Geochemical evidence for combustion of hydrocarbons during the K-T impact event

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It has been proposed that extensive wildfires occurred after the Cretaceous–Tertiary (K-T) impact event. An abundance of soot and pyrosynthetic polycyclic aromatic hydrocarbons (pPAHs) in marine K-T boundary impact rocks (BIRs) have been considered support for this hypothesis. However, nonmarine K-T BIRs, from across North America, contain only rare occurrences of charcoal yet abundant noncharred plant remains. pPAHs and soot can be formed from a variety of sources, including partial combustion of vegetation and hydrocarbons whereby modern pPAH signatures are traceable to their source. We present results from multiple nonmarine K-T boundary sites from North America and reveal that the K-T BIRs have a pPAH signature consistent with the combustion of hydrocarbons and not living plant biomass, providing further evidence against K-T wildfires and compelling evidence that a significant volume of hydrocarbons was combusted during the K-T impact event.

Cretaceous | PAHs | Tertiary | wildfires

It is widely held that an asteroid hit the Earth *ca.* 65 Ma (1) and that the Chicxulub crater on the Yucatan Peninsula in Mexico is the most likely K-T impact structure (2). Initial results from a nonmarine K-T site nearest to the impact crater showed evidence of wildfires in the latest Cretaceous and early Paleocene coals but nothing unusual in the K-T BIRs (3). Belcher et al. (4–6) revealed that K-T boundary impact rocks (BIRs) from 8 sites, spanning the length of the western interior of North America, contain significantly less charcoal than the associated Cretaceous and Tertiary rocks. Furthermore, on average 99% of organic matter in the K-T BIRs is not charred. Comparisons of previously described soot from marine K-T BIRs (7, 8) with modern soot from wildfires suggests that its morphology is inconsistent with a biomass source, but that it is characteristic of soots produced from partial combustion of hydrocarbons (6). Moreover, it has recently been revealed that both marine and nonmarine K-T BIRs contain carbon cenospheres, which are known only to be formed by combustion of hydrocarbon material (9).

pPAHs can arise from a variety of combustion sources, especially partial combustion of vegetation (10, 11), coal (12) and oil (13), whereby modern pPAH signatures may be traceable to their source (14). Wildfire is the dominant source of pPAHs in the fossil record throughout the majority of geological time, as a contribution from combustion of hydrocarbons is likely to be limited before anthropogenic inputs (15). However, the K-T impact vaporized a huge volume of rock that is known to have contained hydrocarbons and a significant fraction of organic material (16, 17) making these a potential source of pPAHs found at the K-T boundary.

This article evaluates the hypothesis that pPAHs found at several marine K-T sites are more consistent with partial combustion of hydrocarbon material in the target rocks at Chicxulub rather than global wildfires. Six of the original 8 nonmarine K-T sites from Belcher et al. (4, 6), stretching from Colorado to Saskatchewan, were also analyzed for pPAHs. All sites studied contain an Iridium anomaly, fern spike, shocked minerals and 2 K-T BIR clay layers (lower Ejecta layer and upper Fireball layer) marking the K-T event (4, 6). The K-T BIRs are shown in Fig. 1, which highlights the distinctive microstratigraphy of the K-T BIRs. Individual K-T BIR

Fig. 1. The K-T BIRs at Clear Creek North. (A–C) (A) K-T BIRs on a polished slab of rock across the K-T boundary. (B) The Ejecta Layer. (C) Fireball Layer. (D) “Re-worked” fireball layer. (B–D) All layers viewed in a polished block of rock using reflected light microscopy. Vitrinite laminae (non charred, coalified plant material) are indicated in C and D.

layers were sampled separately and each whole layer processed for pPAHs. The pPAH abundances have been directly compared with the charcoal abundances published by Belcher et al. (6). This not only provides the first extensive record of pPAHs across nonmarine

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Site		Environment of deposition	Overall Description
Colorado	Madrid East South Clear Creek North Berwind Canyon	Swamp Pond Pond	Late Cretaceous-Vermejo Fm. Interbedded sandstone, siltstone, shale, carbonaceous shale and conglomerate. Deposited in an alluvial plain environment (46)
North Dakota	Mud Buttes	Pond	Latest Cretaceous–Hell Creek Fm. Stratified sandstones with abruptly shifting facies and fining upwards sequences of siltstones and claystones. Typical of a channel floodplain environment. Earliest Tertiary–Ludlow Fm. Thick well-developed peat swamps and large ponds across a floodplain environment (47, 48)
Saskatchewan	Rock Creek East Wood Mountain Creek	Pond Large Swamp	Latest Cretaceous–Hell Creek Fm. Well-drained floodplain environment, becoming wetter towards the uppermost parts of the Late Cretaceous. This increasingly wet environment brought about the initiation of peat forming prior to the K-T, with more open swamps following (49, 50)

Intense K-T Conflagrations as a Potential Source of the pPAHs in the K-T Rocks. Robertson et al. (20) argued that the K-T fires were of such high intensity ($>800^{\circ}\text{C}$) that they destroyed any charcoal produced. It has been shown that charcoal can be created and persist at temperatures of the order of $1,000^{\circ}\text{C}$ (6) and that even delicate charred plant parts (e.g., moss) remain when combusted in ambient O_2 conditions at temperatures of $\approx 800^{\circ}\text{C}$ (21). The relative concentrations of individual pPAHs are known to be related to either the intensity of the wildfire or the type of fuel (22). Increasing number of hydrocarbon rings within the compound reflect an increased temperature of formation. A dominance of 2–3 ringed forms is typically consistent with low-moderate intensity fires whereas hotter fires will produce elevated concentrations of 5–6 ringed forms (22). The pPAH signature (i.e., the variety of pPAHs

Fig. 3. Average pPAH signature (as % total abundance of pPAHs) of the K-T BIRs. Showing dominance of 3 and 4 ringed pPAH forms. Key to pPAH names: Flu, fluorene; Phen, phenanthrene; Anth, anthracene; Pyr, pyrene; Fluor, fluoranthene; Ret, retene; 11(H)BbFlu, 11(H)benzo(b)fluoranthene; 11(H)BaFlu, 11(H)benzo(a)fluoranthene; Benz(g,h,i)Fluor, benzo(g,h,i)fluoranthene; Benz(a)anth, benzo(a)anthracene; Chyr/Tri, chrysene/triphenylene; Benz(a)pyr, benzo(a)pyrene; Benz(b)Fluor, benzo(b)fluoranthene; Diben, dibenz(a,h)anthracene; Ind(cd)Pyr, indeno(1,2,3 cd)pyrene; Benz(g,h,i)pery, benzo(g,h,i)perylene; Anth, anthanthrene; Coro, coronene.

and their relative proportions to one another) in the rock layers (Table S1) was analyzed to assess the likely temperature of formation of the pPAHs (Fig. 3). It can be seen that fluorene and phenanthrene are the dominant pPAHs in all of the K-T BIRs; these forms both have a 3-ringed aromatic structure. 5-ringed forms are very limited in their abundance and no quantifiable levels of 6-ringed forms found in the samples. The lack of high-molecular-weight pPAHs argues against high temperatures of formation and therefore against postulated high intensity (charcoal destructive) K-T wildfires.

Vaporization of Hydrocarbons as a Potential Source for the pPAHs in the K-T Rocks. It has been shown that the K-T soot record resembles soot produced from the combustion of hydrocarbons (6) and that both marine and nonmarine K-T BIRs contain carbon cenospheres, known only to be formed by combustion of hydrocarbon material (9). These findings, coupled with the lack of charred remains and the abundance of noncharred plant material found in K-T sites across North America (4, 6) suggests that hydrocarbons might provide a more likely source for the K-T pPAHs. Venkatesan and Dahl (23) reported the abundance of 28 pPAHs in marine K-T BIRs, found an increase in the total abundance of PAHs at the K-T boundary and concluded that the K-T pPAH distributions were consistent with the suggestion of global fires. However, Venkatesan and Dahl (23) also concluded that the signatures of pPAHs at Woodside Creek and Gubbio were similar to those from the combustion of wood or kerosene while the Stevns Klint signature was analogous to the combustion of coal.

The abundance of pPAHs in the marine and nonmarine K-T BIRs was compared (Table S2) and reveals that the marine K-T BIRs contain a significantly lower abundance of pPAHs than the nonmarine K-T BIRs. Chicxulub crater is 2,303 km from the nearest site in this study, it has been shown that pPAHs are concentrated at or close to their source (18) this can explain the lower pPAH abundance in distant ($\approx 10,000$ km) marine sites. It is also apparent in Fig. 2B that the peak in pPAH abundance is recorded in the lower K-T BIRs in the more southern sites (Madrid East South, Berwind Canyon, and Clear Creek North) and in the upper K-T BIRs in the more northern sites (Mud Buttes, Rock Creek East, and Wood Mountain Creek). This is consistent with the interpretation that the K-T pPAHs are sourced from combustion of hydrocarbons at Chicxulub, because impact related pPAHs might be expected to be delivered to sites more proximal to the impact more promptly than more distal sites.

The pPAH signatures (i.e., the variety of pPAHs and their relative proportions to one another) in the rock layers analyzed in this work (Table S1) were compared with the signatures of pPAHs from the combustion of coal (12), lignite (12), oil (13), diesel (13), angiosperms (11), and gymnosperms (10). A cluster analysis (Fig.

4) [performed using the palaeontological statistical program PAST v1.73 (24)] of these data reveal that 71.5% of the K-T BIRs group with hydrocarbon combustion sources (Table 2). The pPAH signature in the K-T BIRs from Wood Mountain Creek and Madrid East show similarity to combustion of lignite as does the fireball layer from Rock Creek East. At Wood Mountain Creek and Madrid East South the K-T BIRs occur in a coal sequence (which at the time of deposition would have been peat); it is unlikely that burning of the peat surface is the source of the K-T pPAHs at these sites as we would expect to see either a charred peat surface below the K-T BIRs or an increase in charcoal in the K-T BIRs. Moreover, the Cretaceous and Tertiary rocks (that are known to contain charcoal resulting from fires) ought to cluster with this group if this were the case.

The pPAH signature in the K-T BIRs from Clear Creek North shows similarity to that from combustion of diesel or oil and the Ejecta Layer from Mud Buttes shows a similarity to those from combustion of coal. Oddly none of the K-T layers from Berwind Canyon reveal evidence of combustion of hydrocarbons, even though Berwind Canyon contains the highest abundance of pPAH per weight % carbon. We cannot explain why this site should differ from the others. If Berwind Canyon is removed from the analysis, 90.1% of the K-T BIRs would group with hydrocarbon sources. No Cretaceous or Paleogene rocks show any evidence of hydrocarbon combustion. The K-T BIRs reveal that the spike of pPAHs found within them are likely to be a result of combustion of hydrocarbon material.

Ancient or Modern PAHs? pPAHs are ubiquitous in ambient air and occur both in particulate and gaseous phases (25). Particles are deposited slowly from the atmosphere (staying airborne for days) (25) and are often transported over long distances (26).

To check and account for, any modern contamination, blanks were run through the GCMS and blank extractions (without rock samples present) were performed. Both produced essentially blank/clean results. Therefore, pPAHs have not been added to the samples as contamination during processing in the laboratory.

Considering that pPAHs are ubiquitous in ambient air it might be suggested that pPAHs could be adsorbed by the rocks from the modern atmosphere before reaching the laboratory. If modern contamination from ambient air was the source of the pPAHs then the Clear Creek North samples might be expected to contain both the highest abundance and the most compounds because it is situated 16 km from the nearest power station and is located on the interstate highway, where vehicle emissions ought to be a significant input into the surrounding air. Yet the rocks from Clear Creek North contain the lowest abundances of pPAHs measured at any of the sites. Moreover there is no relationship between pPAH abundance or signature based on the sites' proximity to roads, cities or

South reveal that the K-T BIRs simply interrupt an otherwise apparently continuous episode of peat formation.

The K-T BIRs are considered to have been deposited in minutes to hours (28) for the ejecta layer, and in hours to days (29) or days to months (30, 31) for the fireball layer. Based on the calculations of Kring and Durda (32) the particles that formed the K-T BIRs would have taken between 0.1 and 1,000 h (according to different sized particles) to settle through 20 m depth of freshwater. Any charcoal formed ought to have been washed into these ponds or fallen directly into the peat forming mires. Fresh charcoal has a bulk density less than that of water and so initially floats (33) but with continued immersion becomes waterlogged and sinks. The time taken for a variety of charred remains to become waterlogged and sink ranges between 24 and 288 h (33). This is of a similar order of magnitude to the time taken for the K-T ejecta material to settle in a freshwater environment, further confirming that there is no taphonomic reason that charcoal should not have been incorporated into the K-T BIRs as both the charcoal and ejecta should have been deposited at the bottom of the ponds and/or mires at similar times.

Macroscopic charcoal abundances in the K-T BIRs are typically 20× less than those produced by single modern fire events (6) and considerably less than probable fire events elsewhere in the sequence studied. If there was intense conflagration, then it is probable that the proportion of microscopic charcoal (6) (usually transported in the smoke plume) would be greater; if the macroscopic charcoal (6) was formed at >800 °C it would be more fragile and likely to break in to smaller size fractions and become part of the microscopic fraction (34, 35, 36). Moreover, the reflectance of the K-T charcoals is moderate and certainly does not indicate extremely high temperatures of formation (35).

Lack of evidence for postfire erosion features. Extensive burning of all vegetation, particularly from surface fires, would have lead to extensive postfire erosion. Burning the surface vegetation allows for extensive overland flow to occur after the first rainstorms after a fire (37). In addition, there can also be a heat effect on the soils that may enhance a soil's hydrophobic layer and contribute to extensive sediment erosion, transport and ultimately deposition (38, 39). For example, in peatlands, fires can result in peats being replaced by clastic fire splay deposits [e.g., as seen in the Carboniferous Cherokee Group coals of eastern Kansas (40)]. Partings in the Eocene lignites of southern Texas have been interpreted as being the results of fire splays that formed by the rupture of river levees because of the burning-off of surrounding peats during dry periods (41). Clay partings can be seen throughout the sequence at Wood Mountain Creek, however, there are no such partings immediately above the K-T BIRs. The closest parting is 5.7 cm above the top of the K-T BIRs. Based on peat accumulation rates and subsequent coal compaction, this clay parting was deposited of the order of 500 years after the K-T event. Increased deposition might be seen in some areas e.g., as fire splays as described above, but extensive erosion is also a key feature after wildfire events, for example significant peat erosion has been shown after severe fires (42). There is no evidence of erosion (e.g., erosion surfaces) in either of the coal/lignite sequences in this study, the K-T BIRs simply interrupt a continuous episode of peat accumulation.

Fire related erosion events have been shown to initially increase aggradation in fluvial systems, however, this is often followed by down cutting because of increased flow velocities in the river channel (43). Increased deposition or erosion ought to be apparent in siliciclastic K-T sites. Increased deposition into the water bodies in which the K-T BIRs were deposited ought to (i) have diluted the impact debris that formed the K-T BIRs, so that they would not be recognizable or (ii) be present as a clear depositional event shortly after the K-T BIRs. However, coal overlies the K-T BIRs at all of the sites. These 2 observations suggest that increased deposition, associated with extensive wildfires, is unlikely.

Lack of energy delivered by the impact. Melosh et al. (44) conducted detailed modeling of the amounts of energy likely to have been released by the K-T impact and deduced 50 kW·m⁻² to be the total thermal power radiated by reentering ejecta. Approximately half of this is presumed to have radiated upwards into space and some would have been absorbed in the atmosphere by water vapor and carbon dioxide (43). Melosh et al. (44) suggested that ≈1/5 of the total thermal power generated would reach the Earth's surface, therefore, delivering 10 kW·m⁻², which translates to ground temperatures of the order of 400–450 °C (6). Kring and Durda (32) modeled the power delivered to the atmosphere above specific geographical locations and how this diminished with time after the impact, providing a model that considered the duration of the thermal pulse after the K-T event. Belcher et al. (6) used this data to calculate the ground temperatures experienced in Colorado during the first 24 h after the K-T impact event and revealed an average ground temperature of 266 °C. These estimates are likely to represent upper limits as the calculations assume a cloudless sky, which is unlikely especially because the atmosphere is predicted to have been choked with impact dust (29). Neither of these models predict ground temperatures extreme enough, or of sufficient duration, to spontaneously ignite vegetation (6) and so argue against conflagration.

Abundance of soot and carbon cenospheres. Soot found in the K-T BIRs shows a morphology consistent with soots produced from the combustion of hydrocarbons (6). Moreover, both marine and nonmarine K-T BIRs contain carbon cenospheres (9). Carbon cenospheres are thought to derive solely from incomplete combustion of pulverized coal or fuel-oil droplets, which suggests that the impact may have combusted an organic-rich target crust. Harvey et al. (9) highlight that the Chicxulub impact crater is located adjacent to the Cantarell oil reservoir, one of the most productive oil fields on Earth, suggesting that an abundance of organic carbon in the Chicxulub target crust was likely to have been above global mean values. Even if Chicxulub's organic-rich location is discounted, it has been shown that the global mean crustal abundance for fossil organic matter is more than adequate to account for the observed concentrations of both carbon cenospheres and soot (9), therefore making the global wildfire hypothesis unnecessary.

pPAH signature. We have shown herein that the pPAHs found in the K-T BIRs lack high-temperature pPAH species, which are inconsistent with predictions of an intense K-T conflagration (Fig. 3). Moreover, the signature of pPAHs from multiple K-T boundary sites resembles those formed by the combustion of hydrocarbons but not plant material (Fig. 4). The delayed delivery of pPAHs to sites further from the impact site also points to the impact at Chicxulub as being a source of the K-T pPAHs.

Conclusions

The rock record from 6 nonmarine K-T sections from North America reveals a spike in the abundance of pPAHs in the K-T BIRs. The pPAHs found within the K-T BIRs (from 5 of the sites) are shown to have a distinctive signature comparable to that produced by the combustion of hydrocarbons and not plant material. These data, coupled with the limited amount of charcoal found in K-T BIRs from across North America (4–6), the lack of sufficient thermal radiation delivered by the K-T impact to ignite vegetation (6, 32, 44), the lack of post fire erosional features, the morphology of the K-T soot (6) and the presence of carbon cenospheres in both marine and nonmarine K-T BIRs (9) do not support the suggestion of global wildfires and in fact provide compelling evidence that a significant volume of hydrocarbons were combusted during the K-T impact event. An old saying goes that “there's no smoke without fire” but in the case of the K-T event the geological record suggests that there was most likely smoke without fire.