

Spike of pyrosynthetic polycyclic aromatic hydrocarbons associated with an abrupt decrease in $\delta^{13}\text{C}$ of a terrestrial biomarker at the Cretaceous-Tertiary boundary at Caravaca, Spain

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ABSTRACT

The first vertical high-resolution record of polycyclic aromatic hydrocarbons (PAHs) of pyrosynthetic origin and the corresponding $\delta^{13}\text{C}$ profile of a terrestrial biomarker across the Cretaceous-Tertiary (K-T) boundary at Caravaca, Spain, reveals the following. In comparison with adjacent Cretaceous marlstones, the first thin horizon (0 to +0.5 cm; 0 = the K-T boundary) of the boundary-clay layer is (1) enriched as much as 112 to 154 fold in typical pyrosynthetic PAHs such as coronene, benzo(g,h,i)perylene, and benzo(e)pyrene and (2) shows an abrupt $\delta^{13}\text{C}$ decrease of 1.4‰–1.8‰ in terrestrial higher plant-derived $n\text{-C}_{29}$ alkane. The spike of pyrosynthetic PAHs associated with an abrupt decrease in $\delta^{13}\text{C}$ value of a terrestrial biomarker is interpreted to reflect the prevalence of extensive fires with subsequent $\delta^{13}\text{C}$ decrease in atmospheric CO_2 . It is estimated that the geologically instantaneous combustion of ~18%–24% of the terrestrial above-ground biomass would be necessary to account for the measured negative isotopic shift at the K-T boundary, on the basis of carbon mass balance between terrestrial above-ground biomass and atmosphere.

INTRODUCTION

A large number of investigations have been conducted to integrate geological, paleontological, and geochemical data on the mass-extinction event at the Cretaceous-Tertiary (K-T) boundary of ca. 65 Ma. Extraterrestrial impact is invoked as the cause for the mass-extinction event (e.g., Alvarez et al., 1980), whereas the alternative hypothesis attributes the event to Earth-derived extensive volcanism (e.g., Officer and Drake, 1985). Either scenario could induce a global environmental change and profoundly affect the biosphere. The first hint of fire at the K-T boundary was observed at the Raton basin K-T site in Colorado, where large amounts of fusinite were found in the basal coal layer containing the Ir anomaly (Tschudy et al., 1984). Soot layers were discovered by Wolbach et al. (1985, 1988, 1990a, 1990b) and Heymann et al. (1998) at widely separated geographical boundary sites; these workers claimed that the layers provide evidence of global fires ignited by the meteorite impact. Heymann et al. (1994, 1998) found fullerenes (C60 and C70) in samples from K-T boundary sites around the world and asserted that they were probably formed by wildfires. Venkatesan and Dahl (1989) found pyrosynthetic polycyclic aromatic hydrocarbons (PAHs), predominantly nonalkylated species, in the boundary clay at Woodside Creek (New Zealand), Gubbio (Italy), and Stevns Klint (Denmark). Kruger et al. (1994) found larger PAHs such as fluoranthene, pyrene, chrysene, benzo(a)anthracene, and several penta-aromatic compounds, typical of the products of partial combustion, in calcareous sandstone samples from the upper part of a deep-water tsunami deposit, which marks the biostratigraphically defined K-T boundary at Arroyo el Mimbral, Tamaulipas, Mexico.

Ivany and Salawitch (1993) presented an interpretation of the documented negative gradient in $\delta^{13}\text{C}$ value of 0.4‰ (global area-weighted average) from surface water to deep water based on data from Deep Sea Drilling

Project (DSDP) and Ocean Drilling Program (ODP) sites in the South Atlantic, North Atlantic, Pacific, and Antarctic Oceans. They maintained that the negative $\delta^{13}\text{C}$ gradient could not be explained by the cessation of primary production alone, and they suggested that biomass burning with subsequent transfer of isotopically light carbon to surface waters was the most likely cause of the negative gradient in $\delta^{13}\text{C}$ value, on the assumption that this transfer occurred on a shorter time scale than that of oceanic mixing. They estimated that the combustion of ~25% of terrestrial above-ground biomass at the end of the Cretaceous would have been necessary to account for the negative gradient in $\delta^{13}\text{C}$ value of 0.4‰.

Consistent with this scenario, Schimmelmann and DeNiro (1984) found a negative $\delta^{13}\text{C}$ shift of 1.8‰ in bulk organic matter from a terrestrial Ir-enriched K-T boundary sequence at the York Canyon exposure of the Raton basin, New Mexico.

These earlier studies strongly suggest the presence of wildfires and resulting depletion in ^{13}C of atmospheric CO_2 at the K-T boundary, but have not had the resolution sufficient to contain the timing of wildfires.

We provide here the first high-resolution profiles of changes in (1) concentrations of pyrosynthetic PAHs and (2) $\delta^{13}\text{C}$ values of $n\text{-C}_{29}$ alkane (terrestrial higher plant-derived biomarker) for environmental analysis across the K-T boundary at Caravaca (lat 38°04'35"N, long 1°52'40"W) in south-eastern Spain. We believe that this supports the contention that extensive fires influenced the $\delta^{13}\text{C}$ values of the atmosphere on a global scale.

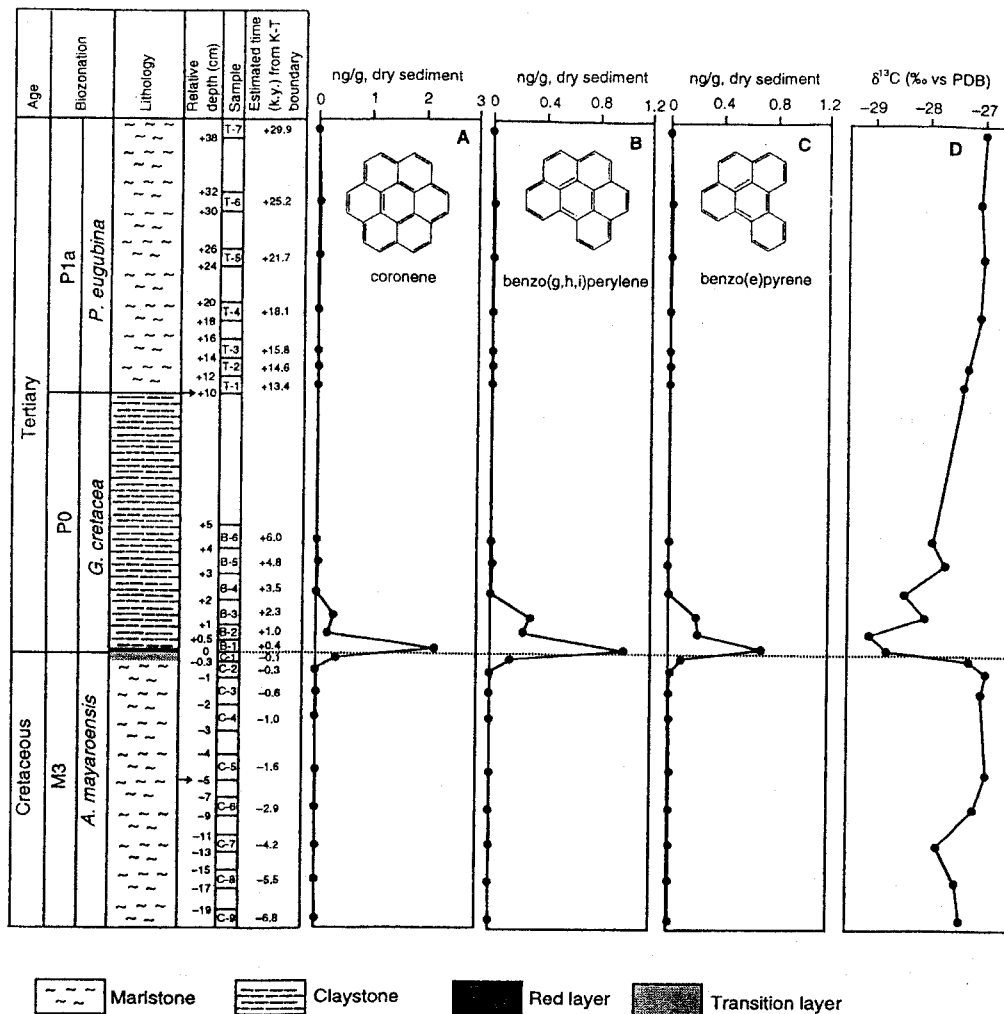
STRATIGRAPHY AND TEMPORAL RESOLUTION

In the K-T section at Caravaca, marlstones of Cretaceous age are lithologically separated from marlstones of Tertiary age by a dark ~7–10-cm-thick clay-marl bed (boundary-clay layer). This section represents one of the most complete and least disturbed K-T boundary sections in the world (Canudo et al., 1991; MacLeod and Keller, 1991), although the upper parts (5–10 cm above the K-T boundary) of the boundary-clay layer are disturbed, and there are some preserved burrows of several centimeters in length in the Cretaceous layer. A 1–2-mm-thick rust-orange basal layer, referred to as the red layer (or fallout lamina), contains the Ir spike (Smit and Ten Kate, 1982). In addition to the high goethite content, an obvious anomalous lithologic feature of the red layer is its high content of small spherules (Smit and Romein, 1985; Schmitz, 1988). This fact was initially emphasized by proponents of an impact origin of the clays because the spherules were interpreted to be pseudomorphs after microtektites (Smit and Klaver, 1981; Montanari et al., 1983). However, additional studies have indicated that the spherules are probably authigenic constituents (e.g., Hansen et al., 1986; Izett, 1987; Schmitz, 1988). Of particular interest is an ~3-mm-thick greenish transition layer just below the red layer. Terminal Maastrichtian–basal Paleocene sediments at Caravaca were deposited in a middle-bathyal environment (depth of 200–1000 m), as indicated by benthic foraminiferal assemblages (Coccioni and Galeotti, 1994; MacLeod and Keller, 1994). In this paper, the base of the red layer is defined as the K-T boundary; its depth is designated as 0 cm, and the depth of lower and higher strata are referenced to it.

As shown in Figure 1, 22 unweathered samples were precisely sliced off from 21 cm below to 40 cm above the defined K-T boundary. On the

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Figure 1. Stratigraphic variation across the Cretaceous-Tertiary boundary at Caravaca (Spain) of (A) coronene, (B) benzo(g,h,i)perylene, (C) benzo(e)pyrene, and (D) $\delta^{13}\text{C}$ values of *n*-C₂₉ alkane. Note changes in resolution of relative depth scale, as indicated by arrows. PDB—Peedee belemnite.



basis of an established, well-dated geomagnetic polarity column of the Caravaca section (Smit, 1982), the C30N-C29R and C29R-C29N boundaries correspond to depths of 11.7 m below and 5.1 m above the K-T boundary, respectively. The durations of the Maastrichtian and the Paleocene parts of C29R are 377 ± 20 k.y. and 296 ± 41 k.y., respectively (Herbert et al., 1995). The average sedimentation rates of the Maastrichtian and Paleocene parts of C29R are therefore estimated to have been 3.1 and 1.7 cm/k.y., respectively. However, the contents of CaCO_3 are lower in the Caravaca boundary-clay layer (average 37.9% by weight) relative to the lower Paleocene marly section (average 70.7% by weight). If it is assumed that the depositional flux of the residual mineral matrix was constant, the average sedimentation rate in the boundary-clay layer could have been approximately half that of the Paleocene marly lithology. The average sedimentation rate in the boundary-clay layer is calculated to have been 0.8 cm/k.y., except for the red layer, which is assumed to be essentially instantaneous. Thus, the interval from -21 cm to +40 cm encompasses the last 6.8 k.y. of the Cretaceous and the first 29.9 k.y. of the Tertiary.

METHODS

The surfaces of rock chips were cleaned twice by ultrasonic agitation with a benzene and methanol solvent mixture (6:4 by volume) for 2 min. Samples (~35 g) were treated with 6N HCl to remove carbonate. The residues were extracted three times with a benzene and methanol solvent mixture (in the same proportion) by ultrasonic agitation. The extracts were centrifuged at 3000 rpm and the supernatants were composited 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 neutral compounds were extracted with *n*-hexane and ether (in the same proportion) three times. The extracts were fractionated into neutral and acidic compounds by liquid-liquid separation. The neutral compounds were fractionated into aliphatic hydrocarbons, PAHs, and other classes of compounds by silica-gel column chromatography (silica gel contained 1% water; column size was 50 × 5 mm internal diameter). The aliphatic hydrocarbons and PAHs were analyzed by GC-MS (gas chromatography-mass spectrometry). The oven temperature was held at 60 °C for 2 min, then allowed to rise from 60 to 120 °C at 30 °C/min and from 120 to 310 °C at 5 °C/min, and finally held isothermally for 18 min. Identification was achieved by comparison of mass spectra and relative GC scan numbers with those of standards and/or published data. The $\delta^{13}\text{C}$ values of *n*-alkanes were analyzed by GC-IRMS (gas chromatography-isotope ratio mass spectrometry). The GC oven temperature for *n*-alkanes was increased from 50 °C to 240 °C at a ramp rate of 30 °C/min, and then increased to 310 °C/min at 5 °C/min. The separated compounds that emerged from the GC column were continuously introduced into the combustion oven and combusted to CO_2 . The intensities of masses 44, 45, and 46 were measured simultaneously, from which the $\delta^{13}\text{C}$ value of the sample relative to that of the Peedee belemnite (PDB) standard was determined.

RESULTS

In almost all Caravaca horizons analyzed, pyrene is the most abundant PAH, followed by phenanthrene, fluoranthene, and methylpyrene. PAHs

detected in Caravaca samples are essentially the same as those reported in the boundary-clay layer samples of the Stevns Klint and Gubbio K-T sections (Venkatesan and Dahl, 1989). Figure 1 (A-C) gives the vertical concentration profiles of coronene, benzo(g,h,i)perylene, and benzo(e)pyrene for the Caravaca section. The abundances are very low in Cretaceous marlstones from samples C-9 to C-2 (~6.8 k.y. to ~0.3 k.y. before the K-T boundary), increase slightly at the transition layer (sample C-1, ~0.1 k.y. before the K-T boundary), and reach maximum values in sample B-1 (during ~0.4 k.y. after the K-T boundary), which includes the red layer. The abundances of coronene, benzo(g,h,i)perylene, and benzo(e)pyrene are 2.20, 0.97, and 0.70 ng/g (dry sediment), respectively, in sample B-1, exhibiting 154-, 112-, and 116-fold increases in concentration, respectively, relative to their average amounts in Cretaceous marlstones from samples C-9 to C-2. Above the horizon at +2 cm (~2.3 k.y. after the K-T boundary), the amounts are similar to those in the underlying Cretaceous marlstones.

As shown in Figure 1D, the $\delta^{13}\text{C}$ value of *n*-C₂₉ alkane, which is a typical terrestrial higher plant-originated hydrocarbon, increased slightly in samples C-6 (~2.9 k.y. before the K-T boundary). The $\delta^{13}\text{C}$ value decreased slightly by 0.4‰ at the transition layer, and dropped markedly by 1.4‰ in sample B-1, resulting in a total negative shift of 1.8‰ in samples C-1 to B-1 (during ~0.5 k.y. across the K-T boundary). The *n*-C₂₉ alkane deposited in sample B-2 (~1.0 k.y. after the K-T boundary) became isotopically lighter by 0.4‰ compared to the next lower sample, and then became heavier by 1.0‰ in sample B-3 (~2.3 k.y. after the K-T boundary).

DISCUSSION

Highly pericondensed PAHs, such as coronene, benzo(g,h,i)perylene, and benzo(e)pyrene, are typical pyrosynthetic compounds formed by forest fires (Masclot et al., 1995) and combustion of organic matter (Blumer, 1975), hydrocarbons (Commins, 1969), gasoline (Kamens et al., 1988), and wood (Ramdahl, 1983; Li and Kamens, 1993), because rapid thermal quenching prevents further equilibration (Blumer, 1975). Such highly pericondensed PAHs are relatively rare in petroleum (Venkatesan and Dahl, 1989), but have been detected in significant amounts in sea-floor hydrothermal mounds (Simoneit and Lonsdale, 1982; Simoneit and Fetzer, 1996). These studies indicated that the production of highly pericondensed PAHs requires high temperatures. There is no evidence of any hydrothermal activity during the K-T event at this locality, hence we believe that the most likely origin for these PAHs is combustion of terrestrial organic matter.

Any variation in the distributions must be due to different pyrolysis conditions and/or differing stabilities of individual PAHs during postdepositional conditions (Killops and Massoud, 1992); the temperature of and exposure time to pyrolysis during PAH formation are the probable factors affecting variation of PAH composition (Youngblood and Blumer, 1975; Commins, 1969). For PAHs resulting from natural vegetation fires, postdepositional factors may be important in controlling the distributions observed in sediments and rocks (Killops and Massoud, 1992). The coronene is relatively resistant to oxidation (Campbell and Andrew, 1979). The highly pericondensed PAHs, exemplified by coronene, benzo(g,h,i)perylene, and benzo(e)pyrene, seem to be preferentially preserved under prevailing sedimentary conditions (Killops and Massoud, 1992).

The presence of considerable amounts of highly pericondensed PAHs just above the K-T boundary is consistent with the idea of massive global fires, as evidenced by the presence of soot. Soot is a polymer of poly-benzenoid radicals, and highly pericondensed PAHs are products of early termination of polymerization (Venkatesan and Dahl, 1989). Almost all of the airborne PAHs produced during combustion are likely to be associated with soot through hydrogen bonding on its surface (Commins, 1969). The duration of the peak in pyrosynthetic PAHs at Caravaca is similar to that of the Ir anomaly (Smit and Ten Kate, 1982), which would be geologically instantaneous. The smearing of these anomalies may be interpreted to reflect the prevalence of bioturbation or other sediment mixing, which blur the geochemical peaks.

The sudden decrease in the $\delta^{13}\text{C}$ value of *n*-C₂₉ alkane coincides with the significantly enhanced amounts of pyrosynthetic PAHs in sample B-1. The distribution of the long-chain *n*-alkanes in sample B-1 shows an odd carbon-number predominance, as indicated by the carbon preference index (CPI) value of 5.1, calculated using the equation $[(C_{27} + 2 \times C_{29} + C_{31}) / (C_{28} + C_{30})] / 2$. We speculate that such a high CPI value is indicative of input from unburned higher plant-derived *n*-alkane, because a contribution from burned vegetation would have reduced the odd-to-even predominance of *n*-alkane (O'Malley et al., 1997) as results of thermally cracking process. The $\delta^{13}\text{C}$ value of terrestrial biomass (and hence *n*-C₂₉ alkane) grown in the atmosphere infused with isotopically light CO₂ from burning would have been depleted. This regrowth organic matter (and *n*-C₂₉ alkane) would subsequently be transported to marine sediments via erosion and mixed with combustion products (pyrosynthetic PAHs) during the ~0.4 k.y. represented by the thickness of sample B-1. Hence, the terrestrially derived organic matter in sample B-1 represents a combination of burn byproducts and unburned post-Cretaceous organic matter.

We estimated the extent of terrestrial above-ground biomass burning on the basis of a simple carbon mass balance between terrestrial above-ground biomass and the atmosphere, using the starting conditions employed by Ivany and Salawitch (1993) in their model of end-Cretaceous biomass burning and carbon cycling. For our estimation, we have assumed the following. (1) The $\delta^{13}\text{C}$ shift for the *n*-C₂₉ alkane across the K-T boundary is a direct reflection of the shift (S) in $\delta^{13}\text{C}$ value of atmospheric CO₂ (S = -1.4‰ to -1.8‰). (2) The amount of end-Cretaceous terrestrial above-ground biomass (TB) was 1.0×10^{18} g of carbon (ΣC_{TB} ; based on Maastrichtian biome reconstructions by Ivany and Salawitch, 1993), and end-Cretaceous biomass had a $\delta^{13}\text{C}$ value of -25.66‰ ($\delta^{13}\text{C}_{\text{TB}}$; Ivany and Salawitch, 1993). (3) The amount of atmospheric carbon (AT) present at the end of the Maastrichtian was 1.09×10^{18} g (ΣC_{AT} ; Ivany and Salawitch, 1993), and the atmospheric carbon had a $\delta^{13}\text{C}$ value of -7.5‰ ($\delta^{13}\text{C}_{\text{AT}}$; Hsü, 1986). (4) The average burning efficiency was 50% (Seiler and Crutzen, 1980). We estimated the percent of terrestrial above-ground biomass burning necessary to account for our observed depletions as follows:

$$\% \text{ burning} = \frac{100 \times 2 \times \Sigma C_{\text{AT}} \times S}{\Sigma C_{\text{TB}} \times (\delta^{13}\text{C}_{\text{TB}} - \delta^{13}\text{C}_{\text{AT}} - S)}$$

As result of the calculation, the geologically instantaneous burning of ~18%–24% of terrestrial above-ground biomass is necessary to account for the negative $\delta^{13}\text{C}$ shift in atmospheric CO₂ of -1.4‰ to -1.8‰. Our estimate of ~18%–24% burning of above-ground biomes suggests that end-Cretaceous wildfires were extensive, perhaps on a global scale, and not simply localized events.

Although the $\delta^{13}\text{C}$ variations of atmospheric CO₂ are interpreted as a response to various climatic and eustatic factors (Gröcke et al., 1999; Kaiho et al., 1996), we believe that the most likely cause of the existence of the spike in the pyrosynthetic PAHs associated with an abrupt decrease in $\delta^{13}\text{C}$ value of *n*-C₂₉ alkane is indicative of extensive fires with subsequent decrease in $\delta^{13}\text{C}$ value of atmospheric CO₂.

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