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Abrupt and massive influx of terrestrial biomarkers into the marine environment at the Cretaceous–Tertiary boundary, Caravaca, Spain

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Abstract

The mass extinction at the Cretaceous–Tertiary (K/T) boundary ca. 65 million years ago caused a major change in the nature and abundance of global life in Earth history. We present the first vertical high-resolution records of molecular distributions of *n*-fatty acids across the K/T boundary at Caravaca (Spain). The results reveal that the first basal thin horizon (0 to +0.5 cm; 0=K/T boundary) of the K/T boundary–clay layer showed as much as a ~35-fold increase in concentrations of terrestrial long-chain *n*-fatty acids ($\geq C_{20}$), representative of an eight-fold increase in mass accumulation rate, compared with the subjacent Cretaceous layers. Thereafter concentrations rapidly declined back to almost pre-boundary values within +3 cm above the K/T boundary. The abrupt increase in supply of terrestrial organic matter into the marine environment at the K/T boundary could have been caused by an enhanced riverine flux, probably due to heavy rains associated with global warming, combined with enhanced fragments of terrestrial higher-plants withered by acid rain and/or by temporal darkness and cooling.

Keywords: Cretaceous–Tertiary boundary; biomarker; fatty acid; terrestrial influx

1. Introduction

The massive extinction of organisms at the end of the Cretaceous (approximately 65 million years ago) is one of the most significant biological events in Earth history. Specific organic compounds (biomarkers) are indicative of specific biogenic sources. Studies of biomarker distributions can help to identify the organisms

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contributing to sedimentary organic matter. Thus molecular organic geochemistry can be regarded as another, complementary palaeontological approach (Yamamoto et al., 1996). Organic geochemical studies of the Cretaceous–Tertiary (K/T) boundary sediments have found evidence for wildfires (Wolbach et al., 1985, 1988; Venkatesan and Dahl, 1989; Heymann et al., 1994, 1998; Mita and Shimoyama, 1999; Arinobu et al., 1999). Other organic geochemical studies examined microbial hydrocarbons and fatty acids and terrestrial resin acids in the sediments above and below the claystone at Stevns Klint, Denmark (Meyers and Simoneit, 1990).

We provide here the first high-resolution profiles of changes in molecular distributions of *n*-fatty acids across the K/T boundary at Caravaca, which represents one of the most complete and least disturbed K/T sections in the world (MacLeod and Keller, 1991; Canudo et al., 1991). The results of our study provide the first detailed information about the timing and scale of transport of terrestrial organic substances into the marine environment across the K/T boundary.

2. Sample description

The Caravaca K/T section is located in the Betic Cordillera of southeastern Spain (lat. 38°04′35″N, long. 1°52′40″W). In the K/T section at Caravaca, marlstones of Cretaceous age are lithologically separated from marlstones of Tertiary age by a thick (~7–10 cm) dark clay–marl bed (the boundary–clay layer). Within the boundary–clay layer, a 1–2 mm, rust-orange, basal layer referred to as the red layer (or fallout lamina) contains the Ir spike (Smit and Ten Kate, 1982), and is underlain by a ~3 mm greenish transition layer. In this paper, the base of the red layer is defined as the K/T boundary; its depth has been set to 0 cm, with the depths of lower and upper strata being described relative to it. The Caravaca section represents paleodepths of 200 to 1000 m (MacLeod and Keller, 1994; Coccioni and Galeotti, 1994).

We collected the sedimentary rock samples for biomarker analyses after removing the surface of outcrop up to about 40–50 cm. Weathering is low because soft marly rocks are constantly removed in the small creek where samples were taken. This is typical of bad-lands in this Mediterranean climatic region, with no vegetal cover on the exposures studied. The samples were carefully sliced off from −21 cm below to +40 cm above the defined K/T boundary. The interval from −21 cm to +40 cm encompasses the last 6.8 kyr of the Cretaceous and the first 29.9 kyr of the Tertiary (Arinobu et al., 1999).

3. Methods

The surface of rock chips was cleaned twice by ultrasonic agitation with a benzene and methanol mixture (6:4 by volume) for two minutes. Samples (~35 g) were treated with 6 M HCl to remove carbonate. The residues were extracted three times with a benzene and methanol mixture (in the same proportions) by ultrasonic agitation. The extracts were centrifuged at 3000 rpm and the supernatants were combined and subsequently evaporated to dryness under reduced pressure by rotary evaporation. The dried extract was dissolved in *n*-hexane and ether (9:1 by volume) and transformed to a separating funnel. KOH solution and water were also added to the separating funnel. The extracts were fractionated into neutral and acidic compounds by liquid–liquid separation. The acidic component was taken into a 10-ml glass ampoule. After evaporation of the solvent, 0.5 ml of ~14% BF_3-methanol were added to the ampoule, and the ampoule was sealed and heated at 100 °C for 30 min. The methyl esters were analyzed by gas chromatography–mass spectrometry (GC–MS). The oven temperature was programmed to hold at 60 °C for 2 min, then to rise from 60 to 120 °C at 30 °C/min and from 120 to 310 °C at 5 °C/min, and finally to hold isothermally for 18 min.

4. Results

The acid fraction of total lipids from sedimentary rock samples across the K/T boundary at Caravaca was analyzed by GC–MS. Fig. 1 gives the representative partial *m*/*z* 74 mass chromatograms from the selected horizons across the K/T boundary at Caravaca. Saturated *n*-fatty acids ranging from C_{12} to C_{32} were detected in our samples. The total amount profiles of biomarkers studied are shown in Fig. 2, especially long-chain saturated *n*-fatty acids (Fig. 2A),

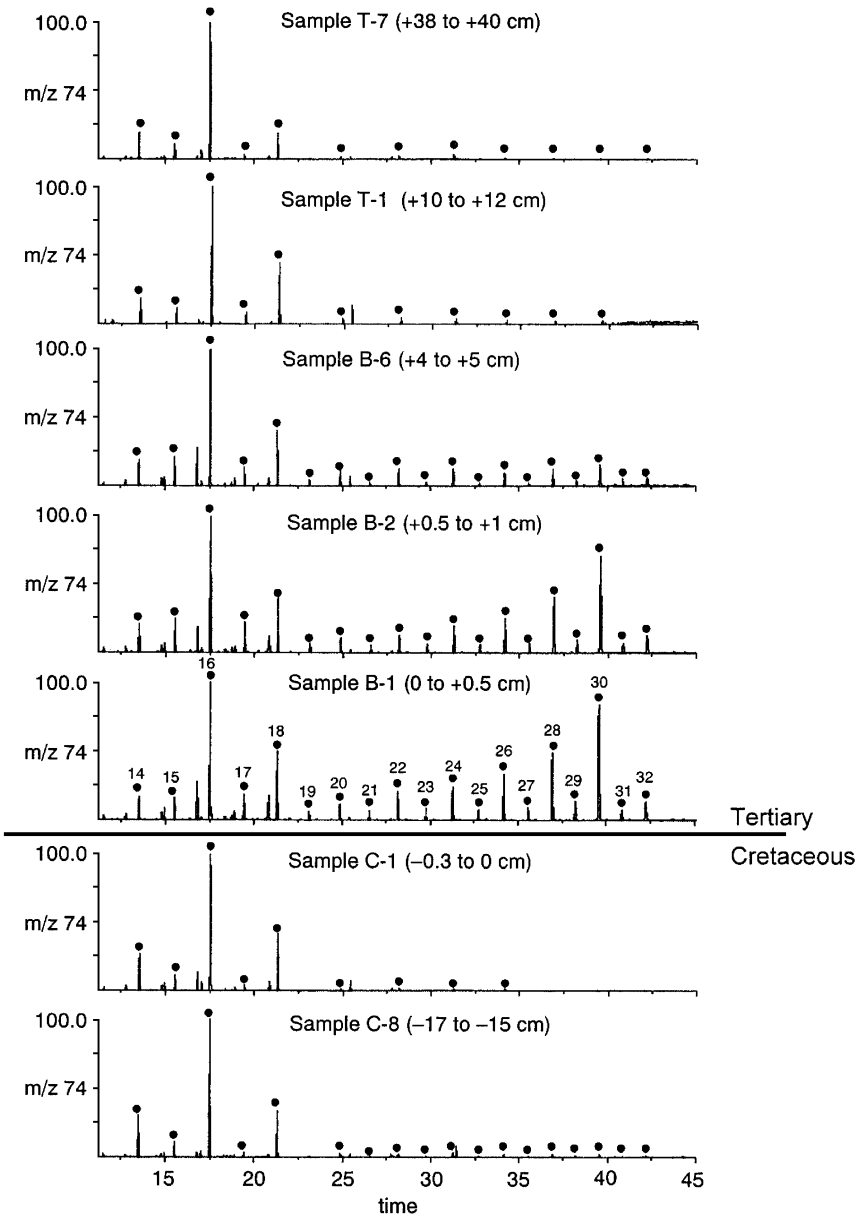

Fig. 1. Partial ion chromatograms of m/z 74 showing the fatty acids of selected horizons across the K/T boundary at Caravaca, Spain. Numbers indicate numbers of carbon atoms of saturated n-fatty acids.

long-chain n-alkanes (Fig. 2C), and some short-chain n-fatty acids, palmitic (C_{16}) and stearic (C_{18}) acids (Fig. 2E). As shown in Fig. 2A, the total amount of long-chain saturated n-fatty acids ranging from C_{20} to C_{30} (LFA), which are considered to originate from terrestrial higher-plant waxes (Cranwell, 1974; Brooks et al., 1976), were very low (<18 ng/g dry sediment) in samples from Cretaceous layers, and dramatically increase in the basal Tertiary sample (B-1; 0 to +0.5 cm) to 384 ng/g dry sediment, about a 35-fold increase in concentration relative to the average amount in Cretaceous samples. Thereafter values decreased and they were similar to the Cretaceous average in sample B-4 (+2 to +3 cm above the

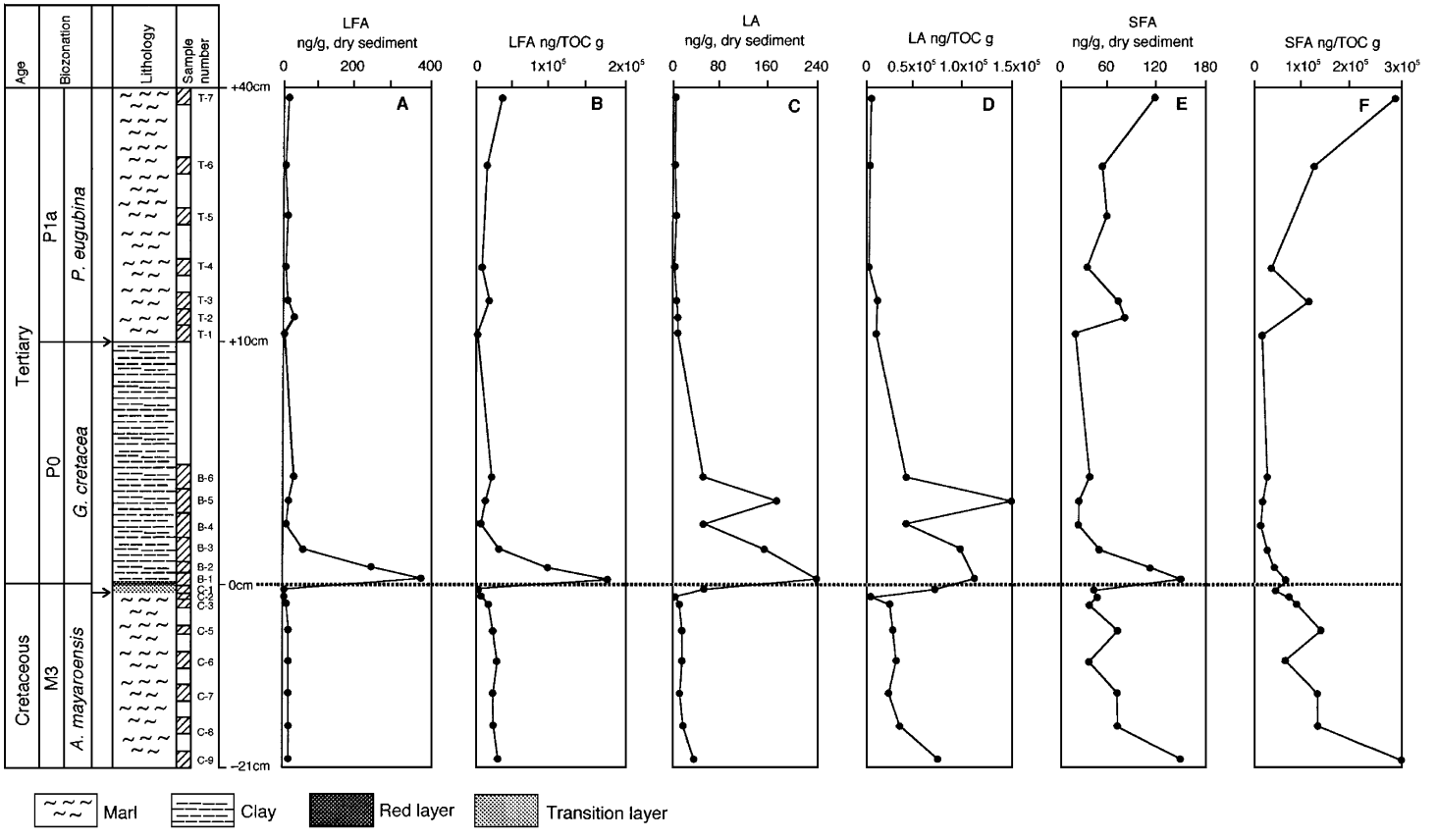

Fig. 2. Stratigraphic variations across the K/T boundary at Caravaca (Spain) of (A) total amounts of saturated long-chain *n*-fatty acids (LFA; C_{20}–C_{30}), (B) the LFA relative to TOC (total organic carbon contents), (C) total amounts of long-chain *n*-alkanes (LA; C_{25}–C_{31}), (D) the LA relative to TOC, (E) total amounts of saturated short-chain *n*-fatty acids (SFA; C_{16}+C_{18}), and (F) the SFA relative to TOC. Note changes in resolution of relative depth scale, as indicated by arrows.

K/T boundary), with two small peaks at samples B-6 (+4 to +5 cm) and T-2 (+12 to +14 cm). Fig. 2C gives the vertical profile of total amount of long-chain *n*-alkanes ranging from C_{25} to C_{31} (LA), which are also derived from terrestrial higher-plants (Prahl et al., 1994), as LFA is. Cretaceous sample values show a decreasing trend up to sample C-2 (−1 to −0.3 cm), whereas sample C-1 had a relative higher value (58 ng/g) compared to the average of the rest of the Cretaceous samples of around 15 ng/g. Danian sample values show a similar pattern to the LFA (Fig. 2C), except a peak in sample B-5 (+3 to +4 cm). The K/T boundary peak was about 15 times the average value of Cretaceous samples, except C-1; the second Danian peak was about 11 times this average.

Palmitic (C_{16}) and stearic (C_{18}) fatty acids have been found in the samples studied. Short-chain *n*-fatty acids (SFA) originated from autochthonous marine organisms (Cranwell, 1974; Brooks et al., 1976), but not exclusively. In this study, SFA were defined as follows; SFA=C_{16}+C_{18} for saturated *n*-fatty acids. As shown in Fig. 2E, the SFA profile shows a minimum value zone in the lowermost Danian samples, just the first 10 cm, with a peak in the K/T boundary similar to, but less significant than those of the other two biomarkers studied. Cretaceous sample values show a clear de-

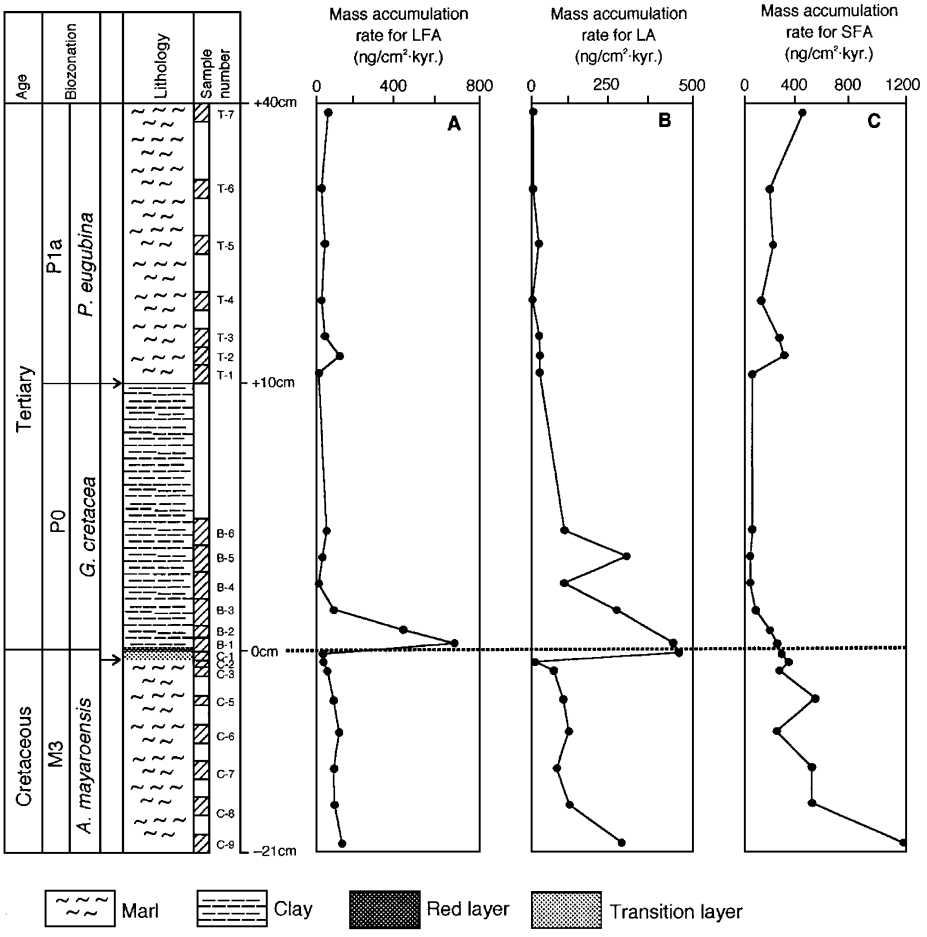

Fig. 3. Stratigraphic variations of mass accumulation rates for (A) saturated long-chain *n*-fatty acids (LFA; C_{20}–C_{30}), (B) long-chain *n*-alkanes (LA; C_{25}–C_{31}), and (C) saturated short-chain *n*-fatty acids (SFA; C_{16}+C_{18}) across the K/T boundary at Caravaca (Spain). Note changes in resolution of relative depth scale, as indicated by arrows.

crease of 73% from sample C-9 to sample C-1. In contrast, Lower Danian ones show more than a five-fold increase from sample B-4 to sample T-7, returning to pre-boundary values.

We have computed the relative abundances of terrestrial higher-plant biomarkers (LFA and LA) to the total organic carbon contents (TOC). The TOC data, except for sample B-1 (TOC = 0.213%) are from Kaiho et al. (1999). Both ratio profiles present a similar pattern (Fig. 2B, D) to their respective absolute abundance curves, with a gradual decrease in Cretaceous samples towards the boundary, except for sample C-1 (transition layer) for the LA/TOC values. A second Danian LA/TOC peak is more evident than the K/T boundary one. The vertical profile of SFA/TOC ratios was quite different in comparison to those of LFA and LA. In fact, the SFA/TOC ratios showed a symmetrical curve, with a minimum value zone from just below the K/T boundary up to 10 cm above it, and no conspicuous peak at the boundary (Fig. 2F).

We calculated the mass accumulation rate (flux) for each biomarker as follows; the average sedimentation rates (ASR) of the Cretaceous, the boundary–clay layer, and the Tertiary parts of C29R at the Caravaca K/T section are estimated to have been 3.1, 0.8, and 1.7 cm/kyr, respectively. The interval from −21 cm to +40 cm encompasses the last 6.8 kyr of the Cretaceous and the first 29.9 kyr of the Tertiary (Arinobu et al., 1999). The average of sediment dry bulk density (DBD) of the Upper Cretaceous marly section, the boundary–clay layer, and the lower Tertiary marly section were 2.51, 2.24, and 2.46 g/cm^3, respectively, at the Caravaca section. Mass accumulation rate (MAR) for individual biomarkers was calculated using the following equation: MAR (ng/cm^2 kyr) for biomarker = ASR (cm/kyr) × DBD (g/cm^3) × concen-concentration of biomarker (ng/g, dry sediment). Fig. 3A, B and C give the vertical profiles of the mass accumulation rates for LFA, LA, and SFA, respectively. All of them show almost similar distribution curves to their respective relative abundances compared with TOC.

5. Discussion

The samples of Cretaceous age taken from below the K/T boundary contained mainly saturated n-C_{16} and n-C_{18} fatty acids, and extremely small amounts of saturated long-chain homologues ($\geq C_{20}$). Interestingly, the molecular distributions of saturated n-fatty acids in the boundary–clay layer exhibit distinctively different distributions from samples of Cretaceous age. The saturated long-chain n-fatty acids with even-to-odd predominance dramatically increase in the basal Tertiary sample (B-1; 0 to +0.5 cm), and thereafter the amounts were gradually reduced. The distributions in samples of Tertiary age from above the boundary–clay layer are similar to those of Cretaceous age. Although it is known that n-C_{30} fatty acid is mostly relative low compared with n-C_{24} and n-C_{26} fatty acids in modern oceanic sediment samples, the long-chain n-fatty acids in estuarine sediment in Sagami Bay in Japan showed a bimodal distribution, the maxima being at C_{24} and C_{30} (Fukushima and Ishiwatari, 1984/1985). It is an interesting fact that long-chain n-fatty acids showed a mono-modal distribution, the maxima being at C_{24}, in sedimentary samples at a location which is far from the estuary in Sagami Bay (Fukushima and Ishiwatari, 1984/1985). The riverine influx may have some effect on their distribution.

As shown in Fig. 2B and D, the terrestrial biomarkers showed an increase in their abundances relative to TOC (LFA/TOC, LA/TOC) in the basal Danian and in the lowermost Danian, marking the enhanced contribution of matter derived from terrestrial higher-plants into marine sediments just after the K/T boundary event. As shown in Fig. 2F, the vertical profile of the SFA/TOC ratio was in contrast to those of the LFA/TOC and the LA/TOC, which showed abruptly higher values around the K/T boundary.

As shown in Fig. 3A, the vertical profile of the mass accumulation rate for the LFA is essentially similar to those for abundance of LFA and LFA/TOC (Fig. 2A and B). The mass accumulation rate for LFA reached a maximum in the basal Tertiary sample (B-1; 0 to +0.5 cm), which exhibited as much as an eight-fold increase in comparison with the average value of subjacent Cretaceous layers, and thereafter the signal was rapidly reduced, and declined back to pre-boundary values within +3 cm of the boundary–clay layer. The vertical profile of the mass accumulation rate for LA (Fig. 3B) is similar to that of LA/TOC (Fig. 2D). The rate for LA reached a maximum in transition layer (C-1; −0.3 to 0 cm) similar to the K/T boundary value, such as has been shown in

previous indices, and a second increase again in 3–4 cm above the K/T boundary. Above +10 cm the rates were lower relative to the Cretaceous layer. The mass accumulation rate for SFA (Fig. 3C) is essentially similar to that of SFA/TOC (Fig. 2F). The mass accumulation rate for SFA showed relatively low values in the lowermost Danian, as much as a half or a third compared with the underlying Cretaceous samples, and no spike across the K/T boundary. Although short-chain *n*-fatty acids are believed to originate largely from autochthonous marine sources (algae and other micro-organisms) (Cranwell, 1974; Brooks et al., 1976), n-C_{16} and n-C_{18} fatty acids are actually ubiquitous. It is also known that short-chain fatty acids are more susceptible to biodegradation, whereas long-chain fatty acids are more stable (Haddad et al., 1992), therefore short-chain fatty acids would be preferentially decomposed by elevated bacterial activity. Therefore, we think it is necessary to pay attention to the use of biomarkers such as SFA. The break down of mass accumulation rate for SFA in the boundary clay layer during the earliest Danian could be interpreted as due to a depression of marine productivity and/or elevated bacterial organic matter degradation. In fact organic matter of algal origin is degraded by bacteria in higher percentages than organic matter of terrestrial higher-plant origin (Lallier-Vergès et al., 1993). This agrees with the proposal of an interruption of primary productivity during K/T boundary times (Zachos et al., 1989; Kaiho et al., 1999, and others), and the hypothesis of the "strangelove ocean" after Hsu and McKenzie (1985).

In this study, it is clear that the relative contribution of terrestrial organic matter increases dramatically at the K/T boundary and thereafter declines more gradually back to pre-boundary values in Tertiary sediments.

Kaiho et al. (1999) reported the percentages of five maceral groups (nonfluorescent amorphous kerogen, nonfluorescent herbaceous kerogen, woody/coaly kerogen, fluorescent amorphous kerogen and weakly fluorescent amorphous kerogen, and fluorescent herbaceous kerogen) across the K/T boundary, at Caravaca. The occurrence of similar percentages of the five maceral groups across the K/T boundary suggested that there was no major change in the origin of kerogen, but the macerals contain many unknown elements.

Evidence of extensive fires at the K/T boundary has been presented from geographically widely separated boundary sites (Wolbach et al., 1985, 1988, 1990a,b; Heymann et al., 1994, 1998; Venkatesan and Dahl, 1989). We also reveal that pyrosynthetic PAHs [coronene, benzo(g,h,i)perylene, benzo(e)pyrene] are enriched as much as 112- to 154-fold in the basal Tertiary sample (B-1; same sample in this study) at Caravaca, in comparison with subjacent Cretaceous marlstone (Arinobu et al., 1999). The molecular distribution of *n*-fatty acids in the basal Tertiary sample (B-1) showed a high even-to-odd predominance. We speculate that such a high even-to-odd predominance is indicative of influx from unburned higher-plant-derived fatty acids, since a contribution from burned vegetation would have reduced the even-to-odd predominance of *n*-fatty acids as a result of thermal cracking processes. An increase in acid rain probably occurred after the K/T boundary event, as evidenced by the abrupt increase in $^{87}Sr/^{86}Sr$ in marine sediments (MacDougall, 1988; Vonhof and Smit, 1997). Acid rain would have had a lethal effect on both terrestrial and surface marine organisms. A greenhouse effect resulting from an increased concentration of atmospheric CO_2 and water vapour after the K/T boundary event may have caused global warming (O'Keefe and Ahrens, 1989), and such environmental changes may have induced an increase in rainfall rate. We presume that the abrupt increase in supply of terrestrial organic matter into the marine environment at the K/T boundary could have been caused by an enhanced riverine flux, probably due to heavy rains associated with global warming, in combination with enhanced fragments of terrestrial higher-plants withered by acid rain and/or by temporal darkness and cooling.

Kaiho et al. (1999) demonstrated that intermediate water oxygen minima were widely developed during earliest Danian time and attributed the cause to an increase in supply of organic matter from terrestrial biomass and sediment redistributed onto continental shelves and slopes. Our new evidence for an abruptly increased influx of terrestrial organic matter into the marine environment at the K/T boundary explains the decreases in dissolved oxygen in the intermediate waters distributed on continental margins.

6. Conclusions

The vertical high-resolution records of organic molecular distributions at Caravaca K/T section, which represents one of the most complete and less disturbed K/T boundary sections in the world, provide strong evidence of an extreme and abrupt increase in supply of terrestrial organic matter into the marine environment at the K/T boundary, as shown by the influx of long-chain *n*-alkanes (C_{25}–C_{31}) and long-chain *n*-fatty acids (C_{20}–C_{30}), especially the latter which shows an eight-fold mass accumulation rate increase in the basal Danian with respect to the subjacent Cretaceous samples. Furthermore, the profile of LFA/TOC shows a similar and consistent pattern. By contrast, the mass accumulation rate of SFA showed a continued decrease across the K/T transition. Those increases of terrestrial origin biomarkers in a marine basin could be related to riverine influx of unburned higher-plants at the K/T event, whereas the depletion of the SFA is consistent with low marine primary productivity and/or bacterial activity during earliest Danian times.

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