

THE GLOBAL CRETACEOUS-TERTIARY FIRE: BIOMASS OR FOSSIL CARBON?

Iain Gilmour* and Frank Guenther†

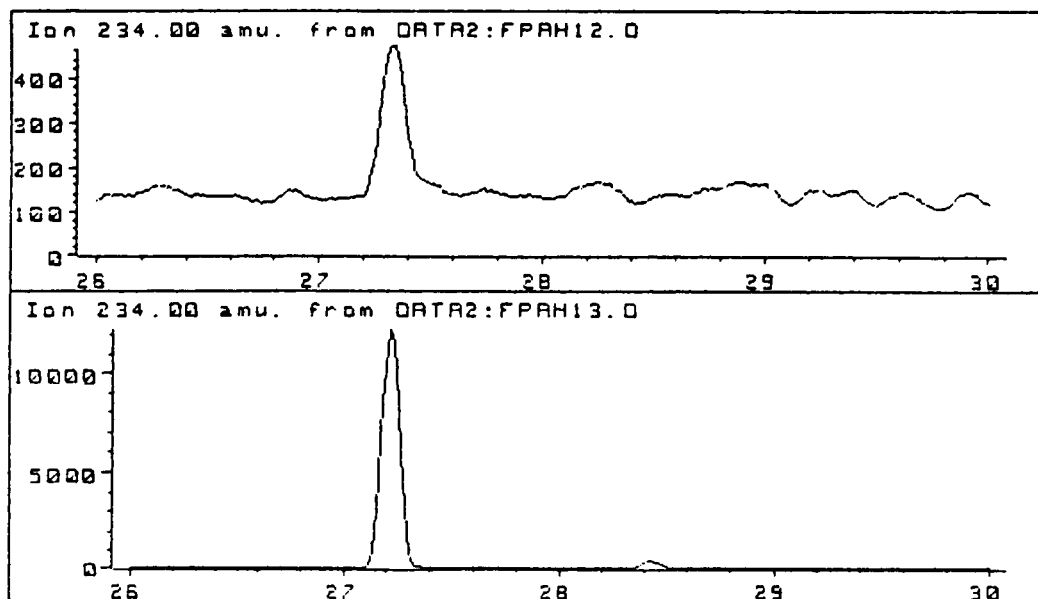
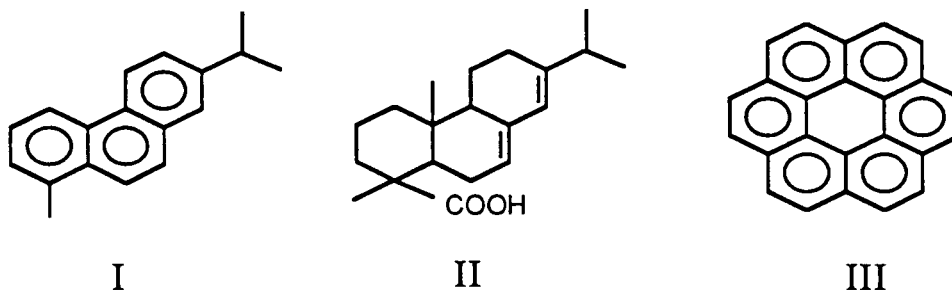
**Enrico Fermi Institute, University of Chicago, Chicago, IL 60637.*†*National Bureau of Standards, Gaithersburg, MD 20899.*

The global soot layer at the K-T boundary^{1,2} indicates a major fire triggered by meteorite impact. However, it is not clear whether the principal fuel was biomass (i.e. forests) or fossil carbon. Forests are favored by $\delta^{13}\text{C}$ ($-25.4 \pm 0.3\%$ at 5 sites worldwide), which is close to the average for trees, but the total amount of elemental C – $7 \times 10^{16}\text{g}$ – is $\approx 10\%$ of the present living carbon (or $>3\%$ of the maximum Cretaceous value), and thus requires very efficient conversion to soot. Also, living trees don't burn well.

We have therefore analyzed PAH at Woodside Creek, in the hope of finding a diagnostic molecular marker. A promising candidate is 1-methyl-7-isopropyl phenanthrene (retene, I), which is probably derived by low temperature degradation of abietic acid³ (II), a common constituent in plant resins. Unlike other PAH (III) that form by pyrosynthesis at higher temperatures, retene has retained the characteristic side chains of its parent molecule (II). A total of 11 PAH compounds were identified in the boundary clay at levels substantially ($10^1 - 10^2$) above background. Most of these PAH are high temperature combustion products that form from any fuel, but in addition, retene is present in substantial abundance (1.2 ppb). The identification was confirmed by analysis of a retene standard (figure).

Retene is characteristic of the combustion of resinous higher plants, the most prolific resin producers being the conifers of temperate climates and the angiosperms of tropical climates. Its formation depends on both temperature and oxygen access, and is apparently highest in oxygen-poor fires⁴. Such fires would also produced soot more efficiently which may explain the high soot abundance. The relatively high level of coronene (1.4 ppb, III) is not typical of a wood combustion source, however, though it can be produced during high temperature ($\approx 900^\circ\text{C}$) pyrolysis of methane⁵, and presumably other H, C-containing materials. This would require large, hot, low O_2 zones (so large ring systems can form), which may occur only in very large fires. The other PAH are all common combustion products and therefore not diagnostic of the fuel. PAH were also detected in a boundary clay sample from Stevns Klint, Denmark, though contamination by large quantities of diatom lipids prevented positive identification of retene. However, Simoneit and Beller⁶ have also observed retene in a K-T boundary sample from DSDP site 605 in the Atlantic ocean, and it would obviously be interesting to check other boundary sites, to see whether the distribution of retene is truly worldwide.

The presence of Retene indicates that biomass was a significant fuel source for the soot at the Cretaceous-Tertiary boundary. The total amount of elemental C produced requires a >3% soot yield, which is higher than typically observed for wildfires (maximum ≈2%). However, retene and presumably coronene imply limited access of O₂ and hence high soot yield.



m/z 234 mass chromatogram for Woodside Creek boundary clay (upper) and retene standard (lower)

References

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GLOBAL FIRE AT THE CRETACEOUS-TERTIARY BOUNDARY

Iain Gilmour, Wendy S. Wolbach, Edward Anders

Enrico Fermi Institute & Univ. Chicago, Chicago, IL 60637-1433, USA

Evidence for a Global Fire. K-T boundary clays from 5 sites in Europe and New Zealand are 10^2 - 10^4 -fold enriched in elemental C (mainly soot), which is isotopically uniform ($\delta C^{13} = -25.4 \pm 0.3\%$) and apparently comes from a single global fire (1,2). The soot layer coincides exactly with the Ir layer, suggesting that the fire was triggered by meteorite impact and began before the ejecta had settled. The carbon-Ir correlation persists in redeposited, secondary fallout above the boundary, implying rapid coagulation of smoke and ejecta (3).

Biomass or Fossil Carbon? The fuel seems to have been mainly trees rather than fossil C, judging from δC^{13} of the soot and especially from the presence of the tricyclic aromatic hydrocarbon retene (4), which is thought to be diagnostic of coniferous wood combustion. However, the total amount of C, $(7 \pm 4) \times 10^{16}$ g, is $\sim 10\%$ of the present biomass or $\sim 3\%$ of the maximum Cretaceous biomass. Thus either most of the Cretaceous forests burned down and were converted to soot with high efficiency ($>3\%$), or part of the soot comes from fossil C. Although living trees do not burn well at $21\% O_2$, they would ignite readily at 24 - $30\% O_2$ (5,6), especially if the trees were killed and dried by the enormous winds following the impact (7).

Events at the K-T Boundary. A time sequence can be reconstructed at undisturbed sites, such as Woodside Creek, NZ, where the boundary clay is laminated and shows large chemical and isotopic differences on a millimeter scale (2). Kerogen rises $15\times$ at the boundary, is strongly enriched in N (8), and varies in structure and δC^{13} (2). These trends may reflect rapid sweepout and burial of plankton by ejecta, with little or no bacterial degradation; perhaps preceded by respiration in darkness and reactions with acid rain (2).

Effects of Fire. A global fire producing 7×10^{16} g of soot would aggravate most of the environmental stresses of the impact. As soot absorbs sunlight more effectively (optical depth = 1800), the darkness and cold would last longer, even if the soot and rock dust had coagulated in the atmosphere (3). Poisons such as NO_2 (9) would be accompanied by CO (~ 100 ppm) and organic pyrotoxins (2), leading to greater selectivity of extinction patterns than darkness alone. Some effects would persist after the skies had cleared: CO_2 (~ 900 ppm) would contribute a greenhouse effect of $-9^\circ C$, and mutagenic pyrotoxins might accelerate evolution among the surviving species, thus speeding up the filling of ecological niches.

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