１－２．n-アルカン、プリスタンおよびファイタン

１－２－１．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 biological events in earth history. A global fallout of debris and dust due to the impact of an extraterrestrial body or bolide6, 7) or to extensive volcanism8, 9) is thought to be the cause of the extinction. Organic geochemical studies on the K/T boundary sediments aimed to find evidence for extraterrestrial organic compounds26) and wild fires triggered by the bolide impact17-22).

Studies of biological organic compounds in the K/T boundary sediments provide useful information on the massive extinction, because they are derived from then-living organisms. However, there are few studies of this kind. Those published to date report traces of microbial hydrocarbons and fatty acids in the K/T boundary claystone and microbial fatty acids and additional terrestrial resin acids in the sediments above and below the claystone at Stevns Klint27-29).

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 boundary claystone is similar in appearance to the well-known “boundary claystone” of the classical K/T boundary in Europe, but is thicker (nearly 14 cm) and can be studied in detail along the depth. Published studies of these sediments dealt with planktonic foraminifera31, 38), palynomorphs30), sulfur isotopes40), Ir accumulation and clay minerals41). In this section, *n*-alkanes, pristane and phytane were analyzed in the sediments above, within, and below the boundary claystone, compared the concentrations, ratios and molecular distributions of those aliphatic hydrocarbons, and related their characteristics to the environmental changes of the K/T boundary sediments at Kawaruppu.

１－２－２．Experiments

1-2-2-1.　Samples

The K/T boundary sediments occur near Kawaruppu Town, Tokachi District, Hokkaido30, 31). The location of Kawaruppu, the lithology and sample horizons of the sediments were described in Section 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. Twelve sediment samples from different horizons within the boundary claystone (0 to 13.7 cm), 5 samples above (40 to 495 cm) and 6 samples below (-395 to 0 cm) the boundary claystone were analyzed for aliphatic hydrocarbons.

1-2-2-2. Analyses

Each rock sample was pulverized in a stainless steel mortar with a pestle. 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.; Keiselgel-60, Merck). Aliphatic hydrocarbons were obtained by eluting with hexane (10 ml). This hexane solution was concentrated to 50 μl under nitrogen flow for the analysis of individual aliphatic hydrocarbons.

A gas chromatograph (GC) combined with a mass spectrometer (MS) (Shimadzu GC-MS QP-5000) was used for separation and detection of the aliphatic hydrocarbons. The GC was equipped with a DB-5ht capillary column (30 m x 0.25 mm i.d.). The oven temperature was programmed to hold at 50 °C for initial 1 min, and then ramp from 50 to 90 °C at a rate of 5 °C min^{-1}, and from 90 to 300 °C at a rate of 4 °C min^{-1}. Helium was used as the 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 of *n*-alkanes, pristane and phytane were generally made by comparison of peak retention times and areas, respectively, on mass fragmentograms for selected ions with those of standard compounds. These compounds used were even carbon numbered *n*-alkanes in the range of C_{12} to C_{24}, and C_{28}, C_{32} and C_{36} besides pristane and phytane.

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.

Total organic carbon contents are determined by an ordinary elemental analysis of carbon, i.e., 850 °C under O_2, with an aliquot of each pulverized sample (ca. 10 mg) by a CHN analyzer (Perkin Elmer, N241-0011).

１－２－３． Results and discussion

1-2-3-1. Concentrations

The total organic carbon contents of the pulverized samples ranged from 0.57 to 1.05 wt% with majority at 0.6 or 0.7 wt% level (Table 1-2-1). They were rather randomly distributed in the rock sequence and showed no enrichment in the boundary claystone.

Normal alkanes ranging from C_{12} to C_{36}, pristane and phytane were identified. For example, the mass fragmentogram (m/z 57) of these aliphatic hydrocarbons in the sediment at the middle horizon (5.5 to 6.3 cm) of the boundary claystone is shown in Fig. 1-2-1. Concentrations of these aliphatic hydrocarbons are listed in Table 1-2-2. The total concentrations of *n*-alkanes within the boundary claystone (0 to 13.7 cm) were in the ranges of 4.7 to 18.2 nmol g^{-1} with the mean value of 8.7 nmol g^{-1}, in the ranges of 14.0 to 17.6 (mean value 16.5) nmol g^{-1} in the sediments above (40 to 495 cm) and 16.4 to 26.5 (mean value 21.7) nmol g^{-1} in those below (-395 to 0 cm) the boundary claystone. The concentrations of pristane plus phytane within the boundary claystone were in the ranges of 0.24 to 1.6 (mean value 0.59) nmol g^{-1}, in the ranges of 1.8 to 3.1 (mean value 2.6) nmol g^{-1} in the sediments above and 2.1 to 3.1 (mean value 2.7) nmol g^{-1} below the boundary claystone. Concentrations of the total *n*-alkanes and pristane plus phytane at each sample horizon are shown in Fig. 1-2-2, together with the total organic carbon contents.

Total concentration of *n*-alkanes decreased significantly at the lowest horizon in the boundary claystone from those in the sediments below the boundary claystone. The decreased concentration of *n*-alkanes continued over the lower two-thirds portion (0 to 10.6 cm) of the boundary claystone and then sharply increased in the upper one-third (10.6 - 13.7 cm) of the claystone. The concentration increase ceased at the top of the boundary claystone, and remained rather constant in the sediments above the claystone. Total concentrations of *n*-alkanes in the sediments above the boundary claystone were about two thirds of those in the sediments below the claystone; therefore, the recovery of the *n*-alkane input to the sediments above did not come back to the input level to the sediments below the claystone. The depth distribution pattern of pristane plus phytane content roughly resembles that of the *n*-alkanes. These two patterns do not coincide with that of total organic carbon contents, showing that the aliphatic hydrocarbons were rather depleted relative to total C within the boundary claystone.

1-2-3-2. Molecular distribution patterns and CPI of n-alkanes

Molecular distribution patterns of *n*-alkanes are shown in Fig. 1-2-3. Concentrations of *n*-alkanes (C_{12} to C_{36}) in most of the sediments within the boundary claystone were roughly similar to each other. In the sediments above and below the boundary claystone, longer chain *n*-alkanes ($> C_{25}$) were more abundant than shorter ones ($< C_{25}$). Lower concentrations of total *n*-alkanes in the sediments within the boundary claystone than above and below it were mainly due to lower concentrations of the longer chain *n*-alkanes.

The concentrations of shorter chain *n*-alkanes (from *n*-C_{15} to *n*-C_{19}) and longer chain *n*-alkanes (from *n*-C_{27} to *n*-C_{31}) are shown in Fig. 1-2-4. The mean value of the shorter chain *n*-alkanes within the boundary claystone was 2.4 nmol g^{-1}, two thirds of the values in the sediments above and below (mean values 3.6 and 3.5 nmol g^{-1}, respectively) the boundary claystone. These values are not so different considering the sources (marine or terrestrial) of the shorter chain *n*-alkanes. The source throughout the K/T sediments was likely marine organisms as discussed in the carbon preference index (CPI) section below. On the other hand, the mean value of the longer chain *n*-alkanes within the boundary claystone was 1.7 nmol g^{-1}, one third of that in the sediments above it (mean value 4.6 nmol g^{-1}) and one fifth of that in the sediments below it (mean value 7.8 nmol g^{-1}). It has been reported that the longer chain *n*-alkanes are major components of terrestrial vascular plant-wax44-46). Therefore, the substantially smaller concentrations of the longer chain *n*-alkanes within the boundary claystone were probably related to smaller inputs of terrestrial organic matter than into the sediments above and below it.

CPIs of the shorter chain *n*-alkanes (from *n*-C_{15} to *n*-C_{19}) were approximately one throughout all the sample horizons at Kawaruppu (Fig. 1-2-5a,b); therefore the major source of those *n*-alkanes was likely marine algae. It was reported that shorter chain *n*-alkanes (from *n*-C_{14} to *n*-C_{20}) with no odd or even carbon number preference were derived from marine algae even when a strong odd carbon number preference of longer chain ones (> *n*-C_{24}) was observed47). CPIs of the longer chain *n*-alkanes (from *n*-C_{27} to *n*-C_{31}) in the sediments below, within and above the claystone were approximately 2.3, 1.7 and 2.1, respectively. The values 2.3 and 2.1 are not significantly different and indicate that no major diagenetic effect to the *n*-alkanes in the sediments below the boundary claystone occurred during the deposition of the claystone. The CPI decrease at the bottom of the claystone was likely due to a small input of terrestrial organic matter.

1-2-3-3. Pristane to phytane ratios

Pristane to phytane (Pr/Ph) ratios were in the range of 2.5 to 3.5 (mean value 3.0) throughout all the sample horizons (Fig. 1-2-5c). The ratios indicate that the Kawaruppu sediments were deposited under an oxic environment, assuming that the Pr/Ph ratio can be used as an indicator of redox potential in sedimentary environment. The higher Pr/Ph ratio (> 1) indicates oxic conditions48). However, the sulfur isotopic record in the K/T boundary sediments at Kawaruppu showed anoxic conditions for sediments from 0 to 60 cm40). On the other hand, a foraminifera study suggested that oxygenic conditions at Kawaruppu were relatively high for the sediments below the -300 cm horizon and above the boundary claystone, low in the sediments between -300 and -10 cm, and medium for the rest of sediments including the boundary claystone[38]. Therefore, it is not appropriate to judge whether oxic or anoxic conditions prevailed in the sedimentary environment at Kawaruppu based on the present information.

1-2-3-4. Implications for the biomass extinction event

An eustatic sea-level drop at the end of the Cretaceous[33, 37], was observed at Kawaruppu by the study of foraminifera[38]. Sediments at -0.5 m accumulated in the lower part of the upper-bathyal zone (depth : 300 - 600 m). Sea bottom shallowing started at -0.5 m and stopped at 0.4 m. Sediments at 0.4 m accumulated in the upper part of the upper-bathyal zone (depth : 150 to 300 m). The shallowing suggests that rather higher concentrations of longer *n*-alkanes could have been found in the sediments above the -0.5 m horizon than in the sediments below the -0.5 m horizon. However, the concentrations of longer *n*-alkanes within the boundary claystone were lower than expected. Therefore, the lower concentrations might have been caused by the devastation of vascular plants at the time the K/T boundary claystone was deposited. Palynological study also suggested the devastation of vascular plants at the K/T boundary time at Kawaruppu[30], similar to the situation in the interior of western North America[39].

Estimated accumulation rates from paleomagnetic study were 1.5 cm kyr^{-1} and 0.9 cm kyr^{-1} in the sediments above and below the boundary claystone, respectively[40]. Rather more rapid sedimentation of the boundary claystone than of the sediments above and below it was proposed from concentrations of benthic foraminifera[30]. Therefore, the duration of a low input of terrestrial *n*-alkanes to the boundary claystone (0 to 10.6 cm) was 7,000 years at most. On the same basis, it took about 2,000 years (10.6 to 13.7 cm) for the recovery of the *n*-alkane input to the level found in the sediments above the boundary claystone. The input recovery time of the longer *n*-alkanes was much shorter than the period of the sulfur isotope anomaly (ca. 70,000 years)[40] and the period of the shallowing (ca. 70,000 years)[38]. It is apparent that the *n*-alkane record in those sediments shows a more rapid response to the environmental change, which took place at the end of the Cretaceous.

１－２－４． Conclusions

Analysis of aliphatic hydrocarbons in the K/T boundary claystone and the sediments above and below it at Kawaruppu found *n*-alkanes (C_{12} to C_{36}), pristane and phytane. Examination of their characteristics led the following conclusions:

1. Concentrations of the individual compounds were mostly at the level of sub-nmol g^{-1} except for longer chain *n*-alkanes (C_{21} to C_{31}) in the sediments above and below the boundary claystone which were present in amounts up to 2.9 nmol g^{-1}.
2. Total concentrations of the *n*-alkanes within the claystone were one third to one half of those in sediments above and below it. These smaller concentrations were mainly due to lower concentrations of the longer *n*-alkanes within the boundary claystone than in the sediments above and below it.
3. CPIs of shorter chain *n*-alkanes (C_{15} to C_{19}) and longer chain *n*-alkanes (C_{25} to C_{31}) suggested that they originated in marine algae and terrestrial plants, respectively.
4. Depth distribution of the total concentrations of *n*-alkanes and their molecular distributions suggest a much smaller input from terrestrial plants to the boundary claystone than to the sediments above and below it.

5. A large concentration decrease of the longer chain *n*-alkanes at the K/T boundary was likely due to a rapid devastation of terrestrial plants, a part of the large biomass extinction at the time. The *n*-alkane concentration change within the boundary claystone indicates the period of the devastation to be ca. 7,000 years at most and the recovery period to the normal level in lower Tertiary to be ca. 2,000 years.

Table 2-1-1. Total organic carbon contents in the K/T boundary sediments at Kawaruppu.

Relative depth / cm	Total organic carbon contents / %
495	0.64
225	0.69
120	0.71
60	0.68
40	0.73
12.7 - 13.7	1.05
11.7 - 12.7	0.74
11.0 - 11.7	0.68
10.6 - 11.7	0.57
8.7 - 10.6	0.72
7.5 - 8.7	0.66
6.3 - 7.5	0.7
5.5 - 6.3	0.85
4.3 - 5.5	0.73
2.8 - 4.3	0.65
1.8 - 2.8	0.69
0.8 - 1.8	0.77
0.0 - 0.8	0.63
-3.0 - 0.0	0.65
-10	0.71
-85	0.69
-165	0.66
-235	0.63
-395	0.65

Table 1-2-2. Concentrations of *n*-alkanes, pristane and phytane in the K/T boundary sediments at Kawaruppu.

Carbon number of *n*-alkane or compound name	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Relative depth / cm	Concentration / nmol g^{-1}													
495	0.29	0.38	0.40	0.65	0.79	0.78	0.77	1.0	0.92	1.0	0.93	1.0	0.83	1.0
225	0.34	0.37	0.41	0.65	0.78	0.85	0.79	0.92	0.86	0.99	0.92	1.1	0.93	1.1
120	0.26	0.32	0.42	0.52	0.68	0.50	0.73	0.85	0.78	0.89	0.80	0.97	0.80	1.0
60	0.23	0.26	0.36	0.49	0.73	0.81	0.84	0.98	0.86	1.0	0.88	1.0	0.86	1.1
40	0.35	0.34	0.36	0.36	0.56	0.45	0.63	0.67	0.68	0.76	0.70	0.88	0.74	1.0
12.7 - 13.7	0.42	0.51	0.62	0.69	0.84	0.91	0.96	1.0	0.91	1.0	0.95	1.0	0.94	1.0
11.7 - 12.7	0.52	0.59	0.67	0.67	0.71	0.65	0.80	0.85	0.80	0.83	0.78	0.80	0.69	0.79
10.6 - 11.7	0.43	0.44	0.46	0.47	0.53	0.63	0.68	0.68	0.62	0.63	0.58	0.62	0.54	0.62
8.7 - 10.6	0.15	0.16	0.17	0.18	0.20	0.23	0.27	0.30	0.29	0.29	0.26	0.26	0.22	0.24
7.5 - 8.7	0.23	0.23	0.27	0.31	0.37	0.39	0.43	0.47	0.42	0.46	0.43	0.46	0.41	0.46
6.3 - 7.5	0.29	0.28	0.30	0.33	0.40	0.31	0.47	0.49	0.45	0.43	0.38	0.36	0.31	0.32
5.5 - 6.3	0.026	0.032	0.088	0.17	0.22	0.26	0.31	0.34	0.33	0.35	0.36	0.36	0.29	0.30
4.3 - 5.5	0.36	0.34	0.31	0.31	0.32	0.33	0.34	0.37	0.35	0.34	0.31	0.31	0.27	0.28
2.8 - 4.3	0.32	0.28	0.28	0.31	0.38	0.28	0.43	0.44	0.41	0.41	0.38	0.38	0.31	0.33
1.8 - 2.8	0.32	0.28	0.27	0.27	0.30	0.31	0.31	0.34	0.33	0.35	0.33	0.34	0.30	0.33
0.8 - 1.8	0.43	0.39	0.38	0.44	0.53	0.55	0.54	0.55	0.51	0.50	0.44	0.43	0.36	0.39
0.0 - 0.8	0.39	0.35	0.36	0.41	0.51	0.60	0.67	0.71	0.66	0.71	0.67	0.38	0.55	0.60
-3 - 0	0.24	0.27	0.36	0.52	0.67	0.52	0.74	0.86	0.78	0.88	0.80	0.97	0.80	1.0
-10	0.18	0.18	0.21	0.31	0.45	0.60	0.70	0.90	0.86	1.2	1.0	1.4	1.2	1.8
-85	0.59	0.28	0.56	0.58	0.75	0.60	0.77	0.94	0.88	1.1	0.98	1.2	1.0	1.4
-165	0.87	0.87	0.91	1.0	0.90	0.92	0.92	1.0	1.0	1.2	1.1	1.5	1.2	1.8
-235	0.36	0.30	0.32	0.44	0.52	0.29	0.55	0.65	0.62	0.83	0.75	1.0	0.8	1.3
-395	0.43	0.39	0.42	0.56	0.61	0.70	0.74	0.93	0.90	1.1	1.0	1.3	1.1	1.6

Table 1-2-2. continued.

Carbon number of *n*-alkane or compound name	26	27	28	29	30	31	32	33	34	35	36	pristane	phytane
Relative depth / cm	Concentration / nmol g^{-1}												
495	0.77	1.2	0.74	1.5	0.34	0.71	0.16	0.21	0.10	0.084	0.035	2.2	0.65
225	0.85	1.2	0.70	1.3	0.39	0.74	0.20	0.27	0.32	0.29	0.031	2.1	0.56
120	0.82	1.4	0.95	1.5	0.49	1.0	0.30	0.34	0.13	0.18	0.091	1.8	0.57
60	0.80	1.3	0.76	1.3	0.38	0.73	0.19	0.27	0.10	0.12	0.039	2.3	0.74
40	0.72	1.1	0.67	1.1	0.34	0.67	0.18	0.23	0.99	0.11	0.032	1.3	0.42
12.7 - 13.7	0.91	1.2	0.83	1.2	0.49	0.76	0.26	0.27	0.11	0.091	0.024	1.2	0.37
11.7 - 12.7	0.65	0.90	0.62	0.95	0.27	0.41	0.11	0.096	0.036	0.038	0.017	0.83	0.28
10.6 - 11.7	0.50	0.65	0.40	0.62	0.22	0.30	0.11	0.10	0.076	0.045	0.023	0.67	0.23
8.7 - 10.6	0.19	0.25	0.16	0.22	0.089	0.12	0.049	0.046	0.020	0.023	0.016	0.24	0.091
7.5 - 8.7	0.38	0.47	0.31	0.42	0.15	0.19	0.067	0.058	0.012	0.005	0.003	0.30	0.098
6.3 - 7.5	0.25	0.28	0.19	0.25	0.081	0.10	0.042	0.034	0.019	0.012	0.004	0.28	0.092
5.5 - 6.3	0.23	0.27	0.17	0.22	0.078	0.093	0.033	0.029	0.012	0.009	0.011	0.17	0.068
4.3 - 5.5	0.22	0.27	0.17	0.22	0.084	0.10	0.044	0.038	0.019	0.014	0.004	0.21	0.076
2.8 - 4.3	0.26	0.33	0.19	0.29	0.076	0.10	0.036	0.031	0.018	0.013	0.001	0.36	0.12
1.8 - 2.8	0.25	0.34	0.20	0.27	0.075	0.096	0.041	0.031	0.015	0.007	0.002	0.25	0.073
0.8 - 1.8	0.30	0.37	0.22	0.30	0.10	0.13	0.057	0.044	0.024	0.018	0.010	0.48	0.14
0.0 - 0.8	0.46	0.62	0.37	0.63	0.20	0.32	0.097	0.10	0.024	0.024	0.010	0.48	0.18
-3 - 0	0.83	1.3	0.86	1.5	0.41	0.92	0.22	0.28	0.27	0.10	0.035	1.7	0.52
-10	1.3	2.3	1.3	2.9	0.83	1.7	0.40	0.57	0.19	0.28	0.079	1.8	0.78
-85	1.0	1.9	1.1	2.5	0.68	1.5	0.32	0.45	0.098	0.11	0.025	2.2	0.82
-165	1.3	2.2	1.2	2.6	0.75	1.5	0.32	0.48	0.17	0.21	0.058	2.2	0.84
-235	1.0	2.0	1.2	2.8	0.73	1.8	0.37	0.55	0.11	0.13	0.036	1.5	0.56
-395	1.1	1.9	1.1	2.4	0.70	1.4	0.33	0.48	0.19	0.27	0.071	2.2	0.83

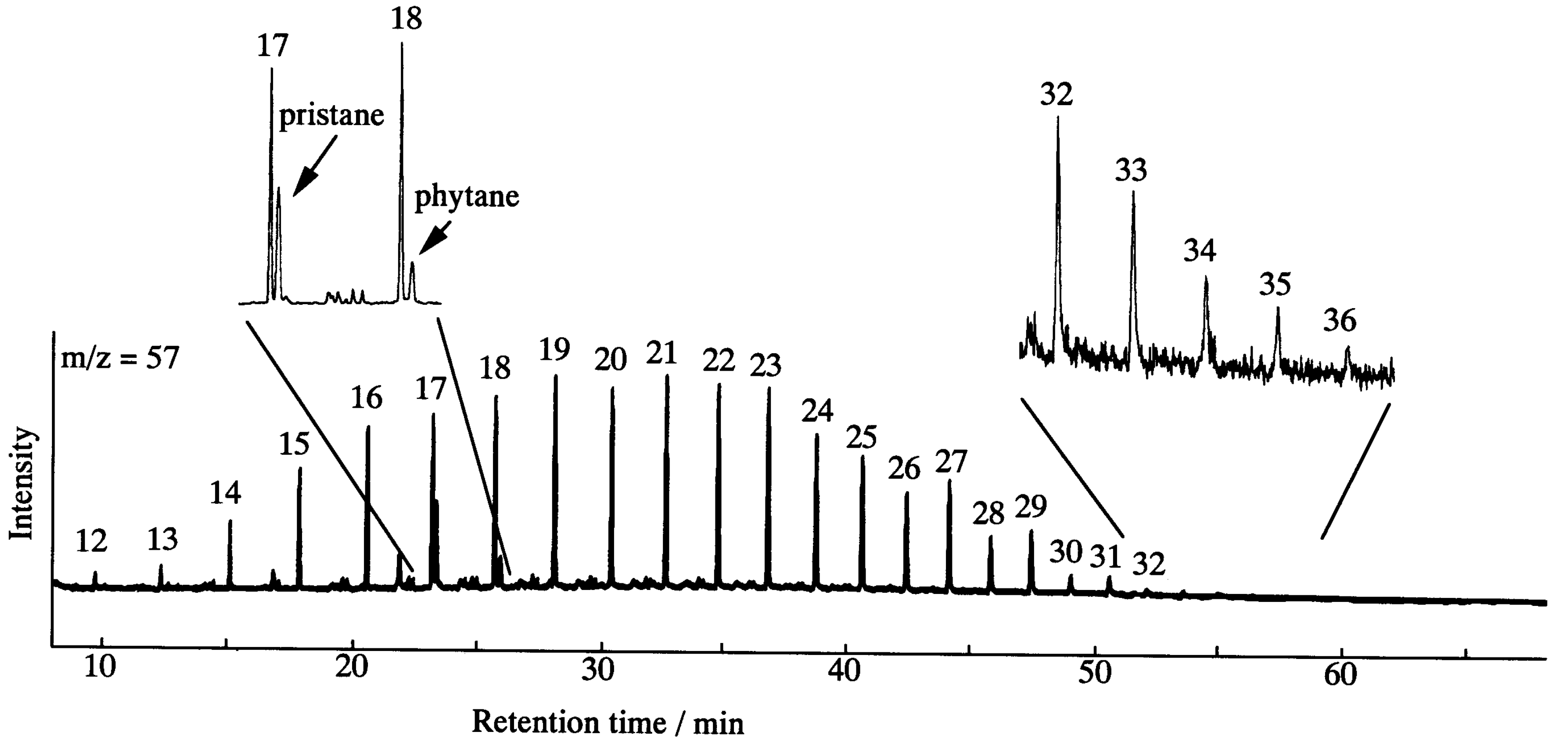

Fig. 1-2-1. Mass fragmentogram (m/z 57) of *n*-alkanes, pristane and phytane in the K/T boundary claystone (5.5 to 6.3 cm). Peak numbers correspond to those of the carbon number of the *n*-alkanes.

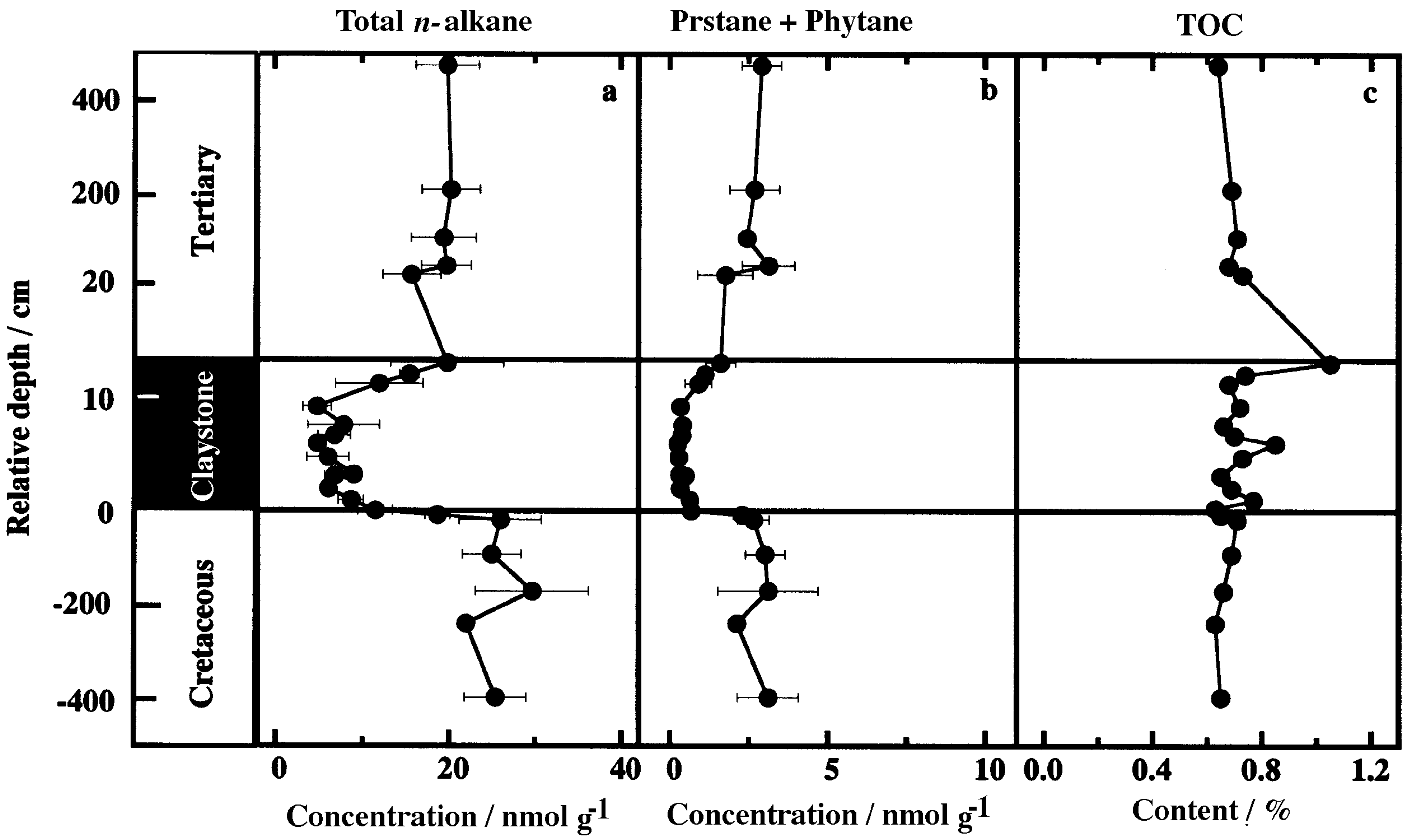

Fig. 1-2-2. Depth distributions of a: total concentrations of *n*-alkanes (C_{12} to C_{36}), b: concentrations of pristane plus phytane, and c: total organic carbon contents (TOC) in the K/T boundary sediments at Kawaruppu.

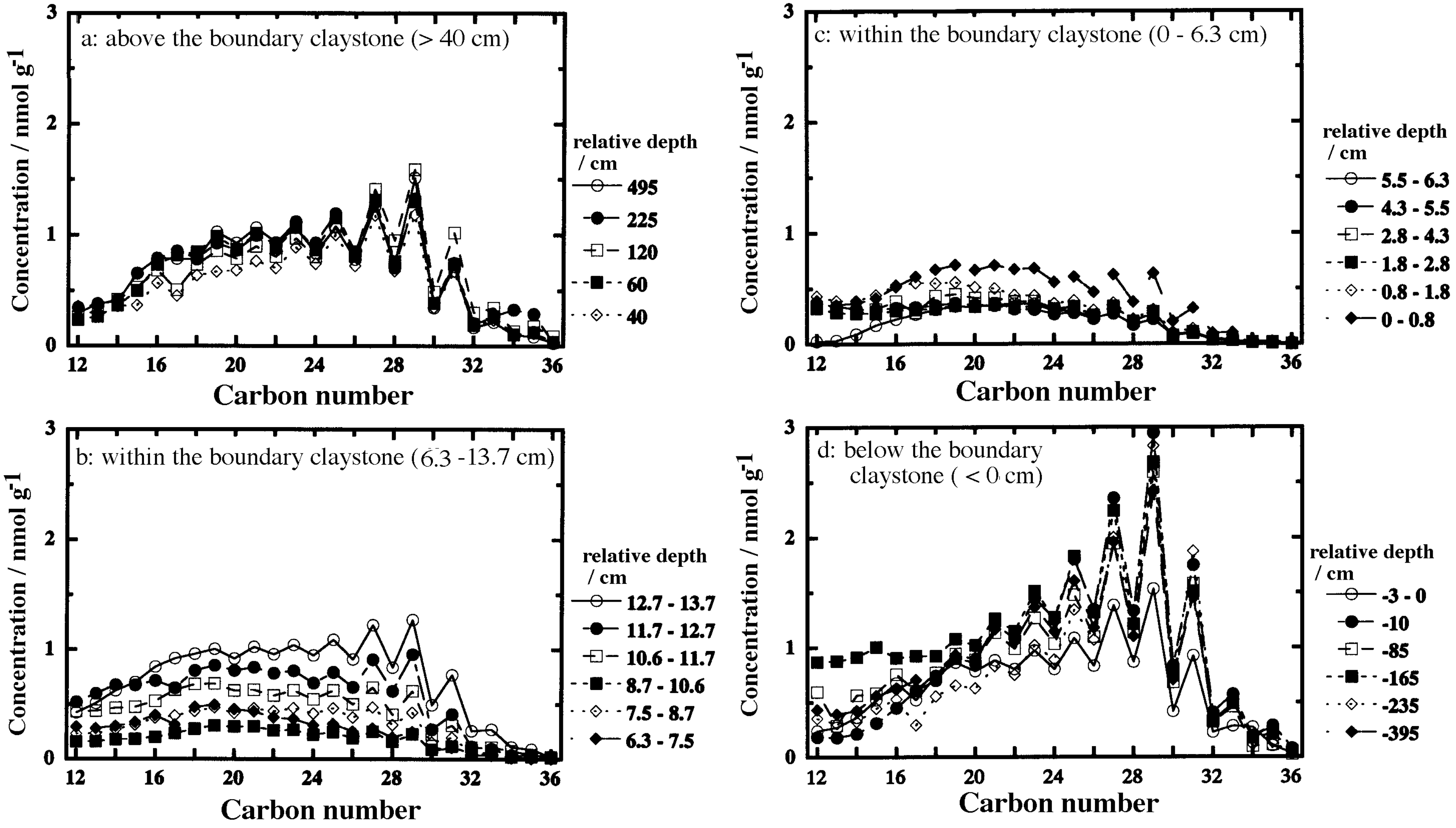

Fig. 1-2-3. Molecular distribution patterns of *n*-alkanes in the sediments a: above (40 to 495 cm), b: within (6.3 to 13.7 cm), c: within (0 to 6.3 cm), and d: below (-395 to 0 cm) the K/T boundary claystone.

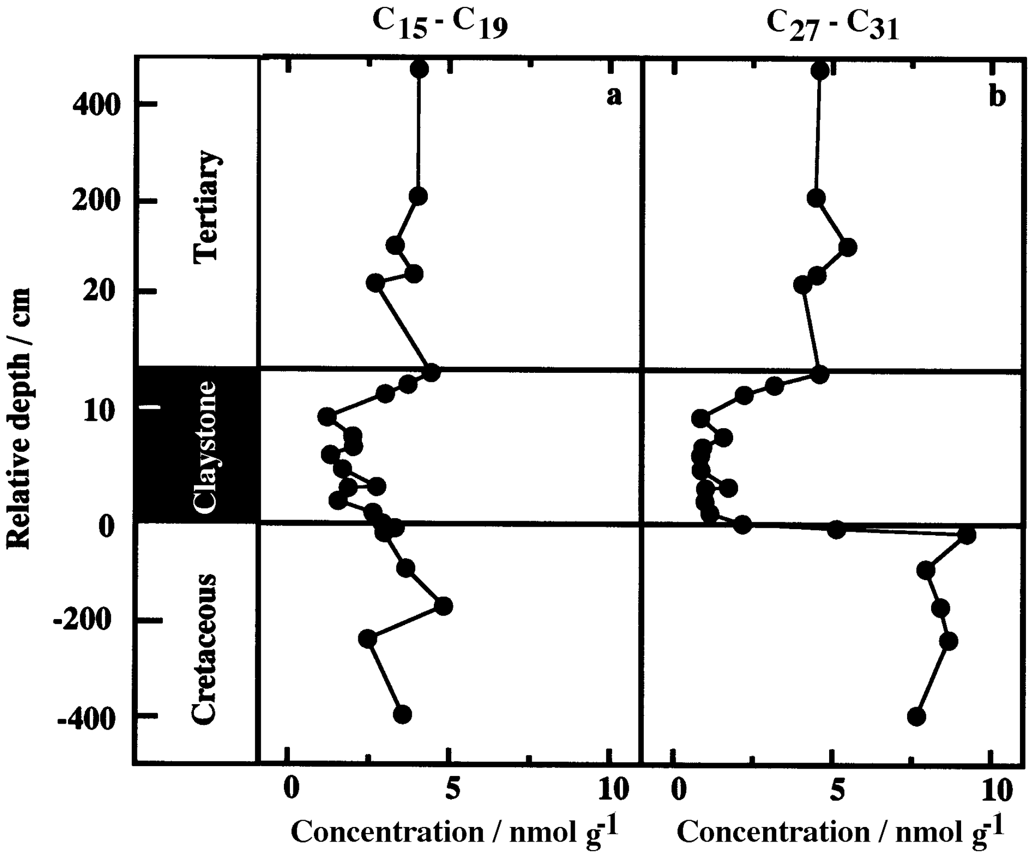

Fig. 1-2-4. Depth distributions of a: concentrations of shorter chain *n*-alkanes (C_{15} to C_{19}) and b: longer ones (C_{27} to C_{31}) in the K/T boundary sediments at Kawaruppu.

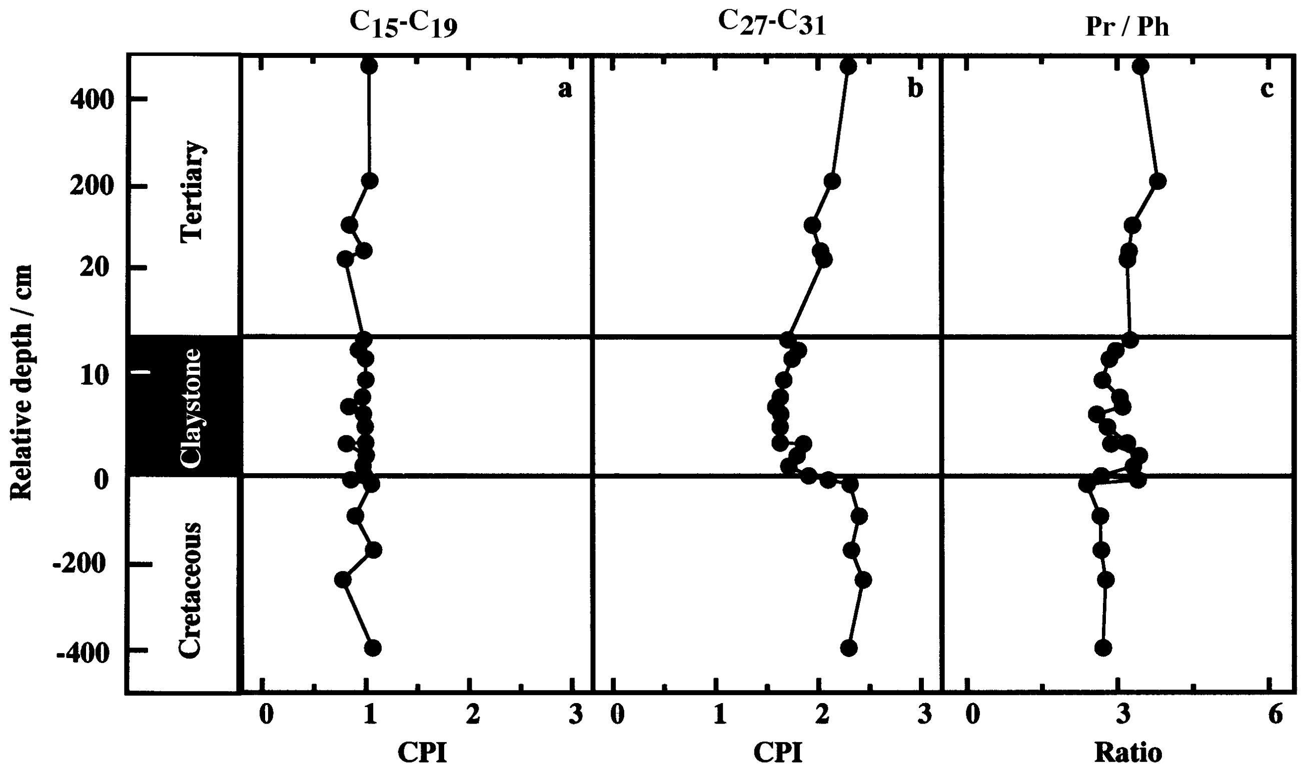

Fig. 1-2-5. Depth distributions of a: carbon preference indices (CPIs) of shorter chain *n*-alkanes (C_{15} to C_{19}), b: CPIs of longer ones (C_{27} to C_{31}), and c: ratios of pristane to phytane (Pr/Ph) in the K/T boundary sediments at Kawaruppu. CPIs for the shorter and longer chain *n*-alkanes are calculated by the equation,

$$\mathrm{CPI} = \frac{\frac{1}{2} C_n + C_{n+2} + \frac{1}{2} C_{n+4}}{C_{n+1} + C_{n+3}}$$

where C_n is the concentration of *n*-alkane with n carbon atoms, and n is 15 for the shorter and 27 for the longer *n*-alkanes.