Search for the elusive end-Permian bolide impact: Exotic carbon – fullerene, as a potential tracer

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Since the Cambrian period, ~ 600 m.y ago, at least five major episodes of mass extinction, respectively during late Ordovician (450 m.y), late Devonian (340 m.y), end Permian (PTB, 250 m.y), end Triassic (T/J, 200 m.y) and end Cretaceous (K/T, 65 m.y) have been recognized. After it came to be known that an impact by a large meteorite was responsible, for at least one of them – the Cretaceous–Tertiary or the K/T extinction event[1], scientists began sifting geologic strata for evidence about similar collisions coinciding with the other four mass extinctions as well. Their expectations for such synchronous collisions appear logical, as earth is known to have been battered by impactors of varying sizes intermittently during those times[2]. So far, they have been unsuccessful in establishing such coincidences. Their hunt, on the contrary, had revealed several other agents that can precipitate mass extinction, such as periodical regression and transgression of sea-level over geological times, development of hostile climatic conditions and environmental changes due to flood volcanism or massive liberation of methane from ocean bottom methane-hydrates[3–10]. Potent extraterrestrial (ET) causes have also come to light like bursts of life-threatening neutrinos from dying stars, muons from neutron stars[11], galactic dark-matter induced flood volcanism and its harsh climatic consequences[12] and so on. In fact, a few studies have even found that the K/T impact was only a chance coincidence that merely hastened the progress of extinction, which had begun due to degradation of environment, ecosystems and other earthbound reasons long before the meteorite hit earth[13,14]. Actually, accumulating data on the five mass extinction events have now shown that except for the ones at K/T and PTB, the others were more events of depletion of the living species, rather than extinction, because these were neither sudden, large or unusual, the yardsticks to measure the magnitude of extinction[15].

In the record of the progress of evolution of life, the end-Permian or the Permian–Triassic boundary (PTB) extinction event is regarded as the worst spell in which bulk of the fauna and flora existing 250 m.y ago were wiped out. Many doubt if this magnitude of damage to life could have resulted just from any of these terrestrial causes alone without the involvement of large ET impact, but so far evidences for the latter have been inconclusive. A 120 km-diameter impact crater with possible Permian–Triassic boundary age was reported two years ago from western Australia (Woodleigh Crater) providing several impact signatures, small and large, but its exact age has remained controversial[16]. Typical impact signatures like shocked quartz and iridium anomaly in the PTB sediments in Australia and Antarctica[17], iridium anomalies in PTB beds in Europe (Dolomite Alps), Soviet Russia[5], China[18], India[19] (Permian section of Spiti Himalayas) have also been reported. But the shocked quartz, without the expected optical strain effects and change in its refractive index due to deformation, were not convincing enough to be considered proofs for impact. Likewise, Ir anomalies were also regarded inadequate to support the impact view, as they were much lower in these areas than in the K/T sediments, though some eucrite type meteorites are known to have low Ir (ref. 19).

In the last few years, a resurgence of activity is noticed in tracking down the elusive bolide strongly suspected to have collided during the PTB times. This flurry of activity is a sequel to the growing interest in rare or exotic form of carbon called fullerenes, with promising properties for use as a tracer for meteorite impact. Fullerenes, whose discovery in 1985 generated much excitement and a Nobel Prize in 1996, represent a new form of natural carbon, besides graphite and diamond. Their association invariably with several types of extraterrestrial materials has been the main reason for the optimism for their use as an impact indicator. Apart from extraterrestrial occurrence, fullerenes are also produced terrestrially at high temperature and pressure that develop when a meteorite impacts earth or in forest fires triggered by such impacts. Fullerenes are noticed in fulgarites, a fusion product, produced when lightning strikes the ground and also during high grade metamorphism of carbonate-rich rocks and low grade metamorphism of silty shales[20–22]. The most commonly found fullerenes (Figure 1) are made up of a cluster of 60 to 70 atoms (C_{60} and C_{70}) linked to form a cage resembling the well-known geodesic dome (developed by the renowned architect Richard Buckminster Fuller, after whom this carbon takes the name).

The presence of fullerene in a rock implies that the sample experienced high pressure and temperature generally associated with meteorite impacts. Their stability even under metamorphic conditions (400°–600°C temperatures) is considered an added advantage for use as a tracer. That fullerenes occur positively at impact sites and at sites related to impact event was established through their discovery at proven impact crater like the Sudbury Crater, Canada[23] and K/T impact-related sediments in New Zealand[24], and last year from India from the clay beds (intertrappean) occurring between Deccan lava flows, at Anjar, Gujarat[25], as well as in the classic Allende and Murchison meteorites[26]. The confirmed relation of this carbon with impact events coupled with the ability to distinguish the forms generated extraterrestrially from those formed on earth through their distinctly diagnostic noble gas ratios (whether in meteoritic or earthly proportions) have encouraged their use as a reliable impact tracer. A breakthrough using this form of carbon as a tracer in the search for the elusive PTB impactor was claimed last year by a team headed by Luann Becker[27], University of Washington, Seattle, USA. They examined a few classic sites exposing PTB formations at Meishan in south China, Sasayama in southwest Japan and Bálvány in northern Hungary, all of which also showed a record of rapid decline of several species of Permian fauna like the marine ammonoids, bivalves and fussulinid foraminifera.

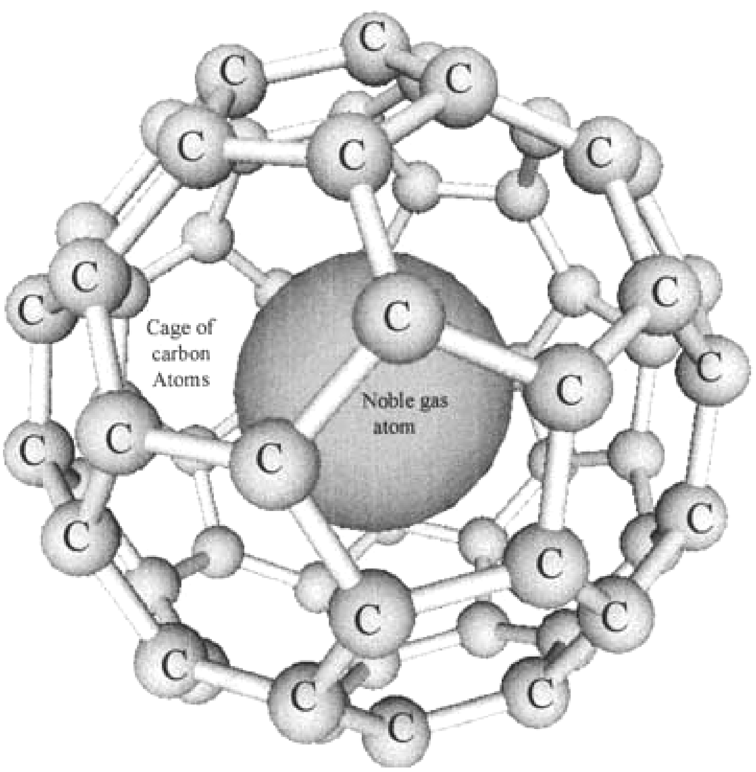

Figure 1. Carbon lattice of molecular fullerene with a trapped atom of noble gas. Most common forms have 60 or 70 carbon atoms arranged as pentagons and hexagons. Association of fullerenes with extraterrestrial materials plus their property to absorb noble gases in their cage-like structure and retain them in the ratios prevailing in the environment of their origin – terrestrial or extraterrestrial, lend support for their use as an impact tracer. Fullerenes have been reported from K/T and PTB localities from around the world including India (figure adapted from: Curl, R. F. and Smalley, R. E., *Sci. Am.*, October 1991).

The PTB sediments were essentially clays (S. China), bedded cherts, shales (Japan) and intercalations of clays in limestone (Hungary). From concentrates of carbonaceous fractions obtained from the sediments, the team extracted the fullerenes using suitable organic solvents and recorded their diagnostic mass spectrum employing Laser Desorption Mass Spectrometer (LDMS). The studies confirmed the presence of C_{60}^{+} and C_{70}^{+} fullerenes in all these boundary beds. Interestingly, the fullerenes were in much lower amounts in the sediment layers above and below the boundary beds, indicating that the deposition of fullerenes took place for a short period only. That the fullerenes were indeed of ET origin was confirmed from their noble gas contents. The ^{3}He and ^{3}He/^{4}He in the fullerenes from Meishan and Sasayama Sections were within the range reported for the ‘planetary’ component in meteorites and were comparable to the range seen in carbonaceous chondrites like the Murchison and Allende meteorites[26]. The results from the Hungarian site were not convincing either because the basin of sedimentation or its post-depositional history was unfavourable for the preservation of fullerenes.

Besides the strong evidence for a bolide impact based on fullerenes at the PTB Sections, the unusual or sudden enhanced amounts of ^{3}He observed in these boundary beds also lends support to their view. Among the various isotopes of helium, only two, ^{3}He and ^{4}He, are stable. Most of earth’s ^{3}He were primordial and they had escaped into space early in earth’s history (though recent findings have envisaged a viable mechanism of ^{3}He production by nuclear fission that can take place in earth’s inner core and its rapid escape outwards[28]). Interplanetary dust particles (IDPs or asteroidal and cometary debris), accumulating continuously on earth are main sources for concentrations of ^{3}He and ^{3}He/^{4}He ratios in sediments, and this ratio in such ET materials is always higher than in the terrestrial materials[29]. Becker’s team found a 50-fold increase in fullerene-accommodated ^{3}He in the Sasayama PTB beds in comparison to the quantity present in the adjacent older and younger beds. Such an increase cannot be accounted just by change in the sedimentation rates at this boundary. Almost 50% of total ^{3}He in the bulk sediments are contained in the PTB fullerenes, and this jump in ^{3}He abundance, they claimed, pointed to an impact event. The distinctly cosmogenic noble gas signature observed rule out possible synthesis of fullerenes at the time of impact on earth. The findings at the Chinese and Japanese PTB sites are therefore interpreted to confirm that the fullerenes were delivered by ET body like an asteroid which crashed over earth during end-Permian times and it was responsible for the mass extinction. Through calculations based on total noble gas contents they estimated the size of the impactor as comparable to the K/T event.

The proposal of fullerene as an alternate signature for ET impacts, besides the Ir anomaly, has produced both skepticism and excitement. If dimensions of preserved meteorite craters on earth[16,30,31] are any guide to the size of the impacting bolide and by corollary its life destroying capacity too, only three craters during the 200–250 m.y span measure 100–120 km-diameter, which is not even half the size of the Chicxulub crater carved by the K/T bolide. The absence from the records of equally large, if not larger, bolide impactor with life annihilating potential exceeding that of the K/T event, as well as rarity of unequivocal impact markers in many of the PTB horizons around the world raise many debatable issues questioning impact-induced mass extinction. Skeptics are also not sure, if fullerenes can survive undisturbed over millions of years of evolving geological scenario and preserve the noble gases, a doubt validated by the observations on the fullerenes from the Hungarian PTB beds. It now looks like the acceptance of this rare form of carbon as an impact signature will have to wait corroboration from more PTB sites. Until then, its claims for a place alongside iridium as an impact tracer will remain a strong but unconfirmed possibility. While fullerene may eventually turn out to be a useful indicator and future work may even confirm an impact event at the PTB, the doubt about the capability of this impactor to produce this immense extinction will persist unless supported by discovery of a large crater, either visible or buried, or explain its absence.

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FROM THE ARCHIVES

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Polyrhachis ants and bacterial symbiosis

While working with the lac insect, *Lakshadia mysorensis* growing on *Shorea talura*, in Bangalore, India, I found the ant, *Polyrhachis rastella* Latr. v. *formicata* Em. intimately associated with it. All the species of Polyrhachis ants I have come across, build their nests underground while the above-mentioned ant lives entirely on trees. I found its nest not only on *Shorea talura* but also on mango and other trees where the leaves were just broad enough to be webbed or rather glued together to serve as small nests for this ant. It seems to have acquired the habit of living on trees in adaptation to an intimate association with scale insects. While surveying the possibilities of spreading itself in a lac plantation, where there was no scarcity of food in the form of honey excreted by the lac insects, I could not imagine why the ant was so scarce there. I never found two nests on the same tree or even a large one so that the greatest search had to be made to discover its nest. What natural factors check this ant from multiplying itself, has never been clear to me.

Polyrhachis formicata is further interesting as secreting a strong odour pleasant to the human nose. While the odour was characteristically allied to amylacetate, traces of a ketone and an amine as well were detectable. An organic chemist kindly suggested the smell might be that of amylformate since most ants produce formic rather than acetic acid. I asked a colleague in the Indian Institute of Science to prepare some amylformate for me which had an unpleasant smell. Many other esters were also tried but the odour of the ant *Polyrhachis formicata* approximated more to amylaceatate than to any other ester tried. I also know another ant which produces the odour of ethyl acetate and where no appreciable smell of formic acid is formed so that the generalization that all ants produce formic acid in some form is not justified.

Polyrachis menelas For. is also found in the lac plantation in Bangalore. It lives underground and as far as the lac culti-