Title	Tetra- and pentacyclic alkanes in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan
Author(s)	Yabuta, Hikaru; Mita, Hajime; Shimoyama, Akira
Citation	Researches in Organic Geochemistry , 17 : 33 - 43
Issue Date	2002-06-30
DOI	10.20612/rog.17.0_33
Self DOI	
URL	https://ir.lib.hiroshima-u.ac.jp/00048603
Right	Copyright (c) 2002 The Japanese Association of Organic Geochemists 本文データは学協会の許諾に基づきCiNiiから複製したものである
Relation	

Res. Org. Geochem. 17, 33 − 43 (2002)

Tetra– and pentacyclic alkanes in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan

Yabuta Hikaru*, Mita Hajime** and Shimoyama Akira***

(Received Dec. 3, 2001 : Revised and accepted Jan. 4, 2002)

Abstract

Twenty two steranes and 17 triterpanes were detected in the Cretaceous–Tertiary (K/T) boundary sediments at Kawaruppu, Hokkaido, Japan. These steranes and triterpanes were detected at a concentration level of 0.001 − 0.1nmol g^{-1}. Their concentrations were smaller within the K/T boundary claystone than in the sediments above and below the claystone, which are likely related to the large biomass extinction event at the end of the Cretaceous. The concentrations of 5α–cholestane and the relative ones of 17α,21β–hopane in the sediments above the boundary claystone were about a half of those in the sediments below the claystone, whereas those of 5α–ergostane, 5α–stigmastane, and oleanane in the sediments above were less than a half abundance level of those in the sediments below the claystone. Diastereomer ratios of steranes and triterpanes were nearly constant over the sediments. No tricyclic alkanes were detected in the sediments.

INTRODUCTION

Steranes and triterpanes have been widely found in geological samples (Seifert and Moldowan, 1979 ; Barrick and Hedges, 1981 ; Suzuki and Shimada, 1983 ; ten Haven et al., 1985 ; Sinninghe Damsté et al., 1995 ; Rangel et al., 2000). They are most popular and useful biomarkers for maturity indices of sediments, oils and coals (Mackenzie, et al., 1980 ; Norgate, et al., 1999) and for biological source materials (Moldowan, et al., 1985 ; Mostafa and Younes, 2001).

Massive extinctions of organisms ranging from dinosaurs to marine plankton occurred at the end of the Cretaceous (approximately 65 million years ago). The extinction event must have left some signatures of biomolecules in the Cretaceous–Tertiary (K/T) boundary sediments. Hopanes in K/T sediments at Stevns Klint were analyzed (Simoneit and Bellar, 1985 ; 1987 ; Meyers and Simoneit, 1989), and it was shown that the sediments were diagenetically immature by $22S/R$ ratios of 17α, 21β–hopanes. Aromatic compounds, which are thought to be derived from triterpanes, were characterized by analysis of K/T coals in Canada and Germany (Heppenheimer, et al., 1992). On the other hand, steranes in K/T sediments have been analyzed little.

---

* Coordination Center for Research and Education, The Graduate University for Advanced Studies, Shonan Village, Hayama, Kanagawa, 240–0193, Japan
** Department of Chemistry, University of Tsukuba, Tsukuba 305–8571, Japan
*** Kochi Gakuen College, Kochi, 780–0955, Japan

K/T boundary sediments occur near Kawaruppu, Hokkaido, Japan. The sediments include 14 cm thick boundary claystone. Such a thick boundary claystone has not been found at other sites (e. g., Stevns Klint in Denmark, Gubbio in Italy, Woodside Creek in New Zealand, and Caravaca in Spain). Therefore, the boundary claystone at Kawaruppu has provided thinly divided samples for detailed studies of fossils (Saito *et al.*, 1986 ; Kaiho and Saito, 1986 ; Kaiho, 1992), inorganic constituents (Kajiwara and Kaiho, 1992 ; Tazaki, *et al.*, 1992), and organic compounds (Mita *et al.*, 1996, 1998 ; Mita and Shimoyama, 1999a ; 1999b ; Katsumata and Shimoyama, 2000 ; Shimoyama, *et al.*, 2001 ; Shimoyama and Yabuta, 2002).

We had analyzed mono– and bicyclic alkanes and diamondoid hydrocarbons in the K/T sediments at Kawaruppu in a previous study (Shimoyama and Yabuta, 2002). Concentrations of these compounds were related to the biomass extinctions at the Cretaceous end. Therefore, for the next step of a cyclic alkane study in the K/T sediments, we analyzed for tetra– and pentacyclic alkanes (esp. steranes and hopanes) as well as tricyclic alkanes. Here we report the results of the analyses and describe characteristic distributions of these compounds 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, and its location and lithology were reported by Saito *et al.* (1986) and Kaiho and Saito (1986). The sedimentary sequence at this locality 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 study and their 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.

Analysis

For each analysis, 1g of a pulverized sediment sample was extracted with 5 ml of a mixture of benzene and methanol (4 : 1 by vol.) for 30 min by sonication and the supernatant after centrifugation was recovered. This extraction and centrifugation process was repeated 3 times. The supernatants were combined, concentrated under reduced pressure, and applied onto a silica gel column (130 mm × 10 mm i. d. ; Keiselgel–60, Merk). Compounds were eluted from the column with 10 ml hexane. The hexane solution was concentrated to 50 μl under a nitrogen flow, and analyzed by a gas chromatograph (GC) combined with a mass spectrometer (MS) (Agilent Technologies, HP 6890–5973 System). The GC was equipped with a HP–5MS capillary column (30 m × 0.25 mm i. d.). The oven temperature was programmed to hold at 50°C for 1 min, to increase 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}, and to hold for 18.5 min at 300°C. The mass spectra were acquired every 0.5s over m/z 40 to 510 in an electron impact ionization mode at 70 eV. Identification and quantification of (20*R*)–5α–cholestane were made by comparison of its peak retention time on a mass fragmentogram and a mass spectrum, and a peak area on the fragmentogram, respectively, with those of the standard compound. For other compounds, identification was made by comparison of relative peak retention times on their mass fragmentograms and mass spectra with data in literature by Seifert and Moldowan (1978, 1979), Philp (1985), Zumberge (1993), and Nytoft and Bojesen–Koefoed (2001). Relative concentrations of these compounds were determined by comparing their peak areas on the fragmentograms.

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 before use to eliminate organic contaminants. A procedural blank was carried out with1g pre–ignited sea sand powder and it was found that there was no significant contamination during the analysis.

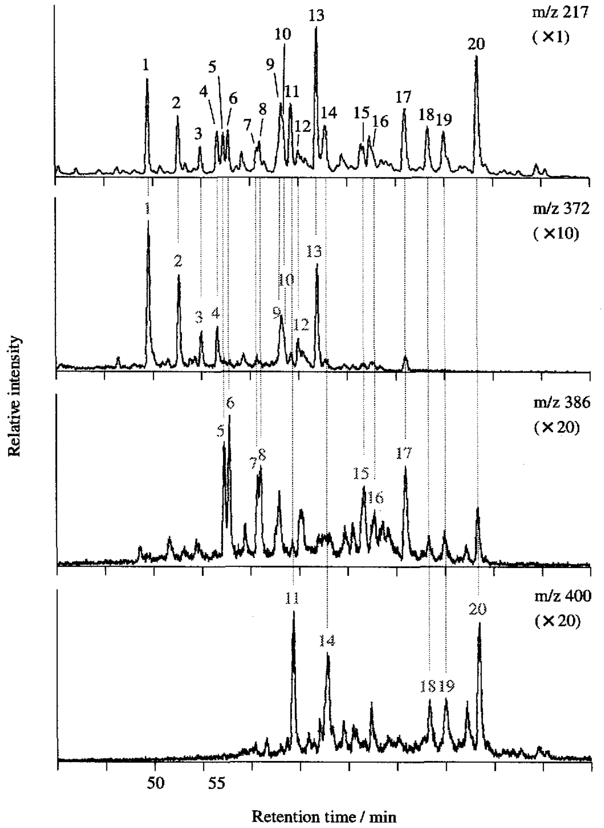

Fig. 1 Mass fragmentograms of m/z 217 for steranes, m/z 372 for cholestanes and diacholestanes, m/z 386 for ergostantanes and diaergostanes, and m/z 400 for stigmastanes and diastigmastanes in the K/T boundary sediment (−10 cm) at Kawaruppu. Peak numbers correspond to those in Table 1.

RESULTS AND DISCUSSION

Identification and concentrations

Tricyclic alkanes were searched for but not detected in the K/T sediments, using their characteristic mass fragment ions of m/z 135, 149, 163, 177, 191, and 219.

Fig. 1 shows mass fragmentograms for steranes recovered from the sediment (−10 cm) below the boundary claystone. The fragmentogram of m/z 217 corresponds to a major fragment ion of steranes. The other fragmentograms are of m/z 372 for molecular ions of diacholestanes and cholestanes, m/z 386 for those of diaergostanes and ergostanes, and m/z 400 for those of diastigmastane and stigmastanes. Diasteranes showed a relatively high intensity of m/z 259 (e. g., peak No. 2 in Fig. 2). Mass spectra of most steranes showed their characteristic ions, $(M–CH_3)^+$ (*e. g.*, peak Nos. 2 and 13 in Fig. 2). Thus, possible 22 steranes were identified and listed in Table 1. They included 3 rearranged steranes tentatively identified (peak Nos. 6, 7, and 14 in Fig. 1).

Fig. 3 shows mass fragmentograms for triterpanes recovered from the sediment (−10 cm) below the boundary claystone. The fragmentogram of m/z 191 corresponds to a major fragment ion of triterpanes. The other fragmentograms are of m/z 370 for molecular ions of trisnorhopanes, m/z 398 for those of norhopanes and norneohopane, m/z 412 for those of hopanes, moretanes, oleanane, and gammacerane, m/z 426 for those of homohopanes, m/z 440 for those of bishomohopanes, and m/z 454 for those of trishomohopanes. Norhopanes showed a relatively high intensity of m/z 177 (e. g., peak No. 23 in Fig. 2) and homomoretane of m/z 205 (peak No. 33 in Fig. 2) compared with those of other triterpanes. Mass spectra of most triterpanes showed their characteristic ions, $(M - CH_3)^+$ (e. g., peak Nos. 23,

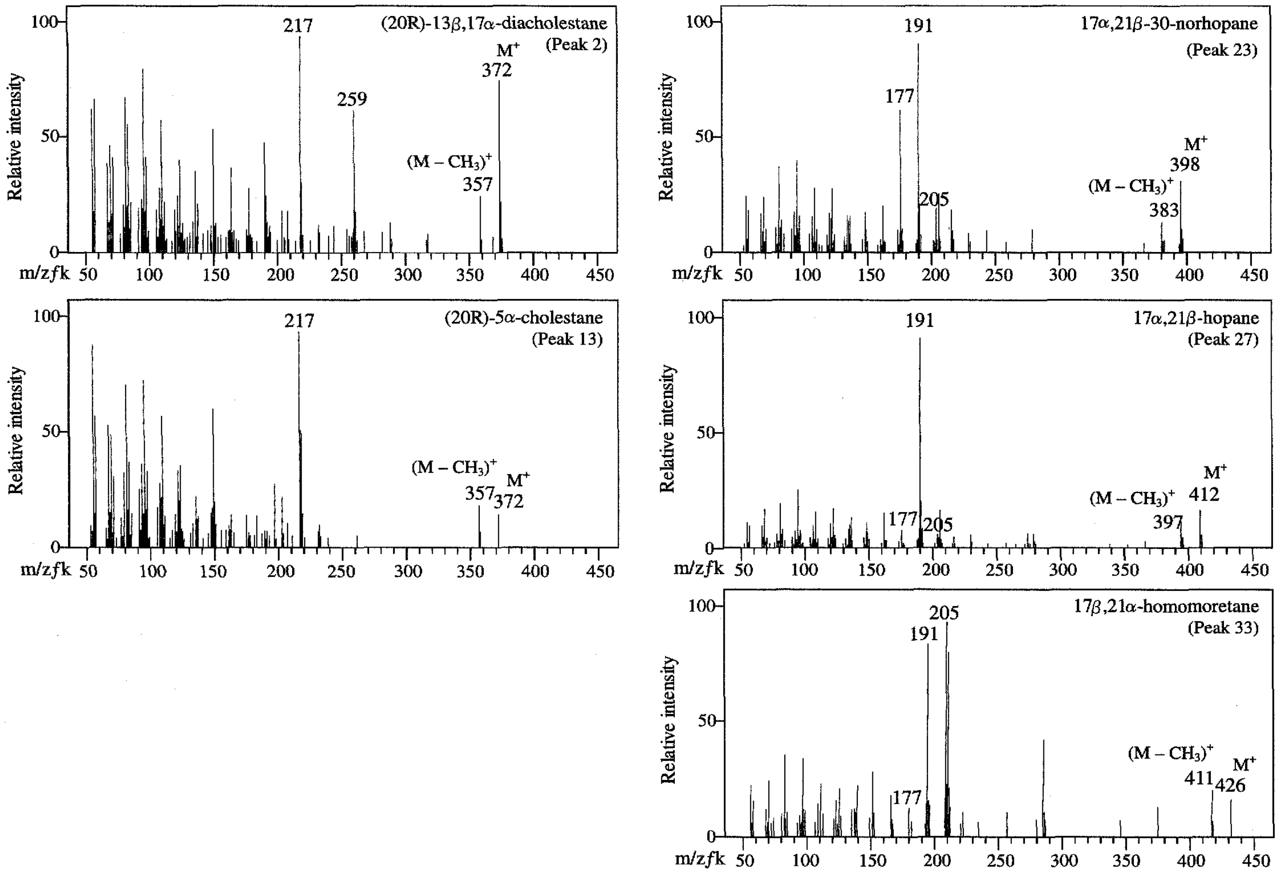

Fig. 2 Mass spectra of steranes and triterpanes in the K/T boundary sediment (−10 cm) at Kawaruppu. Peak numbers correspond to those in Fig. 1 and Table 1.

27 and 33 in Fig. 2). Thus, 17 triterpanes were identified and listed in Table 1.

Concentrations of (20R)–5α–cholestane were in a range of 0.071–0.096 (mean value 0.083, henceforth m.v. stands for mean value) in sediments above, 0.005–0.074 (m.v. 0.019) within, and 0.073–0.23 nmol g^{-1} (m.v. 0.154 nmol g^{-1}) below the boundary claystone (Table 2). These concentrations were at one order of magnitude larger than those of mono– and bicyclic alkanes and diamondoid hydrocarbons in the same sediments (Shimoyama and Yabuta, 2002). Whereas, they were at one order of magnitude less than those of individual *n*–alkanes (Mita and Shimoyama, 1999a). Relative concentrations of (20*R*)–5α–ergostane, (20*R*)–5α– stigmastane, oleanane, and 17α, 21β–hopane were estimated (Table 2). These steranes and triterpanes were likely present at the same concentration level, or at one order of magnitude less than 5α–cholestane, judging from their peak areas on the mass fragmentograms of *m*/*z* 191 and 217, respectively.

Depth profile

The concentrations of 5α–cholestane and relative ones of 5α–ergostane, 5α–stigmastane, oleanane, and 17α, 21β–hopane were plotted with depth of the sediments (Fig. 4a and b). Their concentrations in the boundary claystone were around 10% levels of those in the sediments below the claystone. These small concentrations roughly continued to the second top sediment in the boundary claystone and increased slightly at the top. The concentrations in the sediment above the boundary claystone were nearly equal to those in the top sediment. The concentrations of 5α–cholestane and the relative ones of 17α, 21β–hopane in

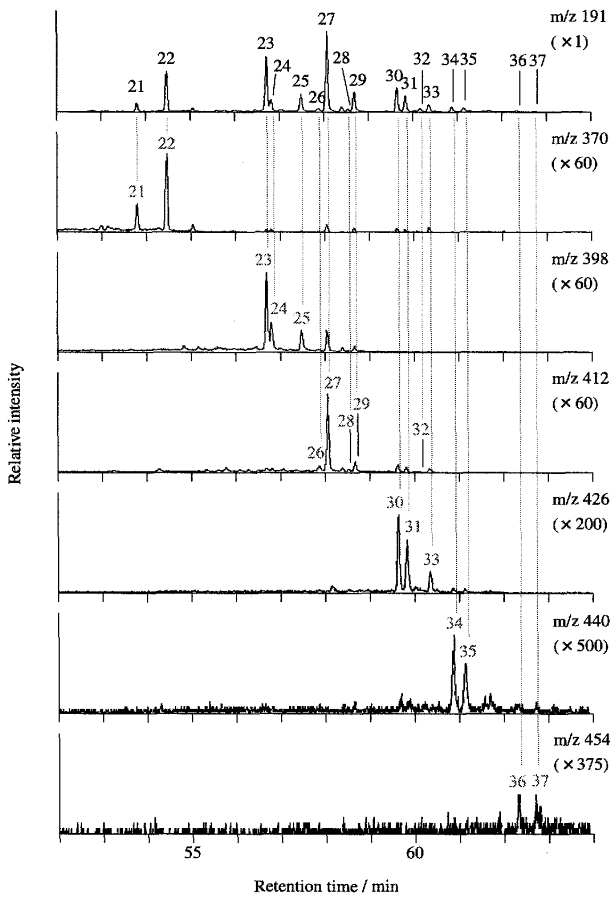

Fig. 3 Mass fragmentograms of *m/z* 191 for triterpanes, *m/z* 370 for trisnorhopanes, *m/z* 398 for norhopanes, and *m/z* 412 for hopanes, moretane, oleanane, and gammacerane, m/z 426 for homohopanes and homomoretane, *m/z* 440 for bishomohopanes, and *m/z* 454 for trishomohopanes in the K/T boundary sediment (−10 cm) at Kawaruppu. Peak numbers correspond to those in Table 1.

the sediments above the claystone were about a half of those in the sediments below it, whereas those of 5α-ergostane, 5α-stigmastane, and oleanane in the sediments above the claystone were less than a half abundance level of those in the sediments below it. These depth profiles did not coincide with that of total organic carbon contents (Mita *et al.*, 1996 ; Mita and Shimoyama, 1999a), showing that the concentrations of steranes and triterpanes were rather depleted compared to total organic carbon contents within the boundary claystone.

Table 1. Steranes and triterpanes identified in the K/T boundary sediments at Kawaruppu.

Peak No.	Compound	Molecular weight
	Steranes (Base m/z=217)	
1	(20*S*)-13β,17α-diacholestane	372
2	(20*R*)-13β,17α-diacholestane	372
3	(20*S*)-13α,17β-diacholestane	372
4	(20*R*)-13α,17β-diacholestane	372
5	(20*S*)-13β,17α-diaergostane	386
6	rearranged C28 sterane	386
7	rearranged C28 sterane	386
8	(20*R*)-13β,17α-diaergostane	386
9	(20*S*)-5α-cholestane	372
10	(20*R*)-5β-cholestane	372
11	(20*S*)-13β,17α-diastigmastane	400
12	(20*RS*)-5α,14β,17β-cholestane	372
13	(20*R*)-5α-cholestane	372
14	rearranged C29 sterane	400
15	(20*S*)-5α-ergostane	386
16	(20*R*)-5β-ergostane and/or	386
	(20*RS*)-5α,14β,17β-ergostane	386
17	(20*R*)-5α-ergostane	386
18	(20*S*)-5α-stigmastane	400
19	(20*R*)-5β-stigmastane and/or	400
	(20*RS*)-5α,14β,17β-stigmastane	400
20	(20*R*)-5α-stigmastane	400
	Triterpanes (Base m/z=191)	
21	18α,21β-22,29,30-trisnorhopane	370
22	17α,21β-22,29,30-trisnorhopane	370
23	17α,21β-30-norhopane	398
24	18α-30-norneohopane	398
25	17β,21α-30-normoretane	398
26	oleanane	412
27	17α,21β-hopane	412
28	17α,21α-hopane	412
29	17β,21α-moretane	412
30	(22*S*)-17α,21β-30-homohopane	426
31	(22*R*)-17α,21β-30-homohopane	426
32	gammacerane	412
33	17β,21α-homomoretane	426
34	(22*S*)-17α,21β-30,31-bishomohopane	440
35	(22*R*)-17α,21β-30,31-bishomohopane	440
36	(22*S*)-17α,21β-30,31,32-trishomohopane	454
37	(22*R*)-17α,21β-30,31,32-trishomohopane	454

Depth profiles of other compounds were also roughly similar to those of the steranes and triterpanes in Fig. 4.

The large concentration decrease of these steranes and triterpanes over the K/T boundary is probably due to a large decrease in the input of their precursors into the boundary claystone, as observed for mono- and bicyclic alkanes (Fig. 4c, Shimoyama and Yabuta, 2002) and *n*-alkanes, pristane, and phytane

Table 2. Concentrations of steranes and triterpanes in the K/T boundary sediments at Kawaruppu.

Relative depth /cm	Steranes			Triterpanes	
	(20*R*)-5α-cholestane†	(20*R*)-5α-ergostane	(20*R*)-5α-stigmastane	oleanane	17α,21β-hopane
Tertiary					
495	0.096	0.024	0.035	0.007	0.287
225	0.071	0.019	0.039	0.008	0.270
120	0.077	0.023	0.039	0.010	0.285
60	0.081	0.034	0.044	0.011	0.292
40	0.091	0.037	0.051	0.011	0.300
Boundary claystone					
12.7 − 13.7	0.074	0.033	0.048	0.005	0.133
11.7 − 12.7	0.021	0.008	0.013	0.002	0.042
10.6 − 11.7	0.022	0.009	0.010	0.002	0.049
8.7 − 10.6	0.009	0.003	0.003	0.001	0.016
7.5 − 8.7	0.007	0.003	0.002	0.001	0.016
5.5 − 6.3	0.019	0.006	0.007	0.001	0.033
4.3 − 5.5	0.005	0.002	0.002	0.001	0.011
2.8 − 4.3	0.008	0.003	0.004	0.001	0.021
1.8 − 2.8	0.017	0.005	0.006	0.001	0.035
0.8 − 1.8	0.010	0.004	0.006	0.001	0.028
0.0 − 0.8	0.018	0.007	0.009	0.002	0.048
Cretaceous					
−3 − 0	0.073	0.021	0.033	0.009	0.252
−10	0.227	0.137	0.153	0.033	0.550
−85	0.188	0.108	0.142	0.032	0.504
−165	0.158	0.088	0.114	0.030	0.517
−235	0.133	0.071	0.097	0.022	0.407
−395	0.144	0.096	0.130	0.046	0.534

† ; Concentrations were determined by standard.
Relative concentrations of the other compounds were estimared by comparison of peak areas.

(Fig. 4d, Mita and Shimoyama, 1999a). Differences in increase among compounds from the claystone to the sediments above the claystone might have been caused by differences in biological source. Hopanes are derived mainly from bacteria (Ourisson, *et al.*, 1979 ; Rohmer, *et al.*, 1980). Their concentrations (Table 2) and depth profiles (Fig. 4b) are probably related to bacteria populations in the K/T sediments. Stigmastanes and oleanane are known to be derived from higher plants, particularly, oleanane from vascular plants (Grantham, *et al.*, 1983 ; ten Haven and Rullkotter, 1988 ; Moldowan, *et al.*,1994). Molecular distribution of *n*-alkanes (Mita and Shimoyama, 1999a) and palynological study (Saito, *et al.*, 1986) indicated the devastation of vascular plants at the K/T boundary time at Kawaruppu. A similar environment was reported in the interior of western North America (Tschudy, *et al.*, 1984). Therefore, the small concentrations of stigmastane and oleanane in the claystone and their relatively low recoveries in the sediments above the claystone were likely related to the devastation of vascular plants due to the massive extinctions.

Diagenetic effect

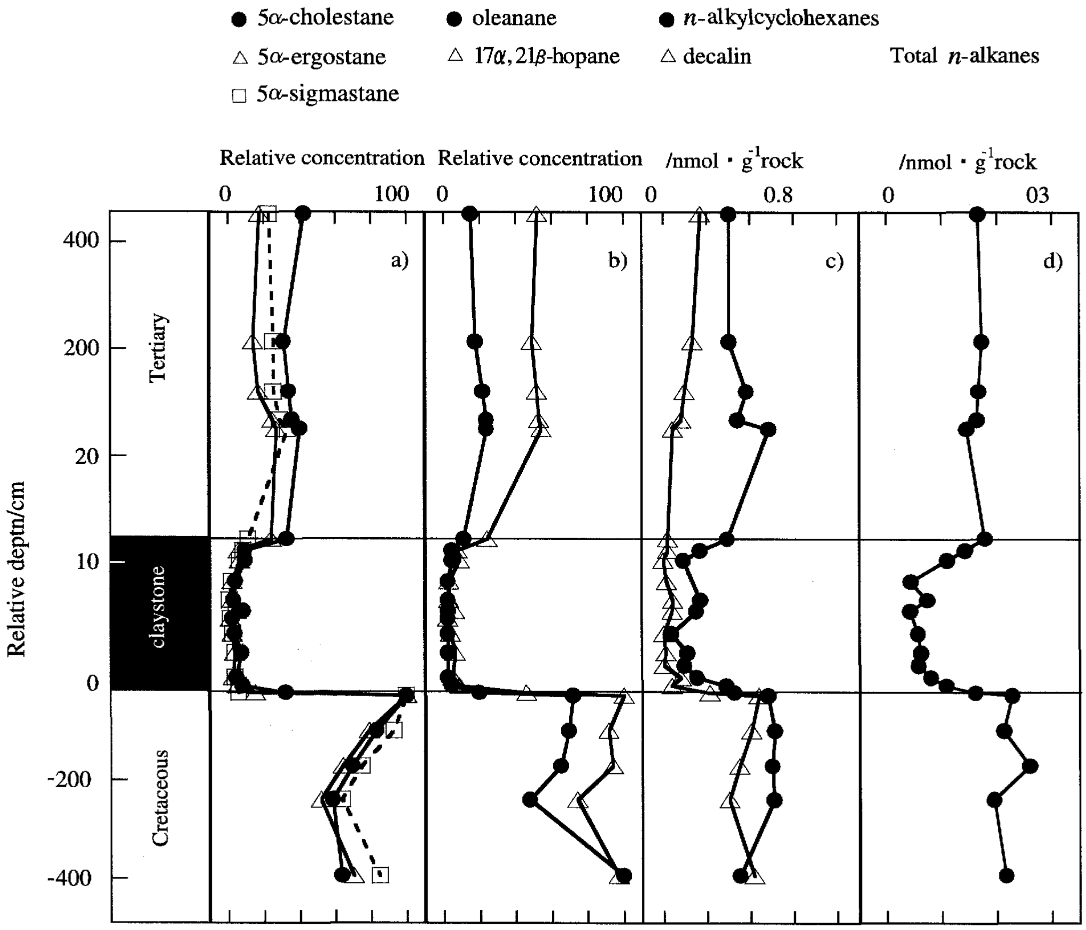

Fig. 4 Depth profiles of a) relative concentrations of (20R)–5α–cholestane, (20R)–5α–ergostane and (20R)–5α–stigmastane, b) oleanane and 17α, 21β–hopanes, c) concentrations of *n*–alkylcyclohexanes and decalins (Shimoyama and Yabuta, 2001), and d) total *n*–alkanes (C12–36) (Mita and Shimoyama, 1999a) in the K/T boundary sediments at Kawaruppu. A maximum concentration was set to 100 in the scale of the relative concentrations.

The diastereomer ratios of 5α–stigmastane (20*S*/(20*S* + 20*R*)) and 17α,21β–30,31–bishomohopane (22*S*/(22*S* + 22*R*)) were calculated and shown in Table 3. The diastereomer ratios of stigmastane were in a range of 0.26 – 0.35 (m.v. 0.30) above, 0.19 – 0.33 (m.v. 0.26) within, and 0.20 – 0.34 (m.v. 0.27) below the boundary claystone. The diastereomer ratios of bishomohopane were 0.55 – 0.59 (m.v. 0.57), 0.50 – 0.56 (m.v. 0.51), and 0.54 – 0.61 (m.v. 0.58), respectively. The two ratios were nearly constant individually over the sediments above, within and below the boundary claystone (Fig. 5), showing similar maturity levels of these compounds. Similar results were observed over the K/T sediments at Kawaruppu by the ratios of β– to α–alkylated PAHs (Mita and Shimoyama, 1999b), β– to α–methyldibenzothiophenes (Katsumata, *et al.*, 2000), alkylmaleimides (Shimoyama, *et al.*, 2001), and cyclic alkanes and diamondoid hydrocarbons (Shimoyama and Yabuta, 2002). 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. In addition, it supports the interpretation that the small concentrations of these steranes and

Table 3 The diastereomer ratios of sterane and triterpane in the K/T boundary sediments at Kawaruppu.

Relative depth/cm	Ratios	
	5α−stigmastane 20*S*/(20*S*+20*R*)	17α,21β−30,31−bishomohopane 22*S*/(22*S*+22*R*)
Tertiary		
495	0.33	0.59
225	0.26	0.59
120	0.28	0.55
60	0.35	0.57
40	0.28	0.57
Boundary claystone		
12.7−13.7	0.26	0.56
11.7−12.7	0.19	0.50
10.6−11.7	0.23	0.50
8.7−10.6	0.25	−
7.5− 8.7	0.30	0.50
5.5− 6.3	0.22	0.50
4.3− 5.5	0.33	0.50
2.8− 4.3	0.20	0.50
1.8− 2.8	0.33	0.50
0.8− 1.8	0.25	0.50
0.0− 0.8	0.25	0.50
Cretaceous		
−3−0	0.34	0.61
−10	0.27	0.57
−85	0.29	0.57
−165	0.26	0.60
−235	0.26	0.60
−395	0.20	0.54

− ; not determined

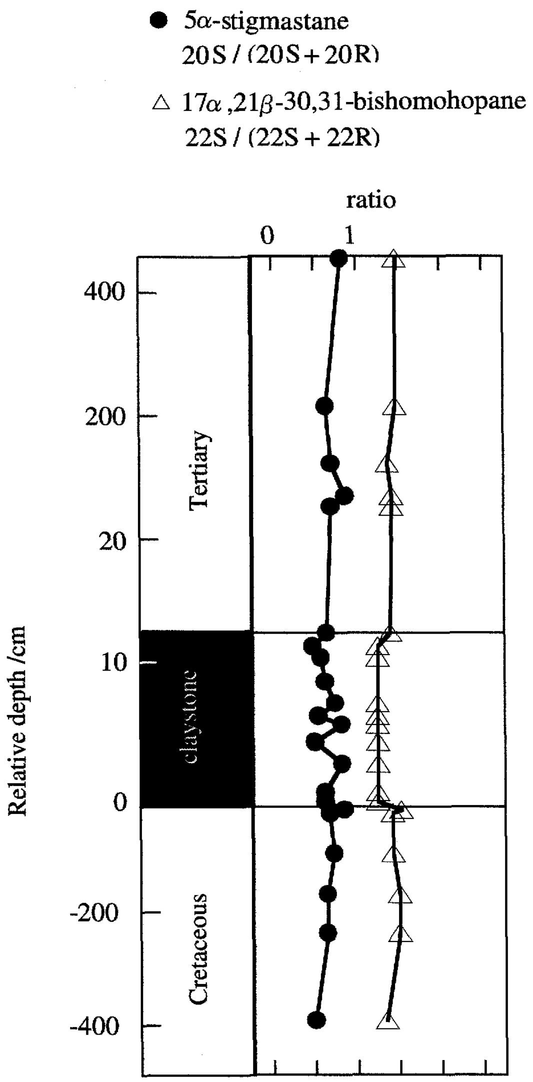

Fig. 5 Depth profiles of diastereomer ratios of 5α−stigmastane (20*S*/(20*S*+20*R*)) and 17α,21β−30, 31−bishomohopane (22*S*/(22*S*+22*R*)) in the K/T boundary sediments at Kawaruppu.

triterpanes within the boundary claystone compared to above and below it were not caused by the selective degradation by clays but caused by the small biomass input into the claystone related to the large biomass extinction event.

CONCLUSIONS

The K/T boundary sediments at Kawaruppu were analyzed for steranes and triterpanes as well as tricyclic alkanes. As a result, 22 steranes and 17 triterpanes were detected at a concentration level of sub−nmol to pmol g^{-1}. However, no tricyclic alkane was detected. Concentrations of most steranes and triterpanes were found to relate to the large biomass extinctions at the end of the Cretaceous. Terrestrial plant devastation was observed by small concentrations of stigmastane and oleanane within the boundary claystone and in the sediment above the claystone. The diastereomer ratios of stigmastanes and bisnorhopanes were nearly constant over the sediments, indicating that diagenetic effect to these compounds was probably unchanged over the sediments. The result of this study coincides with those of other hydrocarbons, such as aliphatic (Mita and Shimoyama, 1999 a) and polyaromatic hydrocarbons (Mita and Shimoyama, 1999b), and mono- and bicyclic alkanes (Shimoyama and Yabuta, 2001).

Acknowledgements - We are grateful to Prof. K. Fukushima of Shinshu University and an anonymous referee for their useful comments to improve this manuscript. This work was supported by the Grant-in-Aid for Scientific Research (B) No. 11440166 from the Ministry of Education, Science, Sports and Culture, Japan and the Research Grant for Fellowship No. 00007064 to H. Y. from Japanese Society for the Promotion of Science.

REFERENCES

Barrick, R. C. and Hedges, J. I. (1981) Hydrocarbon geochemistry of the Puget Sound region-II. Sedimentary diterpenoid, steroid and triterpenoid hydrocarbons. *Geochim. Cosmochim. Acta* **45**, 381-392.

Grantham, P. J., Posthuma, J. and Baak, A. (1983) Triterpanes in a number of Far-Eastern crude oils. In: M. Bjorøy *et al.* (eds.), *Advances in Organic Geochemistry 1981*. 675-683. J. Wiley & Sons.

Heppenheimer, H., Steffens, K., Püttmann, W. and Kalkreuth, W. (1992) Comparison of resinite-related aromatic biomarker distributions in Cretaceous-Tertiary coals from Canada and Germany. *Org. Geochem.* **18**, 273-287.

Kaiho, K. and Saito, T. (1986) Terminal Cretaceous sedimentary sequence recognized in the northernmost Japan based on planktonic foraminifera evidence. *Proc. Jpn. Acad.* **62** (B), 145-148.

Kaiho, K. (1992) A low extinction rate of intermediate-water benthic foraminifera at Cretaceous/Tertiary boundary. *Mar. Micropaleontol.* **18**, 229-259.

Kajiwara, Y. and Kaiho, K. (1992) Oceanic anoxia at the Cretaceous/Tertiary boundary supported by the sulfur isotope record. *Paleogeogr. Paleoclim. Paleoecol*. **99**, 151-162.

Katsumata, H. and Shimoyama, A. (2000) Thiophenes in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan. *Geochem. J*. **35**, 67-76.

Mackenzie, A. S., Patience, R. L., Maxwell, J. R., Vandenbroucke, M. and Durand, D. (1980) Molecular parameters of maturation in the Toarcian shales, Paris basin, France: I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* **44**, 1709-1721.

Meyers and Simoneit (1989) Global comparisons of organic matter in sediments across the Cretaceous/Tertiary boundary. *Org. Geochem.* **16**, 641-648.

Mita, H., Shimoyama, A. and Kajiwara, Y. (1996) Search for extraterrestrial amino acids in sediments at the Cretaceous/Tertiary boundary in Kawaruppu, Hokkaido, Japan. *Geochem. J.* **30**, 89-98.

Mita, H., Fukunaga, N. and Shimoyama, A. (1998) Characterization of dicarboxylic acids in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan and comparison with those of carbonaceous chondrites. *Geochim. Cosmochim. Acta* **62**, 3695-3702.

Mita, H. and Shimoyama, A. (1999a) Characterization of n-alkanes, pristane and phytane in the Cretaceous/Tertiary boundary in Kawaruppu, Hokkaido, Japan. *Geochem. J*. **33**, 285-294.

Mita, H. and Shimoyama, A. (1999b) Distribution of polycyclic aromatic hydrocarbons in the K/T boundary sediments at Kawaruppu, Hokkaido, Japan. *Geochem. J.* **33**, 305-315.

Moldowan, J. M., Seifert, W. K. and Gallegos,

E. J. (1985) Relationships between petroleum composition and depositional environment of petroleum source rocks. *Am. Assoc. Pet. Geol. Bull.* **69**, 1255–1268.

Moldowan, J. M., Dahi, J., Huizinga, B. J., Fago, F. J., Hickey, L. J., Peakman, T. M., and Taylor, D. W. (1994) The molecular fossil record of oleananes and its relation to angiosperms. *Science* **265**, 768–771.

Mostafa, A. R. and Younes, M. A. (2001) Significance of organic matter in recording paleoenvironmental conditions of the Safa Formation coal sequence, Maghara Area, North Sinai, Egypt. *International Journal of Coal Geology* **47**, 9–21.

Norgate, C. M., Boreham, C. J. and Wilkins, A. J. (1999) Changes in hydrocarbon maturity indices with coal rank and type, Buller Coalfield, New Zealand. *Org. Geochem*. **30**, 985–1010.

Nytoft, H. P. and Bojesen–Koefoed, J. A. (2001) 17α,21α–hopanes : natural and synthetic. *Org. Geochem*. **32**, 841–856.

Ourisson, G., Albrecht, P. and Rohmer, M. (1979) The hopanoids, paleochemistry and biochemistry of a group of natural products. *Pure Appl. Chem*. **51**, 709–729.

Philp, R. P. (1985) *Fossil fuel biomarkers. Applications and spectra*. Elsevier, Amsterdam.

Rangel, A., Parra, P. and Nino, C. (2000) The La Luna formation : chemostratigraphy and organic facies in the Middle Magdalena Basin. *Org. Geochem*. **31**, 1267–1284.

Rohmer, M., Dastillung, M. and Ourisson, G. (1980) Hopanoids from $C_{30}-C_{35}$ in recent muds, chemical markers for bacterial activity. *Naturwissenschaft*. **67**, 456–458.

Saito, T., Yamanoi, T. and Kaiho, K. (1986) End–Cretaceous devastation of terrestrial flora in the boreal Far East. *Nature* **323**, 253–255.

Seifert, W. K. and Moldowan, J. M. (1978) Applications of steranes, terpanes, and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta* **42**, 77–95.

Seifert, W. K. and Moldowan, J. M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. *Geochim. Cosmochim. Acta* **43**, 111–126.

Shimoyama, A. and Yabuta, H. (2002) Mono–and bicyclic alkanes and diamondoid hydrocarbons in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan. *Geochem. J., submitted.*

Shimoyama, A., Kozono, M., Mita, H., and Nomoto, S. (2001) Maleimides in the Cretaceous/Tertiary boundary sediments at Kawaruppu, Hokkaido, Japan. *Geochem. J., in press.*

Sinninghe Damsté, J. S., Frewin, N. L., Kenig, F. and De Leeuw, J. W. (1995) Molecular indicators for palaeoenvironmental change in a Messinian evaporitic sequence (Vena del Gesso, Italy). I : Variations in extractable organic matter of ten cyclically deposited marl beds. *Org. Geochem.* **23**, 471–483.

Simoneit, B. R. T. and Bellar, H. R. (1985) Lipid geochemistry of Cretaceous/Tertiary boundary sediments, Hole 577, Deep Sea Drilling Project Leg 86. In : G. R. Heath *et al.* (eds.), *Init. Reports DSDP*. Vol. 86, pp. 671–674.

Simoneit, B. R. T. and Bellar, H. R. (1987) Lipid geochemistry of Cretaceous/Tertiary boundary sediments, Hole 605, Deep Sea Drilling Project Leg 93, and Stevns Klint. Denmark. In : J. Van Hinte *et al.* (eds.), *Init. Reports* DSDP. Vol. 93, pp. 1211–1221.

Suzuki, N. and Shimada, I. (1983) Considerations in epimerization of sterane and triterpane as indicators of thermal history of sedimentary rocks. *Journal of Sedimentological Society of Japan* **17/18/19**, 47–55 (in Japanese with English abstract).

Tazaki, K., Aratani, M., Yanokura, M., Kaiho,

K. and Noda, S. (1992) Singularity of clay minerals and iridium concentration at Cretaceous–Tertiary boundary. *Nendo-kagaku (Clay Science)* **32**, 86–96 (in Japanese with English abstract).

ten Haven, H. L., de Leeuw, J. W. and Schenck, P. A. (1985) Organic geochemical studies of a Messinian evaporitic basin, northern Apennines (Italy) I : Hydrocarbon biological markers for hypersaline environment. *Geochim. Cosmochim. Acta* 49, 2181–2191.

ten Haven, H. L. and Rullkotter, J. (1988) The diagenetic fate of taraxer-14-ene and oleanane isomers. *Geochim. Cosmochim. Acta* **52**, 2543–2548.

Tschudy, R. H., Pillore, C. L., Orth, C. J., Gilmore, J. S. and Knight, J. D. (1984) Disruption of the terrestrial plant ecosystem at the Cretaceous/Tertiary boundary, western interior. *Science* **225**, 1030–1032.

Zumberge, J. E. (1993) Organic geochemistry of Estancia Vieja oils, Rio Negro Norte Block. Correlation with other Neuquen basin, Argentina, oils. In : M. H. Engel and S. A. Macko (eds.), *Organic Geochemistry, principles and applications.* Plenum Press, New York. pp. 461–471.