Mono- and bicyclic alkanes and diamondoid hydrocarbons in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan

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Sixty-two mono- and 4 bicyclic alkanes, and 11 diamondoid hydrocarbons were detected in the Cretaceous-Tertiary (K/T) boundary sediments at Kawaruppu, Hokkaido, Japan. The monocyclic alkanes included series of *n*-alkylcyclohexanes, methyl-*n*-alkylcyclohexanes and *n*-alkylcyclopentanes, and other alkylcyclohexanes. The bicyclic alkanes included bicyclo[3.3.1]nonane, *trans*-decalin, and methyldecalins. The diamondoid hydrocarbons included adamantane, and methyl- and dimethyladamantanes, and diamantane and methyldiamantanes. These mono- and bicyclic alkanes were detected at a level of 0.001–0.1 nmol g⁻¹ and the diamondoid hydrocarbons were at the same or one order magnitude less than those of the cyclic alkanes. Concentrations of all cyclic alkanes within the K/T boundary claystone were markedly small compared to those in the sediments above and below the claystone. The molecular distributions of *n*-alkylcyclohexanes, methyl-*n*-alkylcyclohexanes and *n*-alkylcyclopentanes were relatively smooth within the claystone. On the other hand, those of *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes showed predominances from C₁₅ to C₁₈ and those of *n*-alkylcyclopentanes showed even carbon number predominances from C₁₆ to C₂₂ in the sediments above and below the boundary claystone. These characteristic features in concentration and molecular distribution within the boundary claystone are likely related to the large biomass extinction event at the end of the Cretaceous. Compositions of compounds among trimethylcyclohexanes, methylethylcyclohexanes, decalins, methyladamantanes, and methyldiamantanes were roughly constant over sedimentary sequence. This indicated that diagenetic effect to these compounds had been nearly constant over the sedimentary sequence.

INTRODUCTION

Cyclic alkanes are commonly present in sediments and crude oils. Many studies on these compounds in geochemical materials have dealt with tri-, tetra-, and pentacyclic alkanes such as steranes and hopanes mainly because of the interest in molecular biomarkers in relation to their sources and maturity parameters on organic diagenesis (Farrimond *et al.*, 1998; Alberdi *et al.*, 2001; Inaba *et al.*, 2001). On the other hand, studies of mono- and bicyclic alkanes have been reported rather infrequently. Of these compounds, *n*-alkylcyclohexanes (*n*-alkylCHs, C₁₀–C₂₆), me-

thyl-*n*-alkylcyclohexanes (Me-*n*-alkylCHs, C₁₄–C₂₆) (Rubinstein and Strausz, 1979; Ingram *et al.*, 1983; Fowler and Douglas, 1984; Fowler *et al.*, 1986; Hoffmann *et al.*, 1987; Yamamoto *et al.*, 1990), and *n*-alkylcyclopentanes (*n*-alkylCPs, C₁₀–C₂₆) (Ingram *et al.*, 1983; Yamamoto *et al.*, 1990) in sediments and crude oils have been detected. Cyclic alkanes from C₉ to C₁₁ are present in these geological samples, but their concentrations are in minute probably due to their relatively high volatility (Peters and Moldowan, 1993; Berthod *et al.*, 1998). Diamondoid hydrocarbons have been detected in crude oils and source rocks, and their molecular distributions have been dis-

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cussed (Wingert, 1992; Chen *et al.*, 1996; Dahl *et al.*, 1999; Grice *et al.*, 2000; Jinggui *et al.*, 2000; Schulz *et al.*, 2001).

Massive extinctions of organisms ranging from dinosaurs to marine plankton occurred at the end of the Cretaceous (approximately 65 million years ago). Subsequently, the extinction event must have left notable signatures of biological organic compounds in the Cretaceous-Tertiary (K/T) boundary sediments. The K/T boundary sediments at Kawaruppu, Hokkaido, Japan are suitable for studies of the extinction event, because the boundary claystone is thicker (*ca.* 14 cm) than those at other sites (e.g., Stevns Klint in Denmark, Gubbio in Italy, Woodside Creek in New Zealand, and Caravaca in Spain). Studies of the K/T boundary sediments at Kawaruppu dealt with planktonic foraminifera (Kaiho and Saito, 1986; Kaiho, 1992), palynomorphs (Saito *et al.*, 1986), sulfur isotopes (Kajiwarra and Kaiho, 1992), and Ir accumulation and clay minerals (Tazaki *et al.*, 1992).

The K/T boundary sediments at Kawaruppu are also appropriate for analyses of organic compounds. The 14 cm thickness corresponds to a time span of *ca.* 9000 years based on the studies by Saito *et al.* (1986) and Kajiwarra and Kaiho (1992). This time span might have been enough for some organisms to recover to the abundance level in the Cretaceous as revealed, for example, by *n*-alkanes, pristane and phytane (Mita and Shimoyama, 1999a) or not enough for others as shown by the C₂₅ highly branched isoprenoid thiophene (Katsumata and Shimoyama, 2000). Other studies of organic compounds in the Kawaruppu sediments are of amino acids (Mita *et al.*, 1996) and dicarboxylic acids (Mita *et al.*, 1998) for the search of extraterrestrial compounds, polycyclic aromatic hydrocarbons of combustion origin by wild fires (Mita and Shimoyama, 1999b), and maleimides possibly derived from chlorophyll (Shimoyama *et al.*, 2001).

In this study, we analyzed for mono- and bicyclic alkanes, and diamondoid hydrocarbons (adamantanes and diamantanes) in the K/T boundary sediments at Kawaruppu, using the analytical technique which was employed in our study of the

Neogene sediments (Yabuta *et al.*, 2002). Here we report the results of the analyses and describe characteristic distributions of these cyclic alkanes above, within and below the boundary claystone in relation to the extinction event.

EXPERIMENTAL

Samples

The K/T boundary sediments occurring near Kawaruppu Town, Tokachi District, Hokkaido, their location and lithology were reported by Saito *et al.* (1986), and Kaiho and Saito (1986). 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. These sediment samples were kindly provided by Prof. Y. Kajiwarra of the University of Tsukuba. The sediment sample horizons were shown in previous reports (Mita *et al.*, 1996, 1998). In this study, 11 sediment samples within the boundary claystone (0–13.7 cm), 5 samples above (40–495 cm) and 6 samples below (–395–0 cm) the boundary clay stone were used, in which the bottom of the boundary claystone was set to 0 cm in relative depth.

Analyses

For each analysis, 2 g of a pulverized sediment sample were extracted with 5 ml hexane for 30 min by sonication and the supernatant after centrifugation was recovered. This extraction and centrifugation process was repeated 6 times. The supernatants were combined, concentrated under reduced pressure, and applied to a silica gel column (220 mm × 10 mm i.d.; Keisegel-60, Merk). From the column cyclic alkanes were eluted with 15 ml hexane. The hexane eluate was concentrated to 50 μ l under a nitrogen flow for the analysis by a gas chromatograph (GC) combined with a mass spectrometer (MS) (Hewlett Packard G1800 GCD System). The GC was equipped with a DB-5 (30 m × 0.25 mm i.d., 0.1 μ m thick) or a TC-1 (60 m × 0.25 mm i.d., 0.25 μ m thick) capillary column. The oven temperature was programmed to

hold at 40°C for 10 min, and to increase from 40 to 70°C at a rate of 1°C min⁻¹ and from 70 to 300°C at a rate of 3°C min⁻¹. The mass spectra were acquired every 0.5 s over m/z 45 to 425 in an electron impact ionization mode at 70 eV. Identification and quantification of compounds were made by comparison of peak retention times on the mass fragmentograms of their major or molecular ions and mass spectra, and peak areas, respectively, with those of standard compounds. For compounds without standards, identification was made by comparisons of mass spectra with library data of the National Institute of Standards and Technology (NIST), USA (1992) or data reported in literature. Individual references of these data will be cited in appropriate places in RESULTS and DISCUSSION. Relative concentrations of isomers and homologues were obtained by comparison of peak areas on the mass fragmentograms of their major or molecular ions.

Hexane (Analytical Grade, Wako Pure Chem.) was distilled twice and used. All glassware was heated at 500°C for at least 3 h before use to eliminate organic contaminants. A procedural blank was carried out with 1 g pre-ignited sea sand powder

and it was found that there was no significant contamination during the analysis.

RESULTS

Monocyclic alkanes

Figure 1 shows mass fragmentograms of m/z 83, 97, and 69 for compounds recovered from the sediment (0.8–1.8 cm) within the boundary claystone. *n*-AlkylCHs from C₉ to C₂₆ (m/z 83), Me-*n*-alkylCHs from C₉ to C₂₄ (m/z 97), *n*-alkylCPs from C₉ to C₂₆ (m/z 69), and other alkylCHs of C₉ and C₁₀ (m/z 69, 83, and 97) were detected. Particularly, peaks of *n*-alkylCHs and *n*-alkylCPs with the same carbon numbers were noted as individual compounds by expanding parts of the two mass fragmentograms and the total ion chromatogram, although retention times of some of the two series were very close to each other in Fig. 1. Their mass spectra were also distinguishable from each other by the intensity ratio of the m/z 83 to 69. A series of *n*-alkylCHs and 11 alkylCHs (C₉ and C₁₀) were identified by standard compounds and data by NIST. A series of *n*-alkylCPs was identified by data by Yamamoto *et*

Fig. 1. Mass fragmentograms of m/z 83 for *n*-alkylcyclohexanes and iso-propylcyclohexane, m/z 97 for methyl-*n*-alkylcyclohexanes, and m/z 69 for *n*-alkylcyclopentanes, and tri- and tetramethylcyclohexanes in the K/T boundary claystone (0.8 to 1.8 cm) obtained by GC-MS analysis with a DB-5 capillary column (30 m $\times$ 0.25 mm i.d., 0.1 μ m thick). Peak numbers correspond to those in Table 1.

Table 1. Cyclic alkanes identified in the K/T sediment samples

Peak No.	Compound	Base <i>m/z</i>	Identification
Monocyclic alkanes			
1	<i>iso</i> -Propylcyclohexane	83, 126	Std
2	<i>n</i> -Propylcyclohexane	83, 126	Std
3	<i>n</i> -Butylcyclohexane	83	Std
4	<i>n</i> -Pentylcyclohexane	83	Std
5	<i>n</i> -Hexylcyclohexane	83	Std
6	<i>n</i> -Heptylcyclohexane	83	Std
7	<i>n</i> -Octylcyclohexane	83	Std
8	<i>n</i> -Nonylcyclohexane	83	Std
9	<i>n</i> -Decylcyclohexane	83	Std
10	<i>n</i> -Undecylcyclohexane	83	Std
11	<i>n</i> -Dodecylcyclohexane	83	Std
12	<i>n</i> -Tridecylcyclohexane	83	Std
13	<i>n</i> -Tetradecylcyclohexane	83	Std
14	<i>n</i> -Pentadecylcyclohexane	83	Std
15	<i>n</i> -Hexadecylcyclohexane	83	Std
16	<i>n</i> -Heptadecylcyclohexane	83	Std
17	<i>n</i> -Octadecylcyclohexane	83	Std
18	<i>n</i> -Nonadecylcyclohexane	83	Std
19	<i>n</i> -Eicosylcyclohexane	83	Std
20	3-Methyl-1-ethylcyclohexane (<i>cis</i>)	97, 126	Std
21	4-Methyl-1-ethylcyclohexane (<i>trans</i>)	97, 126	Std
22	} and/or 2-Methyl-1-ethylcyclohexane (<i>trans</i>)	97, 126	Std
23		97, 126	Std
24		97, 126	Std
25	4-Methyl-1-ethylcyclohexane (<i>cis</i>)	97, 126	Std
26	2-Methyl-1-ethylcyclohexane (<i>cis</i>)	97, 126	Std
27	4-Methyl-1-isopropylcyclohexane (<i>trans</i>)	97, 140	Std
28	Methyl- <i>n</i> -propylcyclohexane	97	Fowler <i>et al.</i> (1986)
29	Methyl- <i>n</i> -butylcyclohexane	97	Fowler <i>et al.</i> (1986)
30	Methyl- <i>n</i> -pentylcyclohexane	97	Fowler <i>et al.</i> (1986)
31	Methyl- <i>n</i> -hexylcyclohexane	97	Fowler <i>et al.</i> (1986)
32	Methyl- <i>n</i> -heptylcyclohexane	97	Fowler <i>et al.</i> (1986)
33	Methyl- <i>n</i> -octylcyclohexane	97	Fowler <i>et al.</i> (1986)
34	Methyl- <i>n</i> -nonylcyclohexane	97	Fowler <i>et al.</i> (1986)
35	Methyl- <i>n</i> -decylcyclohexane	97	Fowler <i>et al.</i> (1986)
36	Methyl- <i>n</i> -undecylcyclohexane	97	Fowler <i>et al.</i> (1986)
37	Methyl- <i>n</i> -dodecylcyclohexane	97	Fowler <i>et al.</i> (1986)
38	Methyl- <i>n</i> -tridecylcyclohexane	97	Fowler <i>et al.</i> (1986)
39	Methyl- <i>n</i> -tetradecylcyclohexane	97	Fowler <i>et al.</i> (1986)
40	Methyl- <i>n</i> -pentadecylcyclohexane	97	Fowler <i>et al.</i> (1986)
41	Methyl- <i>n</i> -hexadecylcyclohexane	97	Fowler <i>et al.</i> (1986)

al. (1990) and that of Me-*n*-alkylCHs by Fowler *et al.* (1986). Thus, a total of 62 monocyclic alkanes were identified and they are listed in Table 1.

n-AlkylCHs from C₉ to C₂₆ and other alkylCHs were detected at a concentration level of 0.001–0.1 nmol g⁻¹ (Tables 2 and 3, respectively). All of these compounds were present in most of the

sediments. The total concentration of *n*-alkylCHs in each sediment was in a range of 0.30–0.49 (mean value 0.36, henceforth m.v. stands for mean value) above, 0.09–0.30 (m.v. 0.16) within, and 0.33–0.51 (m.v. 0.45) nmol g⁻¹ below the boundary claystone. The total concentration of other 10 alkylCHs including 6 MeEtCHs in each sediment was in a range of 0.07–0.18 (m.v. 0.14) above,

Table 1. (continued)

Peak No.	Compound	Base m/z	Identification
Monocyclic alkanes			
42	1,1,3-Trimethylcyclohexane	69, 111, 126	Std
43	1,2,4-Trimethylcyclohexane	69, 111, 126	Std
44	<i>n</i> -Butylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
45	1,1,2,3-Tetramethylcyclohexane	69, 125, 140	Lib
46	<i>n</i> -Pentylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
47	<i>n</i> -Hexylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
48	<i>n</i> -Heptylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
49	<i>n</i> -Octylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
50	<i>n</i> -Nonylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
51	<i>n</i> -Decylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
52	<i>n</i> -Undecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
53	<i>n</i> -Dodecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
54	<i>n</i> -Tridecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
55	<i>n</i> -Tetradecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
56	<i>n</i> -Pentadecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
57	<i>n</i> -Hexadecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
58	<i>n</i> -Heptadecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
59	<i>n</i> -Octadecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
60	<i>n</i> -Nonadecylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
61	<i>n</i> -Eicosylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
62	<i>n</i> -Heneicosylcyclopentane	69	Yamamoto <i>et al.</i> (1990)
Bicyclic alkanes			
63	Bicyclo[3.3.1]nonane	67, 124	Lib
64	Decalin (<i>trans</i>)	67, 138	Std
65	Methyldecalin (isomer A)	67, 152	Lib
66	Methyldecalin (isomer B)	67, 152	Lib
Diamondoid hydrocarbons			
<i>Adamantanes</i>			
67	Adamantane	136	Std
68	1-Methyladamantane	135	Wingert (1992); Chen <i>et al.</i> (1996)
69	2-Methyladamantane	135	Wingert (1992); Chen <i>et al.</i> (1996)
70	1,3-Dimethyladamantane	149	Wingert (1992); Chen <i>et al.</i> (1996)
71	1,4-Dimethyladamantane (<i>trans</i>)	149	Wingert (1992); Chen <i>et al.</i> (1996)
72	1,4-Dimethyladamantane (<i>cis</i>)	149	Wingert (1992); Chen <i>et al.</i> (1996)
73	1,2-Dimethyladamantane	149	Wingert (1992); Chen <i>et al.</i> (1996)
<i>Diamantanes</i>			
74	Diamantane	188	Std
75	1-Methyldiamantane	187	Wingert (1992); Chen <i>et al.</i> (1996)
76	4-Methyldiamantane	187	Wingert (1992); Chen <i>et al.</i> (1996)
77	2-Methyldiamantane	187	Wingert (1992); Chen <i>et al.</i> (1996)

Std; standard, Lib; library data (NIST).

0.01–0.18 (m.v. 0.07) within, and 0.13–0.56 (m.v. 0.40) nmol g⁻¹ below the boundary claystone. Although the concentrations of Me-*n*-alkylCHs, *n*-alkylCPs, and 1,1,2,3-tetraMeCH were not estimated, they were likely present at the same level of *n*-alkylCHs, judging from their peak areas on the mass fragmentograms.

Bicyclic alkanes

Figure 2a shows mass fragmentograms of m/z 67 (a major ion for bicyclic alkanes), m/z 124 (a molecular ion for bicyclo[3.3.1]nonane), m/z 138 (decalin), and m/z 152 (methyldecalins) for compounds recovered from the sediment (–10 cm) below the boundary claystone. These four bicy-

Table 2. Concentrations of *n*-alkylcyclohexanes (C_9 – C_{26}) in the *K/T* boundary sediments at Kawaruppu

Relative depth /cm	Concentrations/nmol g ⁻¹ Rock																	
	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}
Tertiary																		
495	0.045	0.027	0.021	0.015	0.016	0.018	0.022	0.029	0.027	0.026	0.010	0.014	0.009	0.010	0.005	0.004	0.003	0.002
225	0.048	0.022	0.010	0.008	0.010	0.012	0.025	0.038	0.035	0.045	0.013	0.012	0.006	0.007	0.004	0.004	0.003	0.003
120	0.035	0.019	0.014	0.013	0.018	0.030	0.048	0.071	0.049	0.047	0.013	0.009	0.005	0.005	0.003	0.002	0.002	0.002
60	0.036	0.022	0.016	0.013	0.017	0.026	0.039	0.054	0.043	0.042	0.009	0.009	0.004	0.005	0.002	0.002	0.002	0.002
40	0.020	0.019	0.018	0.014	0.023	0.036	0.057	0.096	0.072	0.069	0.019	0.014	0.007	0.008	0.004	0.003	0.003	0.002
Clay boundary																		
12.7–13.7	0.031	0.010	0.007	0.012	0.017	0.017	0.019	0.026	0.030	0.028	0.019	0.016	0.017	0.017	0.012	0.007	0.005	0.004
11.7–12.7	0.018	0.002	0.001	0.009	0.008	0.009	0.009	0.019	0.019	0.015	0.012	0.010	0.010	0.009	0.006	0.005	0.004	0.003
10.6–11.7	n.d.	n.d.	n.d.	0.004	0.005	0.004	0.006	0.010	0.008	0.012	0.009	0.010	0.007	0.006	0.005	0.003	0.003	0.003
8.7–10.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7.5–8.7	0.058	0.026	0.011	0.008	0.007	0.006	0.007	0.007	0.007	0.007	0.006	0.005	0.004	0.004	0.003	0.002	0.002	0.001
5.5–6.3	0.036	0.027	0.013	0.010	0.008	0.007	0.006	0.008	0.006	0.007	0.006	0.005	0.004	0.003	0.003	0.002	0.001	0.001
4.3–5.5	n.d.	n.d.	n.d.	n.d.	0.004	0.003	0.004	0.007	0.005	0.005	0.003	0.002	0.002	0.001	0.002	0.0006	0.001	n.d.
2.8–4.3	0.016	0.015	0.013	0.009	0.008	0.008	0.007	0.005	0.006	0.005	0.005	0.003	0.003	0.003	0.002	0.002	0.001	0.001
1.8–2.8	0.017	0.007	0.006	0.005	0.005	0.005	0.005	0.008	0.007	0.007	0.006	0.005	0.004	0.003	0.003	0.002	0.002	0.001
0.8–1.8	0.038	0.026	0.017	0.012	0.008	0.007	0.006	0.006	0.007	0.006	0.005	0.004	0.004	0.003	0.003	0.002	0.001	0.001
0.0–0.8	0.005	0.016	0.013	0.022	0.024	0.025	0.022	0.028	0.030	0.029	0.019	0.015	0.011	0.009	0.008	0.005	0.004	0.003
Cretaceous																		
–3–0	0.040	0.019	0.012	0.010	0.011	0.014	0.027	0.045	0.044	0.039	0.014	0.018	0.011	0.010	0.005	0.003	0.002	0.002
–10	0.047	0.042	0.021	0.015	0.008	0.021	0.042	0.057	0.054	0.068	0.021	0.021	0.015	0.017	0.009	0.008	0.008	0.006
–85	0.19	0.073	0.044	0.027	0.023	0.018	0.018	0.025	0.023	0.019	0.010	0.012	0.008	0.006	0.005	0.004	0.004	0.003
–165	0.12	0.065	0.033	0.034	0.028	0.033	0.030	0.030	0.020	0.020	0.014	0.014	0.010	0.011	0.009	0.008	0.009	0.005
–235	0.13	0.060	0.037	0.046	0.042	0.032	0.026	0.025	0.018	0.017	0.013	0.014	0.010	0.009	0.008	0.007	0.010	0.008
–395	0.091	0.038	0.020	0.025	0.022	0.023	0.020	0.024	0.016	0.014	0.010	0.009	0.008	0.008	0.006	0.005	0.006	0.006

n.d.; not detected, —; not determined.

Table 3. Concentrations of polyalkylcyclohexanes and bicyclic alkanes in the K/T boundary sediments at Kavaruppu

Relative depth /cm	Concentrations/nmol g ⁻¹ Rock												
	Polyalkylcyclohexanes							Bicyclic alkanes					
	1,1,3-TriMe-	1,2,4-TriMe-	2-Me-1-Et- (cis)	2-Me-1-Et- 3-Me-1-Et-(trans) + 3-Me-1-Et-(trans)	3-Me-1-Et- (cis)	4-Me-1-Et- (trans)	4-Me-1-Et- (cis)	4-Me-1-Et- iso-Pr-	4-Me-1-isoPr- (trans)	Decalin (trans)	Me-decalin* (isomer A)	Me-decalin* (isomer B)	
Tertiary													
495	0.041	0.018	0.009	0.012	0.029	0.010	0.005	0.020	0.011	0.066	0.034	0.018	
225	0.038	0.018	0.007	0.016	0.020	0.013	0.009	0.018	0.010	0.054	0.024	0.008	
120	0.044	0.015	0.005	0.008	0.021	0.011	0.006	0.014	0.010	0.060	0.028	0.010	
60	0.056	0.022	0.008	0.011	0.028	0.015	0.007	0.017	0.018	0.042	0.026	0.014	
40	0.019	0.011	0.005	0.004	0.009	0.006	n.d.	0.010	0.007	0.022	0.015	0.008	
Clay boundary													
12.7–13.7	0.009	0.004	0.0003	0.003	0.006	0.003	n.d.	n.d.	0.003	0.016	0.004	n.d.	
11.7–12.7	0.006	0.003	0.001	0.003	0.005	0.004	n.d.	0.003	0.0003	0.013	0.007	n.d.	
10.6–11.7	—	—	—	—	—	—	—	—	—	—	—	—	
8.7–10.6	—	—	—	—	—	—	—	—	—	0.015	—	—	
7.5–8.7	0.050	0.027	0.008	0.013	0.033	0.023	0.004	0.014	0.009	0.030	0.011	0.002	
5.5–6.3	0.025	0.015	0.006	0.008	0.016	0.010	n.d.	0.014	0.008	0.018	0.008	n.d.	
4.3–5.5	—	—	—	—	—	—	—	—	—	0.001	—	—	
2.8–4.3	0.010	0.004	0.001	0.001	0.005	0.002	n.d.	0.005	0.001	0.008	0.003	0.001	
1.8–2.8	0.016	0.006	0.001	0.002	0.008	0.004	n.d.	0.005	0.001	0.003	0.001	n.d.	
0.8–1.8	0.026	0.019	0.010	0.005	0.029	0.009	0.003	0.015	0.011	0.030	0.014	0.006	
0.0–0.8	n.d.	0.002	n.d.	n.d.	0.004	0.001	n.d.	n.d.	0.001	0.024	0.015	n.d.	
Cretaceous													
–3–0	0.034	0.018	0.009	0.009	0.027	0.010	0.005	0.018	n.d.	0.075	0.034	0.017	
–10	0.14	0.078	0.020	0.046	0.084	0.058	0.020	0.078	0.038	0.14	0.063	0.034	
–85	0.12	0.067	0.031	0.034	0.091	0.034	0.016	0.054	0.025	0.14	0.051	0.030	
–165	0.13	0.073	0.010	0.032	0.074	0.044	0.020	0.040	0.024	0.14	0.069	0.033	
–235	0.11	0.050	0.018	0.040	0.079	0.046	0.018	0.042	0.034	0.11	0.066	0.030	
–395	0.072	0.041	0.021	0.034	0.064	0.042	0.014	0.040	0.021	0.14	0.084	0.045	

n.d.; not detected, —; not determined, Me-; methyl-, Et-; ethyl-, Pr-; propyl-.

*Concentrations of methyldecals were determined by the trans-decalin standard.

Fig. 2. Mass fragmentograms of a) m/z 67, 124, 138, and 152 for bicyclic alkanes and b) m/z 135, 136, and 149 for adamantanes and m/z 187 and 188 for diamantanes in the K/T boundary sediment (-10 cm) obtained by GC-MS analysis with a TC-1 capillary column ($60\text{ m} \times 0.25\text{ mm i.d.}$, $0.25\text{ }\mu\text{m}$ thick). Peak numbers correspond to those in Table 1.

clic alkanes are listed in Table 1. The two isomers of methyldecals were arbitrarily named as isomer A for the one at retention time 47.5 min and isomer B for the other at 48.4 min, because the methyl position on the decalin structure could not be determined.

Decalins were detected at a concentration level of $0.001\text{--}0.1\text{ nmol g}^{-1}$ (Table 3). The concentration of decalin (*trans*) in each sediment was in a range of $0.02\text{--}0.07$ (m.v. 0.05) above, $0.001\text{--}0.03$ (m.v. 0.02) within, and $0.08\text{--}0.14$ (m.v. 0.12) nmol g^{-1} below the boundary claystone. The total concentration of methyldecals in each sediment was in a range of $0.02\text{--}0.05$ (m.v. 0.04) above, $0.001\text{--}0.02$ (m.v. 0.01) within, and $0.05\text{--}0.13$ (m.v. 0.09) nmol g^{-1} below the boundary claystone. Bicyclo[3.3.1]nonane was detected in two sediments (495 cm and 225 cm) above, two sediments (0.8–1.8 cm and 7.5–8.7 cm) within,

and most sediments below the claystone. The compound was likely present at the same concentration level of decalins, judging from their peak areas on the mass fragmentograms.

Diamondoid hydrocarbons (adamantanes and diamantanes)

Figure 2b shows mass fragmentograms for compounds recovered from the sediment (-10 cm) below the boundary claystone. These fragment ions are of adamantanes (m/z 135, 136, and 149) and diamantanes (m/z 187 and 188). Adamantane and diamantane were identified by their standard compounds (Peaks 67 and 74, respectively, in Fig. 3). Methyl- and dimethyladamantanes and methyl-diamantanes were identified using data by Wingert (1992) and Chen *et al.* (1996). Mass spectra of these compounds showed that molecular ions M^+ or fragment ions $(\text{M}-\text{CH}_3)^+$ were the most

Fig. 3. Mass spectra of adamantanes and diamantanes in the K/T boundary sediment (−10 cm).

abundant (Fig. 3). Thus, 11 diamondoid hydrocarbons were identified and are listed in Table 1. They included adamantane, 2 isomers of methyladamantanes, 4 isomers of dimethyladamantanes, diamantane, and 3 isomers of methyldiamantanes. Some mass spectra contained ions which were considered to be of other compounds as seen in peaks 74 and 75 in Fig. 3. However, the quantification of these diamondoids was made on their mass chromatograms, so that impurities could be excluded.

Adamantanes were detected at a concentration level of 0.001–0.1 nmol g^{−1} and diamantanes at 0.001–0.01 nmol g^{−1} (Table 4). These concentration levels were same or one order of magnitude less than those of mono- and bicyclic alkanes. Most of these diamondoid hydrocarbons were scarcely present within the claystone, whereas 1-methyladamantane, 1,3-dimethyladamantane, and 4-methyldiamantane were present notably compared with other compounds. The total concentration of 11 diamondoid hydrocarbons in each sediment was in a range of 0.12–0.34 (m.v. 0.21)

above, 0.003–0.06 (m.v. 0.02) within, and 0.09–0.58 (m.v. 0.38) nmol g^{−1} below the boundary claystone.

Mono- and bicyclic alkanes and diamondoid hydrocarbons detected in the K/T boundary sediments were at two orders of magnitude less in concentration than *n*-alkanes (C₁₂–C₃₆) in the same sediments (Mita and Shimoyama, 1999a).

DISCUSSION

Depth profiles

Marked decreases in concentration of all cyclic alkanes were observed from the sediment (−3–0 cm) below the boundary claystone to the bottom sediment (0–0.8 cm) in the boundary claystone (Fig. 4). Over the K/T boundary, the concentrations of *n*-alkylCHs (C₉–C₂₆), Me-*n*-alkylCHs (C₉–C₂₄), and *n*-alkylCPs (C₉–C₂₆) decreased to around the 25% levels of those in the sediments below the boundary claystone (Fig. 4a). These decreased concentrations continued over the lower two-third portion (0–10.6 cm) of the bound-

Table 4. Concentrations of diamondoid hydrocarbons in the K/T boundary sediments at Kawaruppu

Relative depth /cm	Concentrations/nmol g ⁻¹ Rock										
	Adamantane	1-Methyl- adamantane*	2-Methyl- adamantane*	1,3-Dimethyl- adamantane*	1,4-Dimethyl- adamantane (trans)*	1,4-Dimethyl- adamantane (cis)*	1,2-Dimethyl- adamantane*	Diamantane	4-Methyl- diamantane*	1-Methyl- diamantane*	3-Methyl- diamantane*
Tertiary											
495	0.012	0.055	0.019	0.032	0.017	0.015	0.019	0.003	0.003	0.002	0.001
225	0.012	0.060	0.018	0.027	0.012	0.009	0.014	0.001	n.d.	n.d.	n.d.
120	0.025	0.13	0.039	0.060	0.028	0.025	0.031	0.004	0.003	0.002	0.002
60	0.019	0.088	0.022	0.042	0.021	0.017	0.023	0.006	0.006	0.004	0.003
40	0.007	0.039	0.008	0.022	0.009	0.006	0.011	0.006	0.003	0.002	0.002
Clay boundary											
12.7–13.7	n.d.	0.007	n.d.	0.001	n.d.	n.d.	n.d.	0.003	trace	n.d.	n.d.
11.7–12.7	n.d.	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10.6–11.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8.7–10.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7.5–8.7	0.005	0.031	0.003	0.008	0.002	trace	0.002	0.001	trace	n.d.	n.d.
5.5–6.3	n.d.	0.020	trace	0.010	n.d.	n.d.	0.001	n.d.	trace	n.d.	n.d.
4.3–5.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2.8–4.3	n.d.	0.012	n.d.	0.002	trace	n.d.	trace	n.d.	trace	trace	n.d.
1.8–2.8	n.d.	0.004	n.d.	0.002	n.d.	n.d.	n.d.	n.d.	trace	n.d.	n.d.
0.8–1.8	0.004	0.021	0.005	0.012	0.005	0.005	0.006	0.001	0.001	0.001	trace
0.0–0.8	n.d.	0.002	n.d.	0.001	n.d.	n.d.	n.d.	n.d.	trace	trace	n.d.
Cretaceous											
–3–0	0.009	0.036	0.010	0.016	0.007	0.007	0.009	0.001	trace	trace	n.d.
–10	0.041	0.17	0.051	0.081	0.036	0.038	0.044	0.019	0.015	0.011	0.009
–85	0.033	0.13	0.038	0.075	0.035	0.034	0.038	0.008	0.007	0.005	0.004
–165	0.029	0.21	0.060	0.12	0.049	0.047	0.060	0.004	0.003	0.002	0.002
–235	0.021	0.10	0.027	0.045	0.029	0.028	0.033	0.006	0.005	0.005	0.003
–395	0.021	0.11	0.034	0.061	0.033	0.031	0.037	0.009	0.008	0.006	0.005

n.d.; not detected, trace; less than 0.001 nmol g⁻¹.

*Concentrations of methyl- and dimethyladamantanes were determined by the adamantane standard, and those of methyladamantanes were by the adamantane standard.

Fig. 4. Depth profiles of a) concentrations of total *n*-alkylCHs (cyclohexanes, C_{9-26}), and relative concentrations of total *Me-n*-alkylCHs (methyl-*n*-alkylcyclohexanes, C_{9-24}) and total *n*-alkylCPs (cyclopentanes, C_{9-26}) (maximum concentration set to 100), b) concentrations of total other alkylCHs (C_9 and C_{10}), c) total decalins, d) total diamondoid hydrocarbons, and e) short (C_{15-19}) and long chain (C_{27-31}) *n*-alkanes (Mita and Shimoyama, 1999a) in the K/T boundary sediments at Kawaruppu.

ary claystone. Then, they began to increase gradually in the upper one third (10.6–13.7 cm) of the claystone, reaching over the 80% level at the top of the boundary claystone, and remained rather constant in the sediments above the claystone. This depth profile resembled those of short chain *n*-alkanes ($C_{15}-C_{19}$) in Fig. 4e (Mita and Shimoyama, 1999a). Concentrations of other alkylCHs, decalins, and diamondoid hydrocarbons decreased to the 10–15% levels (Figs. 4b, c, and d, respectively). These decreased concentrations roughly remained to the top of the claystone and increased slightly to the 30–45% levels in the sediments above the claystone. This depth profile resembled those of long chain *n*-alkanes ($C_{27}-C_{31}$) in Fig. 4e (Mita and Shimoyama, 1999a).

The large concentration decrease of cyclic alkanes at the K/T boundary is probably due to a large decrease in biomass input into the boundary claystone, which related to the massive extinctions of organisms, as observed in the case of *n*-alkanes, pristane, and phytane (Mita and Shimoyama, 1999a). Differences in decrease among cyclic alkanes in the boundary claystone and in increase in the sediments above the claystone might have been caused by their difference in biological source. According to these depth profiles, living organisms which had been sources of *n*-alkylcycloalkanes had recovered to the abundance level of the Cretaceous at the sediment (40 cm) depositional time (*ca.* 50000 years after the boundary). Whereas, those which had been sources of

other alkylCHs, decalins, and diamondoids had not recovered even to a half abundance level at the sediment (495 cm) time (*ca.* 550000 years after the boundary). The 50000 and 550000 years were estimated using data by Kajiwara and Kaiho (1992).

Both *n*-alkylCHs and Me-*n*-alkylCHs have been detected in various geological samples including mature crude oil (Rubinstein and Strausz, 1979), Ordovician sediments (Fowler and Douglas, 1984; Fowler *et al.*, 1986; Hoffmann *et al.*, 1987) and the fossil alga (*G. priska*) (Hoffmann *et al.*, 1987), Eocene oil shales (Ingram *et al.*, 1983), and ODP Hole sediments of Late Miocene (Yamamoto *et al.*, 1990). It has been suggested that *n*-alkylCHs and Me-*n*-alkylCHs were formed by cyclization of *n*-fatty acids and they were likely derived from marine organisms such as algae (Rubinstein and Strausz, 1979; Fowler *et al.*, 1986; Hoffmann *et al.*, 1987). Rubinstein and Strausz (1979) demonstrated experimentally the formation of *n*-alkylCHs and Me-*n*-alkylCHs mainly in a range of C₁₅ to C₁₈ by heating stearic (saturated) and oleic (unsaturated) acids (C₁₈) in the presence of bentonite. As to *n*-alkylCPs, it was suggested that they were formed by cyclization of unsaturated fatty acids during diagenesis (Philp, 1980). Therefore, it is very likely that these *n*-alkylCHs and Me-*n*-alkylCHs in the K/T sediments at Kwaruppu were derived from biological fatty acids, as it was the case for *n*-alkanes. Furthermore, the similarity in their depth profiles to that of the short chain *n*-alkanes (C₁₅–C₁₉) suggested that they were derived from fatty acids of marine organisms. In addition, it has been suggested that *n*-alkylcyclohexanes were produced by decarboxylation of ω -cyclohexyl fatty acids in thermoacidophilic bacterial products (De Rosa *et al.*, 1972; Oshima and Ariga, 1975; Suzuki *et al.*, 1981). However, contribution from thermoacidophilic bacteria is probably insignificant because of the K/T sedimentary environment at Kwaruppu.

Anders and Robinson (1971) proposed that polyalkylCHs and bicyclic alkanes were derived by degradation of some terpenoids. It was also

reported that polyalkyl-CHs (C₇–C₉) and CPs (C₆ and C₇) were produced by heating 5 α -cholestane in the presence of clay, although in small yields (Kissin, 1990). Diamondoid hydrocarbons are known to be formed by heating with a strong Lewis acid catalyst from some polycyclic alkanes (Petrov *et al.*, 1974), which can be derived from terpenoids in sediments. PolyalkylCHs, bicyclic alkanes, and diamondoid hydrocarbons are likely derived from these terrestrial terpenoids. The similar depth profiles of these compounds to those of long chain *n*-alkanes (C₂₇–C₃₁) support above interpretation. Therefore, precursors and their biological sources of these cycloalkanes are possibly different from those of *n*-alkylcycloalkanes, which might explain the difference in their depth profiles from those of *n*-alkylcycloalkanes.

Molecular distribution of n-alkylcycloalkanes

The molecular distributions of *n*-alkylCHs (C₁₅–C₂₆), Me-*n*-alkylCHs (C₁₅–C₂₄), and *n*-alkylCPs (C₁₅–C₂₆) in each sediment were shown in Fig. 5, together with those of *n*-alkanes (C₁₅–C₃₆) (Mita and Shimoyama, 1999a). The abundances of *n*-alkylCHs in most sediments within the boundary claystone were small and roughly similar to each other. On the other hand, those in the sediments above and below the boundary claystone showed predominances in a range of C₁₅–C₁₈. The molecular distributions of Me-*n*-alkylCHs were roughly similar to those of *n*-alkylCHs in most sediments. *n*-AlkylCPs also showed a similar distribution feature as those of the former two homologues, except that even carbon number predominances in a range of C₁₆–C₂₂, as opposed to rather smooth distributions of the two former homologues in the carbon range.

The molecular distributions of the three series did not resemble those of *n*-alkanes which showed clearly high abundances in a range of C₂₅–C₃₁ (Fig. 5). The difference in predominance of *n*-alkylcycloalkanes (C₁₅–C₁₈) and *n*-alkanes (C₂₅–C₃₁) might be related to the different sources and formation processes from biological fatty acids which are rich in C₁₆–C₁₈ and C₂₈–C₃₀. The cyclization might proceed rather efficiently with

Fig. 5. Molecular distributions with carbon number of *n*-alkylcyclohexanes, methyl-*n*-alkylcyclohexanes (maximum concentration set to 100), *n*-alkylcyclopentanes (maximum concentration set to 100), and *n*-alkanes (Mita and Shimoyama, 1999a) in the K/T boundary sediments at Kawaruppu.

fatty acids of carbon chain length of C_{16} – C_{18} generally derived from marine organisms than the longer one, which produced the *n*-alkylcycloalkane predominances in the carbon range. Whereas, decarboxylation probably takes place nearly evenly over fatty acids with C_{16} – C_{30} , which caused the *n*-alkane predominance in the range of C_{25} – C_{31} due to the abundance of source fatty acids with C_{28} – C_{30} from land plants.

The relatively smooth molecular distributions of the four homologues (including *n*-alkanes) within the boundary claystone seem to indicate that they were older than those above and below the claystone. However, the depth profiles of these series clearly reflected the biomass extinctions. Therefore, the smooth molecular distributions might have been related to the depositional environment of the claystone besides the small biomass input into it. If so, the relatively high concentrations or compositions from C_{15} to C_{18} of three *n*-alkylcycloalkane homologues in the upper two sediments (11.7–13.7 cm) within the claystone were likely related to the recovery processes of the environment as well as their precursors input.

Carbon preference indices (CPIs) of *n*-alkylCHs (C_{15} – C_{26}), Me-*n*-alkylCHs (C_{15} – C_{26}), and *n*-alkylCPs (C_{15} – C_{26}) were calculated in each sediment by the equation

$$CPI = \sum_{i=8}^{13} C_{2i-1} / \sum_{i=8}^{13} C_{2i}$$

where *i* is number of carbon atoms in the molecules.

CPIs of *n*-alkylCHs in the sediments above, within, and below the claystone were in a range of 0.8–0.9 (m.v. 0.9), 0.9–1.3 (m.v. 1.1), and 0.8–1.1 (m.v. 1.1), respectively. Those of Me-*n*-alkylCHs were 0.7–1.0 (m.v. 0.9), 1.0–1.2 (m.v. 1.1), and 1.0–1.3 (m.v. 1.1), respectively. These values are more or less close to 1, indicating that the two homologues once formed from fatty acids received the diagenetic alteration which produced smooth molecular distributions. On the other hand, CPIs of *n*-alkylCPs were 0.3–0.4 (m.v. 0.3), 0.6–0.9 (m.v. 0.8), and 0.4–0.7 (m.v. 0.6), respectively.

These values clearly showed an even carbon number predominance as seen in Fig. 5. If *n*-alkylCPs were formed from unsaturated fatty acids (Philp, 1980), the values should have been close to 1 similarly to those of *n*-alkylCHs and Me-*n*-alkylCHs. Presently it can only be said that the precursors and formation paths were different for *n*-alkylCPs from *n*-alkylCHs and Me-*n*-alkylCHs. This may relate why C_{20} molecule in addition to C_{16} and C_{18} ones were predominant among *n*-alkylCPs, while the C_{20} predominance was not observed for the other two homologues.

Compositions of cyclic alkanes (trimethyl- and methylethylcyclohexanes, decalins, adamantanes, and diamantanes)

Depth profiles of the compound compositions among triMeCHs, MeEtCHs, decalins, methyladamantanes, and methyldiamantanes are shown in Figs. 6a, b, c, and d, respectively. These compositions were roughly constant over the K/T sediments. This indicated that diagenetic effect to these compounds had been nearly the same in the sediments above, within and below the boundary claystone. Similar results were observed by the ratios of β - to α -alkylated PAHs (Fig. 6e, Mita and Shimoyama, 1999b), β - to α -methyldibenzothiophenes (Fig. 6e, Katsumata and Shimoyama, 2000), and of alkylmaleimides (Fig. 6f, Shimoyama *et al.*, 2001). This may be understandable from the age difference of about one million year from the bottom to the top sediment of the K/T sediment we examined whose age as a whole is *ca.* 65 million years. Therefore, the small concentrations of these cyclic alkanes within the boundary claystone were not caused by the selective degradation by clays but by the small biomass input into the claystone. Additionally, the near constant compositions suggest that their precursors were nearly constant in composition over the K/T sediments, but not in abundance due to the massive extinctions.

Decalin (non-substituted) was more abundant than methyldecalins over the sedimentary sequence. This result can be explained by their structural stabilities; i.e., decalin is structurally more

Fig. 6. Depth profiles of a) relative compositions (%) of triMeCHs (trimethylcyclohexanes), b) MeEtCHs (methylethylcyclohexanes), and c) decalins, d) MAIs (methyladamantane index; $1\text{-MA}/(1\text{-MA} + 2\text{-MA})$) and MDIs (methyladamantane index; $4\text{-MD}/(4\text{-MD} + 1\text{-MD} + 3\text{-MD})$) (the two indices were from Chen *et al.*, 1996), e) ratios of β - to α -MN (methylnaphthalene), MP (methylphenanthrene) (Mita and Shimoyama, 1999b), and MDBT (methyldibenzothiophene) (Katsumata and Shimoyama, 2000), and f) 2,3-DMMi (2,3-dimethylmaleimide)/(2,3-DMMi + 2-M-3E-Mi (2-methyl-3-ethylmaleimide)) (Shimoyama *et al.*, 2001) in the K/T boundary sediments at Kawaruppu.

stable than methyldecalins. Among diamondoid hydrocarbons, 1-methyladamantane, 1,3-dimethyladamantane, and 4-methyldiamantane were predominant (Table 4). The three diamondoids are bridgehead-substituted and most stable among adamantanes and diamantanes. Therefore, the predominances also related to the stabilities of diamondoid structures. Chen *et al.* (1996) have introduced maturity parameters using the stabilities of methyladamantanes and methyldiamantanes. However, our results were not in accordance with their maturity evaluation indices. Likewise, Schulz *et al.* (2001) reported that the indices were not applicable to their samples of marine siliciclastic shales, marine carbonates,

and coals. Further studies of diamondoid hydrocarbons are necessary for the evaluation of their sources and maturity.

CONCLUSIONS

The K/T boundary sediments at Kawaruppu were analyzed for mono- and bicyclic alkanes, and diamondoid hydrocarbons. As a result, 62 mono- and 4 bicyclic alkanes, and 11 diamondoid hydrocarbons were detected at a concentration level of sub-nmol or pmol g^{-1} . Concentrations of all cyclic alkanes were found to relate to the large biomass extinction at the Cretaceous end. Among the cyclic alkanes, *n*-alkylcycloalkanes showed a

rather quick recovery of their biological sources. Other alkyl cyclohexanes, decalins, and diamondoid hydrocarbons showed no complete recovery to the abundance levels of the Cretaceous. Such differences in recovery might have been caused by their differences in biological sources. CPIs of *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes indicated that two homologues probably formed from the same biological source. CPIs of *n*-alkylcyclopentanes suggested that their precursors and formation paths were different from those of the above two homologues. Compositions of compounds among trimethylcyclohexanes, methylethylcyclohexanes, decalins, methyladamantanes, and methyladamantanes were constant over sedimentary sequence, indicating that diagenetic effect to these compounds was probably same over the sediments.

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