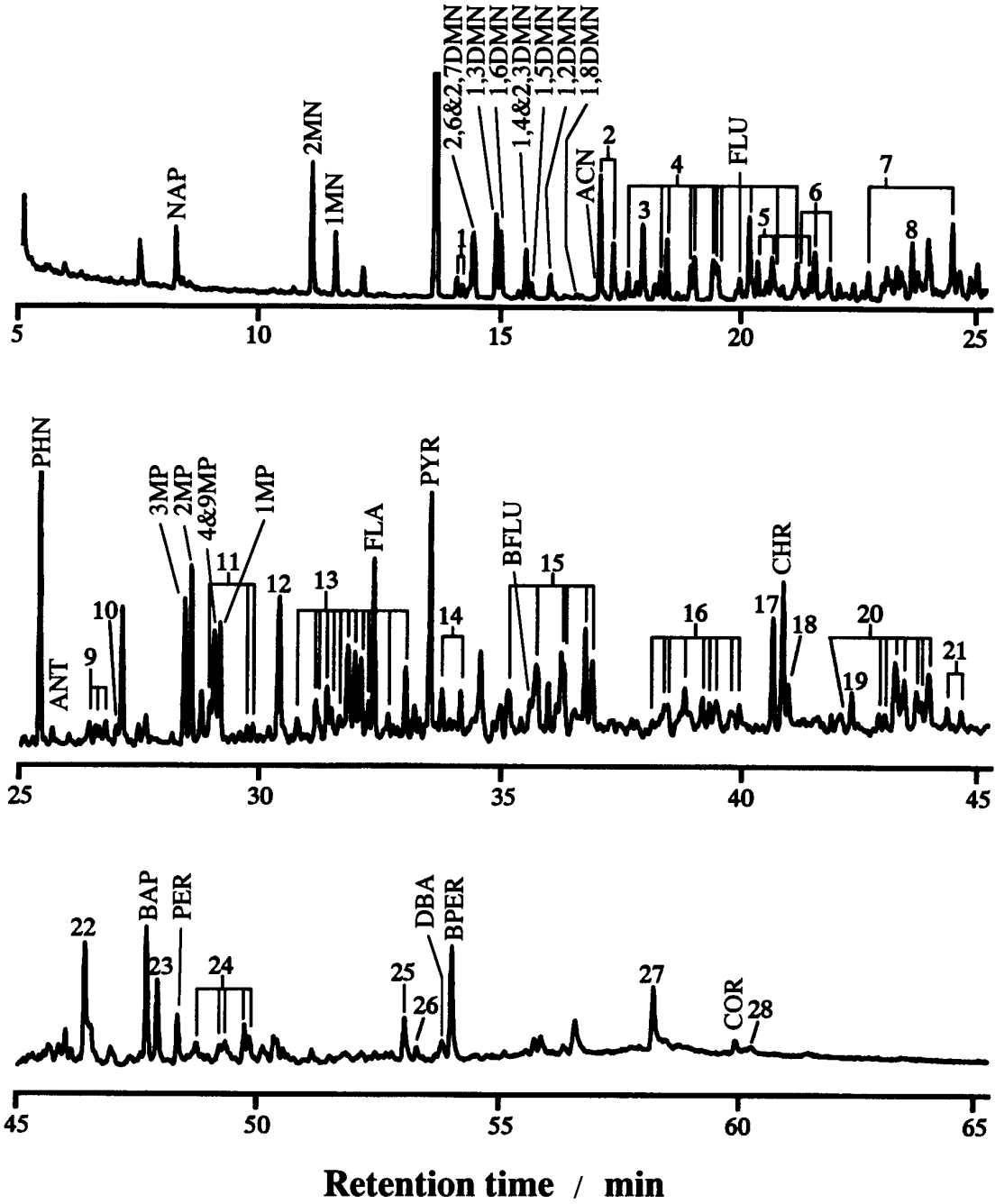


Fig. 1-3-1. Total ion chromatogram of polycyclic aromatic hydrocarbons recovered from the lowest horizon (0 to 0.8 cm) of the K/T boundary claystone at Kawaruppu. Abbreviation correspond those compounds listed in Table 1-3-1. Numbers for peaks correspond to those in Table 1-3-3.

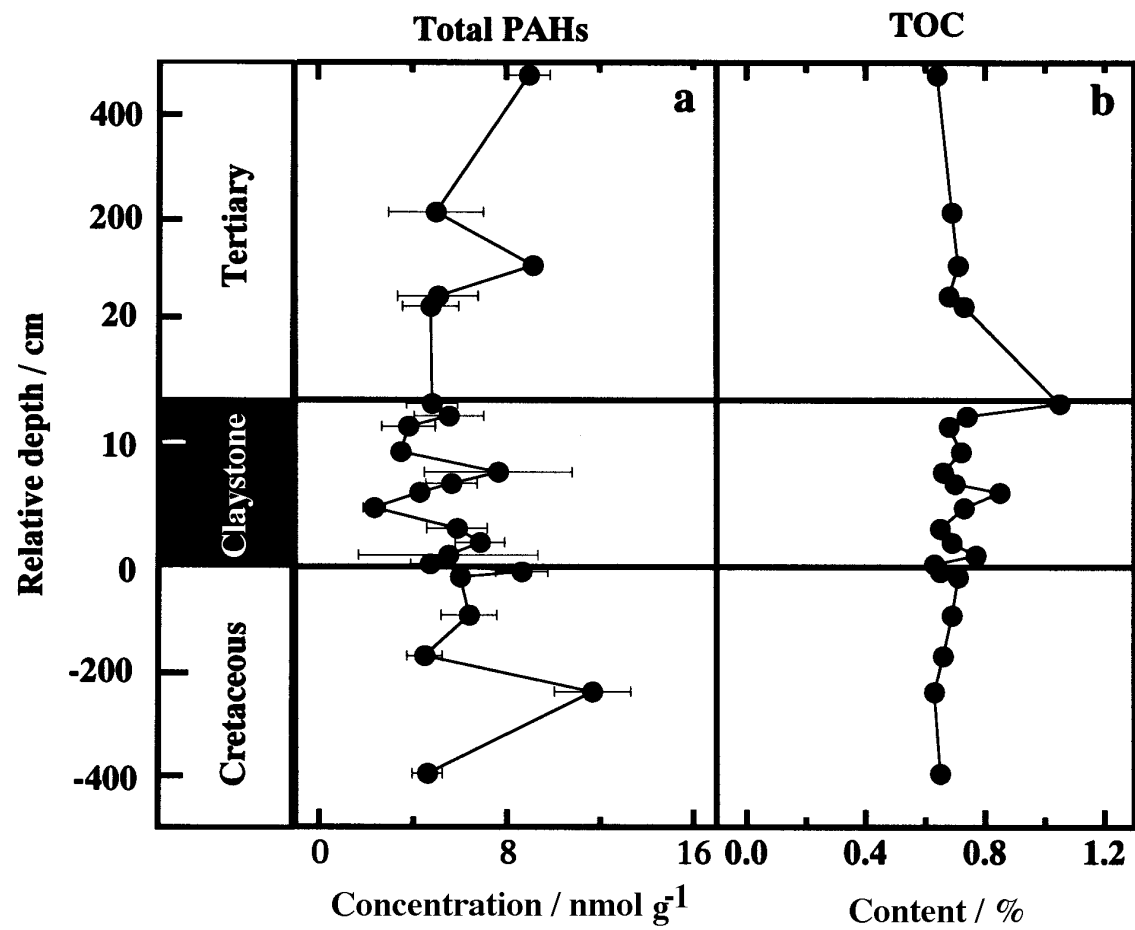


Fig. 1-3-2. Depth distributions of the total polycyclic aromatic hydrocarbon (PAH) concentrations and total organic carbon contents (TOC) in the K/T boundary sediments at Kwaruppu.

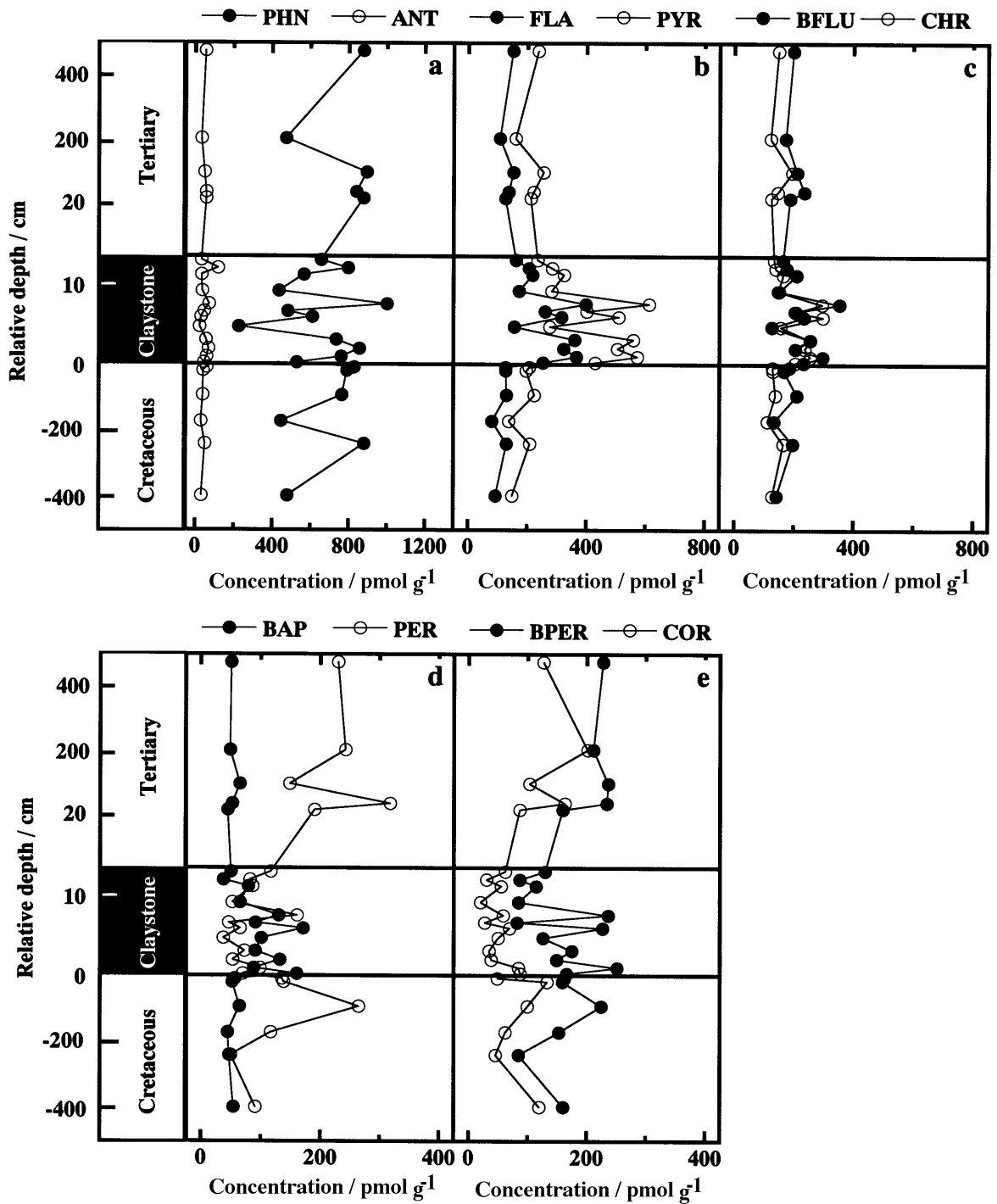


Fig. 1-3-3. Depth distributions of the individual polycyclic aromatic hydrocarbon concentrations in the K/T boundary sediments at Kawaruppu. Abbreviations correspond to those compounds in Table 1-3-1.

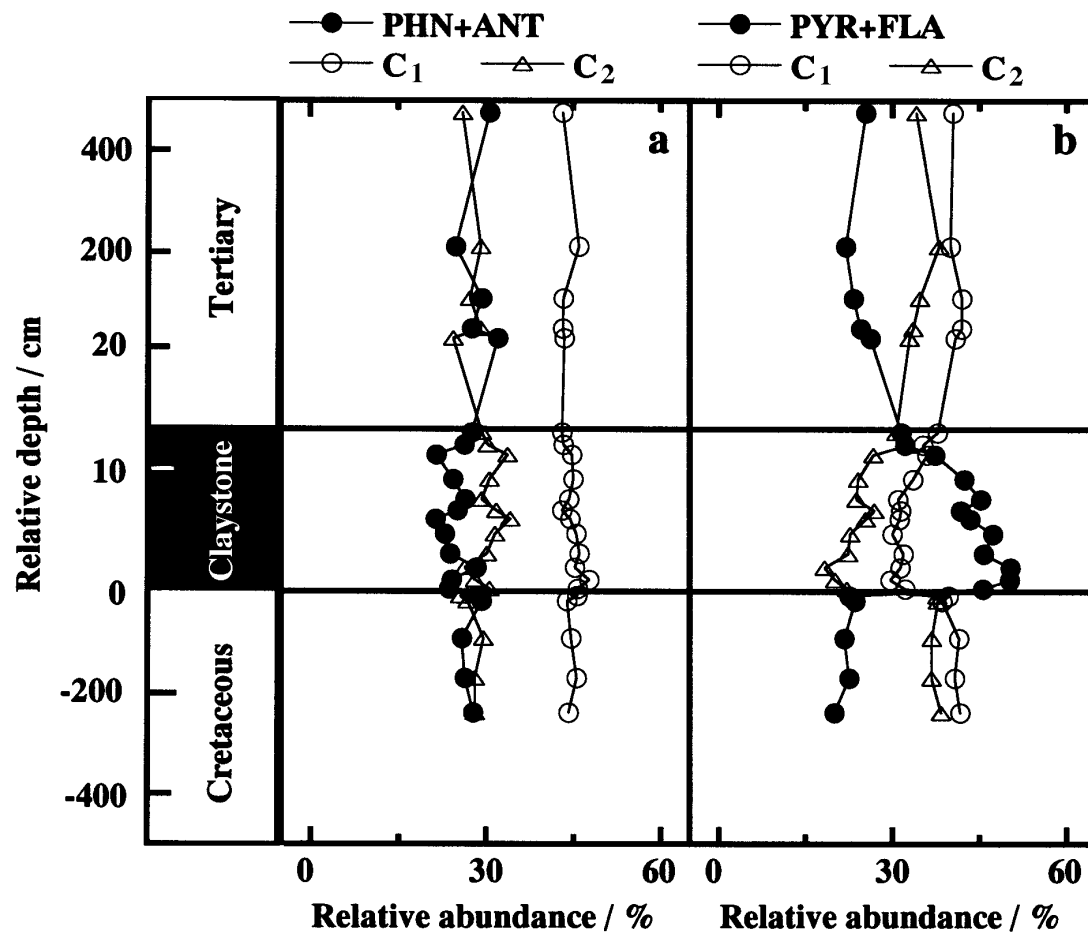


Fig. 1-3-4. Depth distributions of parent and their alkylated polycyclic aromatic hydrocarbons in the K/T boundary sediments at Kawaruppu. Abbreviations correspond to those compounds in Table 1-3-1.

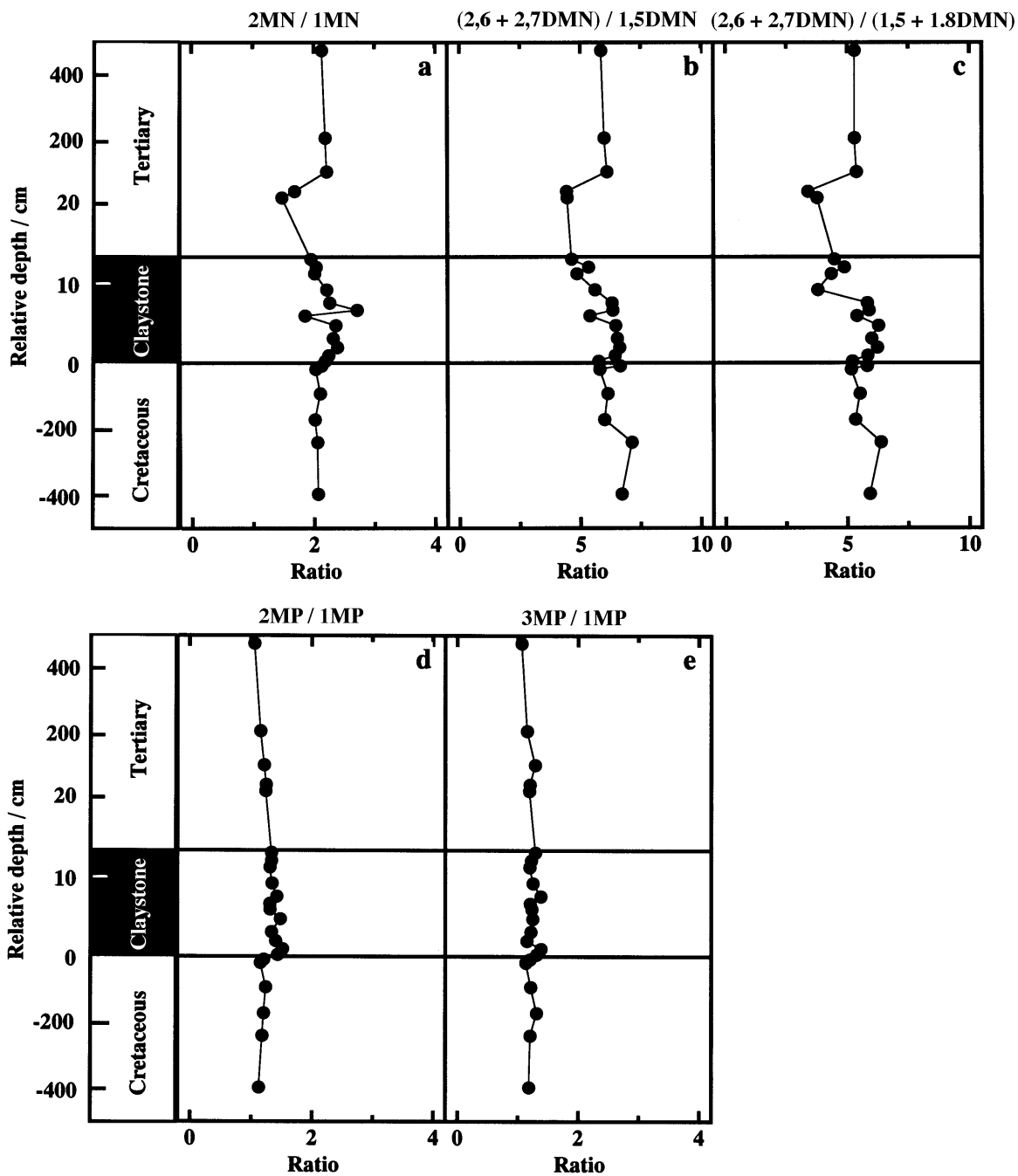


Fig. 1-3-5. Depth distributions of ratios of β - to α -alkylated naphthalene and phenanthrene in the K/T boundary sediments at Kawaruppu. Abbreviations correspond to those compounds in Table 1-3-1.