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Terrestrial and Extraterrestrial Fullerenes

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ABSTRACT

This paper reviews reports of occurrences of fullerenes in circumstellar media, interstellar media, meteorites, interplanetary dust particles (IDPs), lunar rocks, hard terrestrial rocks from Shunga (Russia), Sudbury (Canada) and Mitov (Czech Republic), coal, terrestrial sediments from the Cretaceous-Tertiary-Boundary and Permian-Triassic-Boundary, fulgurite, ink sticks, dinosaur eggs, and a tree char. The occurrences are discussed in the context of known and postulated processes of fullerene formation, including the suggestion that some natural fullerenes might have formed from biological (algal) remains.

Key Words: Fullerenes; Stellar media; Moon; Meteorites; Terrestrial rocks; Biogenic formation.

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1. INTRODUCTION

When Kroto et al.[1] discovered buckminsterfullerene, they predicted that this surprisingly stable carbon molecule should occur abundantly in circumstellar and interstellar media, hence in meteorites. Astronomers almost immediately began searches for fullerenes and fullerene derivatives in interstellar and circumstellar media. When Krätschmer et al.[2] first synthesized macroscopic amounts of C_{60} and discovered that the fullerenes were soluble in organic solvents such as toluene and in CS_2, the search for fullerenes in terrestrial and extraterrestrial rocks became possible and began. All searches had in common not only the excitement of the hunt, but, if fullerenes were found, speculations on how and where these had formed in the first place. There ensued therefore an interesting interaction between geo- and cosmochemists on the one hand and fullerene chemists on the other (see Ref.[3]). In this review we will report the story of the successes and failures of searches for fullerenes in nature and the interpretations of their formation or absence.

The reader of publications on terrestrial and extraterrestrial fullerenes will be confronted with apparently conflicting results. For example, one group of investigators reported the finding of fullerenes in samples of the Allende meteorite[4] while others have failed to find fullerenes in other samples of the same meteorite.[5–10] We will never use the statement "there are no fullerenes in the Allende meteorite" but we shall assume that "group A found fullerenes in their samples of Allende" or "group B found no fullerenes in their samples of Allende". Even when there were doubts expressed about a discovery of fullerenes "in the wild" we will treat every discovery as real unless retracted by its authors.

We have attempted to find and include most relevant publications up to December 31, 2002, including significant conference abstracts. Occasionally such abstracts are the only reports available on a specific topic. The great majority of abstracts cited are from the annual Lunar and Planetary Science Conferences or the annual Meetings of the Meteoritical Society. The former can be ordered from the Lunar and Planetary Institute, Houston, TX, USA; the latter are printed in the regular issues or supplements of Meteoritics (now Meteoritics and Planetary Science) An exception to completeness was made for publications in the fields of fullerene photo- and pressure-polymerization, fullerene synthesis by carbon condensation, and fullerene synthesis by oxygen-starved combustion of organic compounds. The number of papers in each of these fields is so large that we decided to cull for citation only a few papers from each of these. The reference section of this paper lists a large number of entries. This is deliberately done to ease literature researches of future investigators of fullerenes in nature.

2. FULLERENE ASTROCHEMISTRY

Analysis of all manifestations of electromagnetic radiation is the only diagnostic tool that astronomers have to survey for electrons, ions, atoms, molecules, macromolecules and solid grains ("stardust") in the Universe. Every conclusion that one of these is discovered must be confirmed by analogous experimental or theoretical studies in the laboratory. Given the huge number of known atoms, molecules, and minerals, inorganic as well as organic, that seems to be a relatively simple task, but it can also be frustrating when more than one molecule or cluster of molecules emits, absorbs, polarizes, or scatters light at or very near the wavelengths of interest.

When fullerenes were discovered there already existed a number of enigmatic observations concerning radiation received from interstellar media. Foremost among these were the general shape of the interstellar extinction curve for the Galaxy with its strong, but broad feature centered at 217 nm, and the so-called diffuse interstellar bands (DIBs), which are spectral features arising from absorption of light by matter in the diffuse interstellar gas. The strong 217 nm absorption band was variously attributed to graphite, carbonaceous materials, carbon compounds processed on icy grains, or carbon onions, but there are problems with all of these (see for example Ref.[11]). Thirty-nine DIBs were known in 1975 and about 80 in 1988. Today they number more than 200. Diffuse interstellar bands range in frequency from the visible to the infrared. A variety of carbon-bearing compounds was proposed as carriers, but the most widely touted of these were ionized PAHs.[12–15] The initial problem with PAHs was an "embarrassment of riches" because it was concluded that the already known PAHs should give rise to many more DIBs than observed, unless one accepted that only a restricted number of PAHs actually occurred in interstellar media.

Onto this smorgasbord of astrochemical compounds fell the fullerenes and they, as well as some of their derivatives, immediately became potential candidates for the interstellar extinction curve, its 217 nm maximum, and the DIBs. A major observational problem, until after 1990, when macroscopic amounts of C_{60} became available, was that only one absorption feature of C_{60} at 386.0 nm had been determined.[16] All other assignments of fullerenes to specific DIBs had to be checked by theoretical calculations of the unknown energies of electronic and vibrational transitions of fullerenes and fullerene derivatives. Today, the results of searches for fullerenes in interstellar media have achieved very modest, but still much debated results. Perhaps the strongest evidence was the fit of a few DIBs in the infrared with measured absorption bands of C_{60}^{+}[17–24] and of the interstellar extinction curve with its 217 nm maximum with C_{60} and fulleranes, the hydrogenated fullerenes $C_{60}H_{2n}$ ($n = 1 - 30$).[25–30] However, even in these cases there remained strong reservations about the assignments.[31,32] There were also failures to associate specific DIBs with

known electronic and vibrational transitions of fullerenes and fullerene deriva-
tives, especially in the UV.[33–35] A study of light emitted from a proto-planetary
nebula concluded that the observed electromagnetic features could be best
explained by a mixed population of hydrogenated amorphous carbonaceous
grains, fullerenes with different degrees of hydrogenation, partially dehydroge-
nated cationic PAH molecules, and crystalline silicates,[36,37] quite an assortment
of compounds. Nevertheless, that is perhaps much more realistic than claims that
any specific, single carbon compound is greatly dominant in such environments.

If fullerenes occur in interstellar media, how were they formed and from
where did they come? The most widely held view is that interstellar fullerenes
formed initially in atmospheres of carbon-rich, hydrogen-poor stars whence they
are delivered by strong stellar winds to interstellar media. Possible syntheses
include carbon condensation,[1,38–42] but also hydrogenation,[25–30] pyrolysis of
gaseous molecules,[43] and decomposition of hydrogenated amorphous
carbon.[44] Unfortunately, extensive experimental evidence shows that many
other forms of elemental carbon are likely to form alongside fullerenes and it
is still not understood which of these will be the most abundant in any of the
relevant astrochemical environments. Today, most investigators of formation of
fullerenes in stellar atmospheres consider the simultaneous formation of amor-
phous carbon, carbon onions, carbon black, and carbynes in variable proportions.

Once delivered to interstellar media, the fullerenes and fullerene deriva-
tives participate in the complex chemistry of these environments. Detailed
experimental and theoretical studies on this subject have been published.[45–49]
The following is a summary of the pertinent observations and conclusions.
The high ionization energy of C_{60} and the low UV flux in interstellar clouds
essentially preclude direct photoionization, but charge transfer electron
detachment from He^+ or interactions with cosmic ray protons may produce
C_{60}^{2+} and C_{60}^{3+}. The most likely loss process for both species is partial
neutralization with electrons, eventually to C_{60}^+. Whether C_{60}^- ions can form
either by free electron attachment or by electron transfer with negatively
charged PAHs is not clear. Once formed, however, C_{60}^- ions should be quite
stable given the high electron affinity of the neutral molecule. The three
positive ions can react, however, with various molecules in interstellar clouds.
Their reactivity decreases from C_{60}^{3+} to C_{60}^+. The reactants studied include
C_6H_6, $C_{20}H_{10}$, $C_{14}H_{10}$, CH_3OH, HC_3N, NH_3, and many others. With acenes,
the ions, like neutral C_{60}, form $[4 + 2]$ cycloadducts. Adduction with con-
densed PAHs such as corannulene, results in a charge-transfer complex. These
papers do not present any calculated equilibrium distribution of the various
fullerenic molecules because that cannot be done reliably until the reaction of
C_{60} with atomic hydrogen becomes better studied. They suggest, however, that
neutral C_{60} is likely to be the most abundant fullerenic molecule in interstellar
media, if such molecules exist there at all.

In summary, while there are tantalizing hints, there is no solid evidence that fullerene molecules, ions, or their derivatives actually occur in circumstellar and interstellar media. The notion that interstellar media are, hence the solar nebula was rich in fullerenes, available there in abundance to be picked up by meteorites or their precursor materials is unwarranted.

3. FULLERENES IN ROCKS

3.1. Meteorites and Interplanetary Dust Particles

Soon after fullerenes were discovered it was suggested that they might occur in meteorites as a kind of "molecular bottles" for certain isotopically anomalous trapped noble gases.[50] However, it was subsequently found that these gases were actually contained in nanodiamonds.[51] Nevertheless, precisely because the nanodiamonds and the later discovered graphite and silicon carbide grains in meteorites are interstellar, it seemed logical to search for possibly interstellar fullerenes in meteorites also.

There are three major classes of meteorites: the iron-, stony- and stony-iron meteorites. Elemental carbon occurs in meteorites of all three, but the thermal and metallurgical histories of the iron meteorites, whose metals were once molten and many of which contain graphite, mitigates against them containing fullerenes, and no searches for fullerenes were ever made in iron or stony-iron meteorites. Among the stony meteorites it is the carbonaceous chondrites that are the richest in presolar grains, hence are the most likely extraterrestrial rocks to contain presolar fullerenes.

The search for fullerenes in rocks is a comparatively simple geochemical procedure. CS_2 and aromatic organic solvents were used for the extraction of fullerenes from rocks when it became understood that C_{60} and C_{70} dissolve well in them. Most analytical procedures begin therefore with solvent-extraction of either the powdered meteorite or its so-called "acid-resistant residues" (ARRs), carbon-enriched residues obtained by the dissolution of inorganic minerals usually with HF-HCl. One assumes that the fullerenes are not too strongly locked up in the powdered meteorites or ARRs and that the chemical treatments do not destroy them. Studies of the geochemical behavior of fullerenes have shown that the HF-HCl treatments do not degrade them but very strongly oxidizing chemicals such as hot perchloric acid do.[52] Meteorite extracts were always in contact with air at some stage of the analysis but in darkness and even in conditions of moderate light (e.g. lab benches) molecular oxygen does not react detectably with fullerenes. However, ozone swiftly oxidizes fullerenes in solution.[53]

After filtration the extracts are analyzed by HPLC or by mass spectrometry (or, as in a few studies, by both). HPLC has the advantage that fullerenes are

neither formed nor destroyed by this technique and that rather precisely calibrated quantitative data can be obtained. A potential problem is that fullerenes and several organic compounds with closely similar retention times and UV-VIS absorption spectra could be present in the extracts. This problem can be alleviated but not completely removed by the use of different HPLC columns for the analysis of the same sample.[10] mass spectroscopy, the characteristic set of isotopic peaks at $m/z = 720$–724 amu in spectra is used for proving the presence of C_{60} in the sample, but when laser desorption-ionization is used there is the potential risk that fullerene ions are actually formed in the process from carbonaceous matter or hydrocarbons. Also, mass spectrometric methods have not yet yielded precise quantitative data. In one study, the extraction of fullerenes was attempted by sublimation in the range 300–600°C, followed by mass spectrometric analysis.[7] Two papers reported negative results of searches for fullerenes in two meteorites by vacuum pyrolysis.[5,6]

Table 1 presents a summary of the results of all searches for fullerenes in **T1** meteorites. Dr. P. Buseck (personal communication of unpublished results) did not find fullerenes in twelve carbonaceous and ordinary chondrite samples of his own. Obviously some investigations found fullerenes in their samples whilst others did not in theirs.[4–10,54–58] It is still not clear what has caused the

Table 1.   Reported fullerene contents in meteorites.

Meteorite	C_{60} (ppm)	C_{70} (ppm)	Higher[a]	Reference
Allende[b]	100			[4]
Allende	detected	detected	detected	[54]
Allende[c]	all <1			[150,151,157]
Allende	detected	detected		[55]
Allende	detected	detected	detected	[54]
Allende	10			[56]
Allende	10			[56]
Allende	5			[56]
Allende[d]	all <3			[56]
Allende	detected	detected	detected	[57,58]
Murchison	not detect.			[5,6]
Murchison	<2			[7]
Murchison	not detect.			[157]
Murray	not detect.			[5,6]

[a]Higher means $C > 70$
[b]Arranged in order of year of publication
[c]A total of nine distinct samples
[d]A total of seven distinct samples.

253 differences. Chondritic meteorites are known to be mineralogically hetero-
254 geneous clastic breccias, hence the analysis of one large and homogenized
255 sample, or of a number of smaller samples may be required to find any
256 fullerenes present in a given meteorite. Some of the negative results could be
257 due to inefficient fullerene extraction.

258   It appears then that fullerenes occur heterogeneously distributed in ppb
259 quantities in the Allende meteorite. It has not been convincingly demonstrated
260 that they occur in other meteorites. Again the questions are: how and where did
261 the Allende fullerenes form? It was suggested that these had formed around
262 C-rich stars, had made it into interstellar media and eventually via the solar
263 nebula into the meteorites, [4] but it was also suggested that the formation of
264 fullerenes and fulleranes could have occurred in the solar nebula.[55,56] The
265 most recent studies report the occurrence of noble gas atoms trapped in Allende
266 fullerene molecules.[57,58] The composition of the trapped gas is that of the well-
267 known meteoritic component of "planetary noble gases", which were sug-
268 gested to have been trapped in a carbonaceous meteoritic phase in the cooling
269 solar nebula.[59] Some, or even all of the fullerene molecules of Allende may
270 therefore have formed in the solar system but it is still unclear how and where.
271 We suggest here that clues may be found in the nature of the carbonaceous
272 matter of the Allende meteorite. In most carbonaceous meteorites, the bulk of
273 the element carbon occurs as a complex organic polymer. Allende is excep-
274 tional because the element is a poorly ordered carbon, characterized from
275 studies by transmission electron microscopy as "glassy carbon".[60,61] A more
276 recent TEM study of Allende carbon supports this finding and reports the
277 abundant occurrence of "carbon black-like particles" Vis et al.[62] Taken
278 together these observations suggest that Allende carbon formed by pyrolysis
279 of hydrocarbons and polymeric hydrocarbons, in part in a gas phase, in part
280 perhaps on hot mineral surfaces. Such a scenario for the formation of fullerenes
281 is not too outlandish when one considers that fullerenes have been synthesized
282 by the pyrolysis of naphtalene[63] and by the consecutive/multiple cyclo-
283 dehydrogenation of even more complex trimerized PAHs.[64–69]

284   It has been suggested that pre-terrestrial fullerenes are an important carrier
285 phase for the noble gases of the atmospheres of the terrestrial planets.[57,58]
286 That is questionable because it can be shown that the Allende ARR must
287 contain more than 1 g C_{60} per gram to account for all so-called planetary He
288 and that is obviously impossible.

289   Interplanetary dust particles (IDPs) constitute a circumsolar dust system.
290 It is generally assumed that this system must be continuously refreshed with
291 particles from comets and asteroid collisions. The particles have been
292 collected in the Earth's stratosphere and by Earth-orbiting spacecraft but
293 also from the mid-oceanic seafloor and polar ice deposits. Interplanetary
294 Dust Particles range in size from about one micrometer to about 1 mm. It is not

clear why IDPs might contain fullerenes unless one argues that the collisions of and impacts on chondrite parent bodies in the asteroid belt releases fullerene-bearing chondrite dust. Bajt and his coworkers searched for fullerenes in IDPs.[70,71] The result, although seemingly encouraging, was nevertheless inconclusive. More recently, Becker and Poreda[72] have suggested that IDPs contain noble gas-laden fullerenes.

3.2. Fullerenes were not found on the Moon

The discovery of fullerenes on the skin of the Long Duration Exposure Facility (LDEF) spacecraft in Earth orbit, possibly formed by a high-energy impact from carbon of a micrometeorite,[73] suggested that fullerenes might occur in the lunar regolith, the fragmented and unconsolidated outermost rocky layer of the Moon. Impact craters with a large range of diameters are abundant selenographic surface features and some of the impactors are likely to have contained elemental carbon or carbon compounds from which fullerenes could have formed in some of these violent events. A search for fullerenes in samples returned by Apollo missions was therefore undertaken.[74] Two samples of so-called "lunar fines", i.e. <1 mm particles from the regolith, were made available by NASA. One was 5.006 g of fines collected directly at the surface of the Apollo 11 landing site. The other was a 7–17 cm depth subsurface sample of 0.972 g fines collected in the Van Serg trench at the Apollo 17 site. The samples were extracted with toluene and were analyzed by HPLC. No fullerenes were detected at the 1 ppb level or higher.

These negative results must be evaluated in the context of the puny fraction of lunar regolith matter that was actually studied. The regolith content of fullerenes could be grossly heterogeneous with detectable amounts present at young craters but none in older terranes as there are several processes that could dilute or even destroy regolith fullerenes in the course of time. Elemental carbon, including fullerenes, can react with impact-molten silicates to form CO and CO_2 that escape from the Moon, one explanation for the surprisingly small carbon contents of lunar fines and rocks.[75–78] Also, fullerenes can become destroyed on the Moon by thermal decomposition,[79–81] destruction by electrons and ions from the solar wind and cosmic rays[82–86] and become photo- or pressure-polymerized[87,88] in the harsh environment of the lunar regolith. Fullerene multimers, because of their very low solubilities in organic solvents, are very hard to detect. An additional loss mechanism from the equatorial region of the Moon is due to the estimated relatively short sticking time of 270 s of C_{60} at the very top of the regolith of the two landing sites. That time rapidly lengthens towards the cooler lunar Poles, which means that fullerenes could have slowly migrated north- and southward away from the more equatorial

Apollo sampling areas.[89] The diffusional migration can also proceed downward into the regolith because the penetration of the diurnal lunar heat wave is very shallow. That was the reason why the Apollo 17 sample was studied.

3.3. Terrestrial Rocks, Overview

Fullerenes have been reported in two distinctly different kinds of terrestrial rocks: hard, carbon-rich formations and sediments. The hard materials occur in the so-called shungite formation of Karelia, Russia, in the large-body impact structure at Sudbury, Ontario, Canada, and in bitumens among pillow-lavas of the Bohemian massif, Czech Republic, and Coals of the Yunnan province of the People's Republic of China. These materials may have in common that their parent materials were biological remains. The sedimentary rocks come from formations at the Creataceous-Tertiary Boundary (KTB) and the Permo-Triassic Boundary (PTB). These formations are associated with catastrophic mass extinctions of species. Figure 1a shows the locations of fullerenes in hard rocks. Figure 1b shows the locations of fullerenes in sedimentary rocks.

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3.4. Hard Rocks

3.4.1. Shungite

We received valuable guidance and information for the writing of this section from an unpublished manuscript by Dr. Buseck. Buseck et al.[90] reported the serendipitous finding of C_{60} by high-resolution transmission electron microscopy in shungite, a metamorphosed carbon-rich rock within Precambrian sediments of about 1.8 Gy on the Kola Peninsula of Russia. They followed through by analyzing powdered samples with Laser Desorption Mass Spectrometry (LDMS), which confirmed the presence of the fullerene.[91,92] A number of subsequent studies have also found small concentrations of C_{60} in shungite.[93–101] Other investigators have questioned these reports or have failed to find fullerenes in their samples of shungite.[102,103]

The presence of C_{60} in shungite is enigmatic. There is no evidence for any high-energy events at Shunga such as a meteorite impact structure or lightning strikes.[104,105] Because the age of the Karelian shungite could be closely the same as that of the Sudbury impact structure (see below) it seems marginally possible that the shungite C_{60} is due to a world-wide fullerene-bearing dust deposit from the Sudbury event. If, however, the formation was local or in situ, then one must try to understand the origin of the C_{60} in the context of the origin and formation of the carbon itself. The principal sources for the shungite can be either biogenic or volcanogenic.[106] It is not yet known
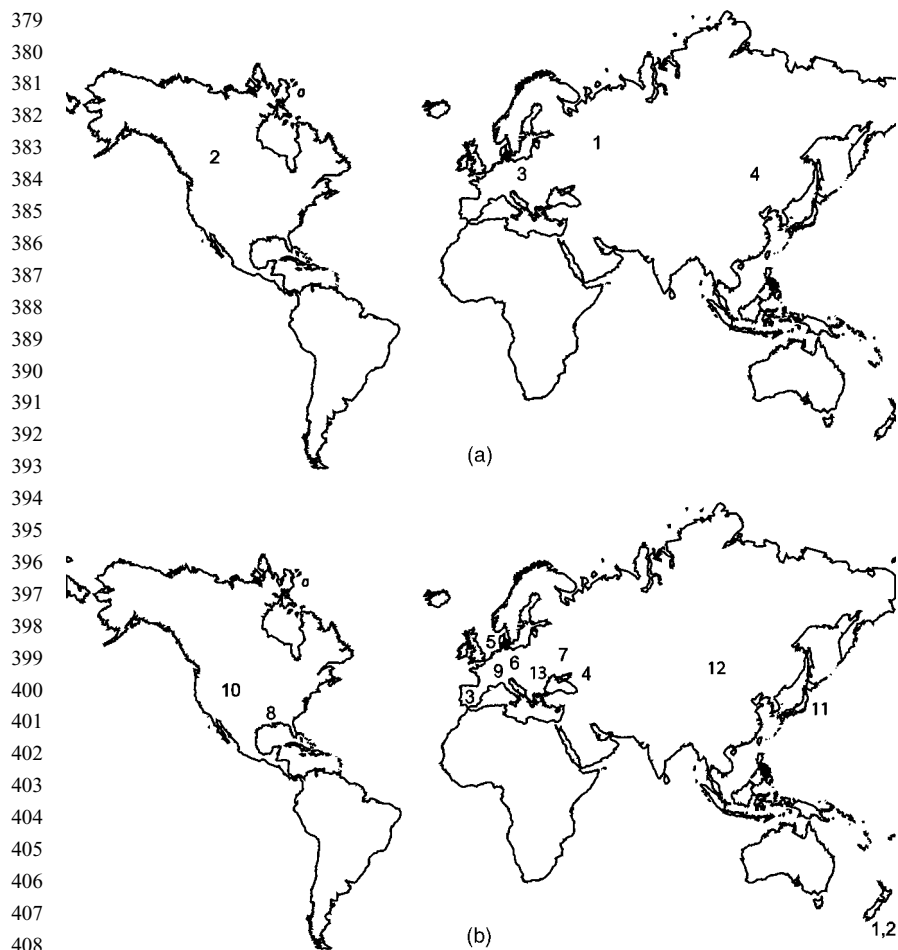
Figure 1. (a) World map showing the locations where fullerenes were reportedly found in hard rocks. 1 = Shunga, Karelia, Russia. 2 = Sudbury, Ontario, Canada. 3 = Mitov, Czech Republic. 4 = Yunnan Province, Peoples Republic of China. (b) World map showing the locations where fullerenes were searched in soft rocks. 1 = Woodside Creek, New Zealand. 2 = Flaxbourne River, New Zealand. 3 = Caravaca, Spain. 4 = Sumbar, Turkmenistan. 5 = Stevns Klint, Denmark. 6 = Elendgraben, Austria. 7 = Tetri Tskaro, Georgia. 8 = Brazos River, Texas, USA. 9 = Gubbio, Italy. 10 = Raton Basin (Boca Raton), Colorado, USA; 11 = Sasayama, Japan. 12 = Meishan, Peoples Republic of China. 13 = Bálvány, Hungary.

whether fullerenes occur in volcanic exhalations. If the C_{60} is a metamorphic product of local biogenic matter, in this case most likely remains of blue-green algae, then one must try to understand its formation in the context of the graphitization of such remains.

   A Science Magazine article that accompanied the discovery paper[107] cites the opinion of several experts that fullerenes cannot form in condensed phases. That may, or may be not so, but the precursor materials of shungite and the later to be discussed bitumens of the Bohemian Massif had probably significant internal gas phases in which fullerenes could have formed at sufficiently high temperatures. Shungite carbon has been characterized as "glassy".[90,106,108–110] Glassy carbon is a pyrocarbon with internal voids that typically forms by the pyrolysis of polymerized hydrocarbons on hot sur-faces.[111,112] Other investigators report "carbon black particles"[113] and "multilayered hollow globules"[114] in shungite. The globules are probably not fullerene-like structures but graphitized carbon black. C_{60} could also have formed during the transformation of algal remains to glassy carbon if a biogenic C_{60} precursor was present early on. PAHs in general have frequently been suggested as potential C_{60} precursors, but very recently it has been shown specifically that the $C_{20}H_{12}$ PAH 4,5-dihydrobenz[1]acephenanthrylene with molten S_8 readily cyclotrimerizes to two possible $C_{60}H_{30}$ isomers of which one, viz. benzo[1,2-e:3,4-e′:5,6-e″]tribenzo[1]acephenanthrylene (C_3 symmetry), possesses the exact carbon atom topology of the C_{60} Schlegel diagram.[64,65] Unfortunately, however, under the S_8-mediated cyclotrimeriza-tion conditions the wrong $C_{60}H_{30}$ isomer, viz. benzo[1,2-e:3,4-e′:6,5-e″] tribenzo[1]acephenanthrylene, which possesses C_1 symmetry and thus a carbon atom topology that does not match the C_{60} Schlegel diagram is the prevalent product (Fig. 2). Hence, upon cyclodehydogenation, i.e. constru-ctive H_2 losses and ring closures, of the S_8 cyclotrimerization reaction mixture under MALDI TOF-MS (positive ion mode) conditions only the curved PAH $C_{60}H_{10}$ and $C_{60}H_{12}$ were obtained. No evidence for the formation of C_{60} was found.[64] Fortunately, an independent regio-chemically controlled synthesis of the proper $C_{60}H_{30}$ cyclotrimer became available[115] and it was recently shown that under similar MALDI TOF-MS (positive ion mode) conditions this $C_{60}H_{30}$ isomer fully dehydrogenates to C_{60}.[64–67,69] The viability of the stepwise zipping up of the proper $C_{60}H_{30}$ PAH (C_3 symmetry) to C_{60} is supported by semiempirical (AM1, PM3) as well as ab initio calculations (Fig. 3).[67,69] It is interesting to note that C_{70} cannot form by a related cyclotrimerization/dehydrogenation process of single PAH precursors because suitable precursors do not exist ($70 : 3 = 23.33!$).[68,116] Exactly which condi-tions the shungite formation has experienced is still unresolved. If that was greenschist facies metamorphism, then any algal remains were exposed to temperatures in the range 300–500°C for several 10^5, perhaps 10^6 years.

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$C_{60}H_{30}$, C_3 $C_{60}H_{30}$, C_1
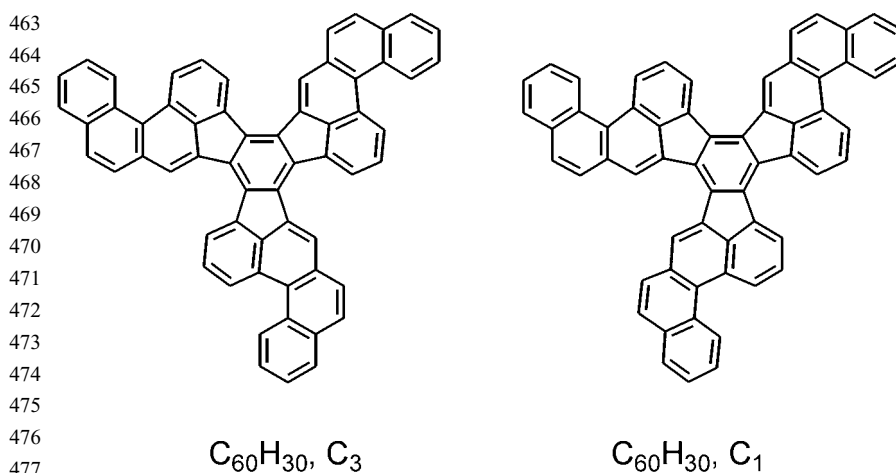
Figure 2. The "propeller-shaped" C_{60} progenitor benzo[1,2-e:3,4-e′:5,6-e″]tribenzo[1] acephenathrylene (C_3 symmetry) and its isomer benzo[1,2-e:3,4-e′:6,5-e″]tribenzo[1] acephenanthrylene (C_1 symmetry).

Elemental sulfur should be present in such systems, but it is not known whether $C_{20}H_{12}$ forms during algal decay. Formation of glassy carbon in laboratories and graphitization of carbon black requires higher temperatures than the conditions of greenschist facies metamorphism, but the long duration of the metamorphism might offset this drawback. Could C_{60} form in small amounts under these natural conditions? The answer is not yet known unless one accepts the natural fullerenes as evidence that it does.
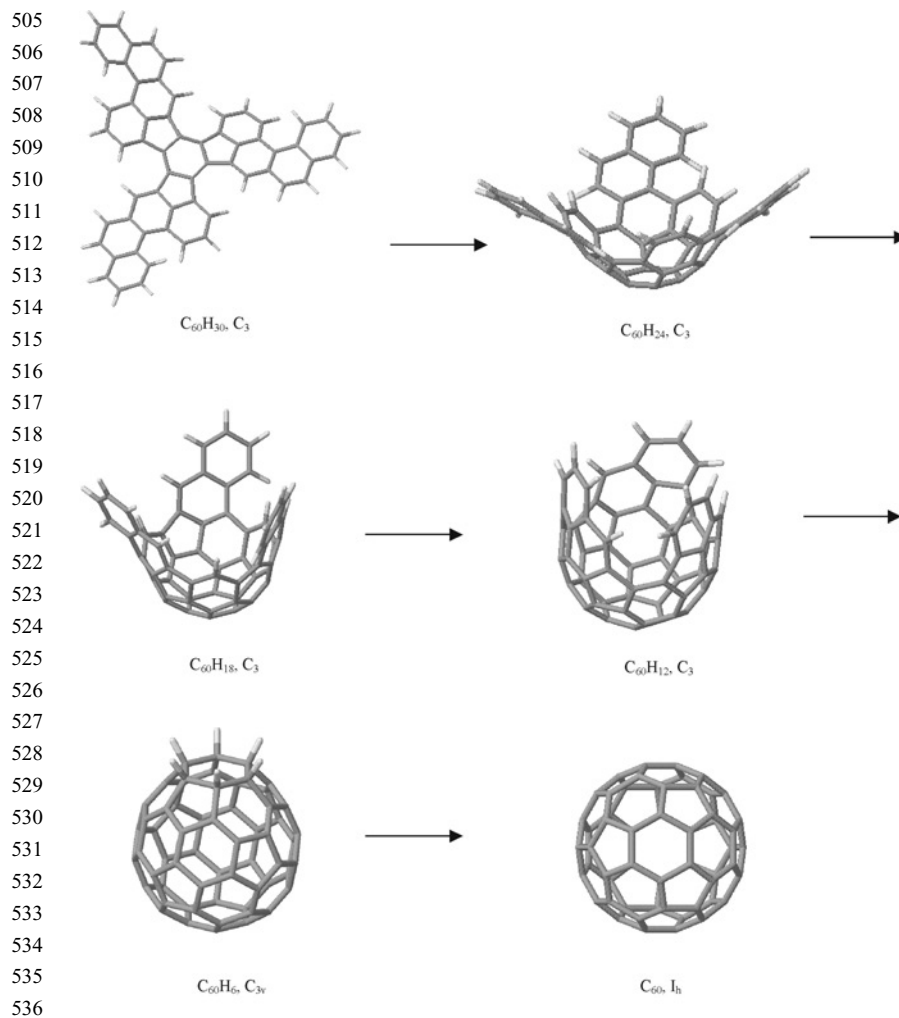

3.4.2.   Sudbury

The search for fullerenes in rocks from the huge Sudbury impact structure was undertaken because it suggested an LDEF kind of event only numerous orders of magnitude bigger.[117] The Sudbury multi-ring, tectonically deformed impact structure in Ontario, Canada is 1.85 Ga in age.[118,119] The Precambrian date is significant because not enough combustible plant-life was then available to sustain the kind of global wildfires which raged following the catastrophic impact at the end of the Cretaceous and which are thought to have produced fullerenes (see section on sedimentary rocks). The estimated diameter of ∼180–250 km of the Sudbury structure is among the largest on Earth.[120–122] The carbon-rich rocks of interest occur within a canoe-shaped ∼1600 m thick sequence of heterolithic breccias of the Onaping Formation[123]

C$_{60}$H$_{30}$, C$_3$

C$_{60}$H$_{24}$, C$_3$

C$_{60}$H$_{18}$, C$_3$

C$_{60}$H$_{12}$, C$_3$

C$_{60}$H$_6$, C$_{3v}$

C$_{60}$, I$_h$

Figure 3. Zipping up "the crushed fullerene" C$_{60}$H$_{30}$: C$_{60}$ by fifteen-fold, consecutive intramolecular H$_2$ losses and ring closures under MALDI TOF-MS (positive ion mode) conditions[67,69] (Ref.[66]). All structures were obtained by semiempirical (AM1 and PM3) calculations. Both methods give similar results[67–69,116].

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547 which is overlain by ∼600 m of mudstones of the Onwatin Formation,[124] and
548 ∼850 m of wacke-turbidites of the Chelmsford Formation,[124] all making up
549 the Whitewater Group.[125] Figure 4 is a schematic representation of this   **F4**
550 Group, showing also the traditional subdivision of the Onaping Formation. It
551 was in rocks from the Black Member of this Formation that fullerenes were
552 found in ppm concentrations.[117] It was subsequently reported that the C_{60}
553 was actually an endohedral molecule with isotopically anomalous He enclosed
554 within the cages.[126] Other investigators have failed to find fullerenes in their
555 samples of the same formation.[127] Table 2 lists the results of all searches for   **T2**
556 fullerenes in rocks from the Sudbury structure. Clearly some samples
557 contained fullerenes whilst others did not.

558   The rocks of the Black Member of the Onaping Formation in which the
559 fullerenes were found contain approximately one percent of overwhelmingly
560 elemental carbon. Raman spectra show that the carbon is highly disordered.[127]
561 Various theories about the origin of this carbon exist, but extensive $^{13}C/^{12}C$
562 measurements have now conclusively demonstrated that the Black Member
563 carbon is isotopically the same as carbon from the Onwatin and Chelmsford
564 Formations, hence is biogenic. The carbon proper is not from the impactor, but
565 postdates the formation of the crater.[127] Algal remains, formed within the
566 crater's lake, were later graphitized by low-grade greenschist facies metamorph-
567 ism. Hence the C_{60} molecules were not formed during the impact event from
568 some carbon-bearing matter of the impactor or from the very sparse local target
569 sources of carbonates and carbonaceous matter, but were already contained
570 within the impactor prior to its collision with Earth, or were formed much later.
571 This raises a number of salient issues. Did the impactor contain enough
572 fullerenes to explain an estimated C_{60} content of the Black Member? Why is
573 the fullerene distribution of the Black Member so patchy? Could the fullerenes
574 have survived contact with a superheated atmosphere and hot rocks? What
575 fraction was blasted into the stratosphere to fall back to the Earth's surface at
576 large distances from the crater? Could the He in He@C_{60} have survived the   **Q2**
577 greenschist metamorphism? None of these were ever significantly discussed.

578   The estimated pre-deformation, circular diameter of the Onaping Forma-
579 tion is about 50 km and its thickness about 1 km. This yields a total volume of
580 roughly 2000 km^3, somewhat larger than an earlier estimate.[128] The reported
581 C_{60} contents of Black Member rocks are in the range 1–10 ppm.[117] The only
582 extraterrestrial matter for which C_{60} was reported were meteorites, samples of
583 which contained from a few to about 100 ppb C_{60} (see Table 1). Let us assume
584 a uniform C_{60} content of 10 ppb for the impactor of which only an estimated
585 0.1 ppb remained behind at the impact site (from an estimated Ir content at the
586 Chicxulub Cretaceous/Tertiary age impact site, compared to the estimated
587 total, world-wide iridium deposits; Dr. B. C. Schuraytz, private communica-
588 tion, 2000). The remaining 99.9 ppb would have been dispersed globally, like
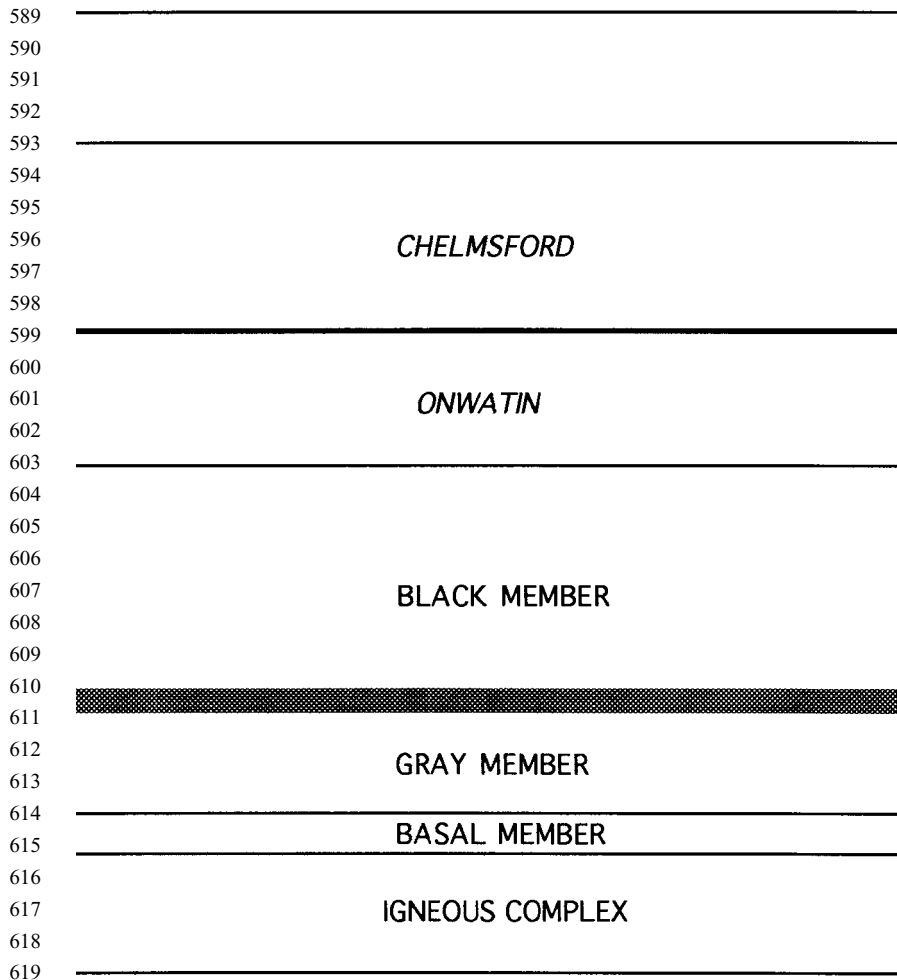
CHELMSFORD

ONWATIN

BLACK MEMBER

GRAY MEMBER

BASAL MEMBER

IGNEOUS COMPLEX

Figure 4. Schematic representation of the Formations of the Whitewater Group rocks of the Sudbury Impact Structure. From bottom to top: Igneous Complex. Then: Basal Member, Gray Member, Green Member (the thin white band above the Gray Member), and Black Member, all of the Onaping Formation. Then: Onwatin Formation and Chelmsford Formation.

Table 2. Fullerenes in rocks from the Sudbury impact structure.

Sample Location ONAPING FORMATION	C_{60} (ppm)	Reference
BLACK MEMBER		
High Falls[a]	1	[117]
High Falls	6–7	[117]
High Falls[b]	not found	[127]
Onaping River	10	[117]
Dowling	found[c]	[126]
Dowling	not found	[127]
Capreol	found[c]	[126]
Capreol[d]	not found	[127]
Nelson Lake	not found	[127]
South Chelmsford	not found	[127]
Nickel Offset Road	not found	[127]
GREY MEMBER		
High Falls	not found	[127]
ONWATIN FORMATION		
Dowling	not found	[127]

[a]Names of sampling locations on the Black Member of the Onaping Formation.
[b]Eight different rocks from High Falls.
[c]He@C_{60} reported.
[d]Three different rocks from Capreol.

iridium in the case of the Chicxulub event. In order for the Black Member to have a uniform C_{60} content of at least 1 ppm, the volume of the impactor must have been $\{10^{-6}/10^{-9}\} \times 2000 = 2 \times 10^6$ km^3 and its radius at least on the order of 100 km, clearly outside the estimated impactor radius of 10–20 km (Dr. B. French, private communication, 2000). Obviously, the fullerene content of the Black Member is too large to be consistent with a maximum dimension of the impactor.

The survival during impact and patchiness of C_{60} in the Black Member can perhaps be understood in the context of fallback and accumulation of the unconsolidated, still carbon-poor Onaping breccia that eventually became the Black Member rocks. Numerous experimental and theoretical studies of large impacts have demonstrated that significant fractions of large impactors can become scrambled with the target rocks and some impactor matter may be found among the local, so-called fallback material. Most experts on Sudbury have concluded that the fallback layers, i.e. deposits of material that was lifted up only to fall back into the crater, are the Basal, Gray and Green Members of

673 the Onaping Formation, all three *below* the Black Member in which the
674 fullerenes were found.[129] It has also been argued that the rock fragments
675 and glasses of the Black Member were actually stream-carried from outside the
676 central depression into the central depression where redeposition occurred
677 under euxinic aquatic conditions.[127,130] When did the first rains come after the
678 impact? Did they cool the surface sufficiently to allow preservation of full-
679 erenes? Perhaps so; nevertheless the substantial abundance of once-molten
680 glasses in the Onaping rocks is worrisome. Fortunately, the deduced solubility
681 of C_{60} in water is only on the order of only 10–11 ng/mL.[131]

682 Arguably the greatest problem for the He@ C_{60} origin from the impactor
683 is that helium loss rates as a function of temperature can be calculated from the
684 thermal release experiments carried out with these molecules.[126] When such
685 rates are applied to the temperature range and duration of the greenschist
686 metamorphism, 300–500°C during hundreds of thousands of years, it follows
687 that the helium should have been quantitatively lost. Perhaps fullerenes at
688 Sudbury also formed from algal remains late during the metamorphism that
689 would avert the potential problems of heat, pressure, and radiation of the
690 impact environment. Perhaps isotopically anomalous helium, released from
691 older minerals was occluded by the fullerene precursors and later firmly
692 trapped in the fullerene molecules.

693
694
695 ### 3.4.3.   The Bohemian Massif
696
697 At Mitov in the Bohemian Massif, Czech Republic, there occur pillow
698 lavas of andesitic basalt that contain hard solid bitumens with C_{60} at a level of
699 0.2 ppm as determined by HPLC and mass spectrometry.[132] C_{70} was not
700 found. It is thought that algal organic remains of Precambrian age were the
701 parent materials for the bitumens. The highly carbonized material is char-
702 acterized as glassy carbon. Once again it is remarkable that fullerenes were
703 found in materials with a biologic ancestry in the absence of any evidence that
704 C_{60} could have come "from the outside". It is this discovery that strengthens
705 the earlier mentioned hypothesis of conversion of certain PAHs to C_{60} but not
706 C_{70} during geologic metamorphism.

707
708 ### 3.4.4.   Coal
709
710 Coals have been investigated for the production of fullerenes (see for
711 example Ref.[133]). There are two reasons why one may expect fullerenes to
712 occur in coal. Coal is another material formed by metamorphism of biologic
713 remains and underground fires in coal deposits are common. Analyses are
714 generally encumbered by substantial amounts of organic compounds co-extracted

with possible fullerenes. C_{60} fullerene has been reported in a coal from Yunnan province, China.[134]

3.4.5.   Summary of Terrestrial Hard Rocks

There is considerable evidence that C_{60} molecules are associated at the 0.1–10 ppm level with highly carbonized matter in shungite, in rocks from the Sudbury structure, and from the bitumens at Mitov. Evidence for the occurrence of C_{70} in these materials is weak. Only at Sudbury was C_{60} found in rocks from an ancient impact crater and evidence that some, or all of the fullerenes are extraterrestrial. No such claim can be made for the fullerenes reported in shungite and bitumen. How did these form? And did some, or all of the fullerenes at Sudbury perhaps form in the same manner?

The carbons in which the fullerenes were found seem to have one property in common. It has been suggested here that every one these was derived from algal remains via metamorphic carbonization. For the carbon in the Black Member of the Onaping Formation that has been proven[127] but investigators of shungite are divided on the biogenic origin of its carbon.[106] The discoverers of fullerenes in the Czech bitumens claim a biogenic origin for these also.[132] Are there any reasons to expect formation of small quantities of fullerenes from algal remains? As we have argued in Section 3.4.1, biogenic PAHs might have been transformed to C_{60}.

The report that fullerenes at Sudbury contain isotopically anomalous helium seemingly precludes a terrestrial biogenic origin for the fullerenes in the Black Member of the Onaping Formation. However, only 1 in about 10^5 C_{60} molecules contains a helium atom; therefore a significant fraction of the remaining C_{60} molecules could be biogenic.

Some samples from Shunga and Sudbury were shown not to contain C_{60}. In one case at Sudbury a fullerene-containing sample was only about 10 cm removed from a fullerene-free sample.[127] Obviously, the fullerene distribution in these rocks is very patchy. An attractive feature of the hypothesis of PAH-trimerization/dehydrogenation with sulfur is that it may explain this patchyness.[64,116] Only in spots where the correct PAHs and hot sulfur both occurred could fullerenes form at all and perhaps only very inefficiently.

3.5.   Soft Rocks

3.5.1.   Cretaceous-Tertiary Boundary

In 1980, Alvarez and his collaborators discovered a thin global layer of clay-like geologic deposits greatly enriched in iridium.[135] They concluded

that a large extraterrestrial, iridium-rich body had collided with the Earth and that this event had triggered the catastrophic biologic extinctions at that time. The existence of a large buried crater at the tip of the Yucatan peninsula of Mexico was established as early as 1950[136] but it was not until 1990 that the crater, widely known as Chicxulub, was firmly identified as the KT impact site.[137] The time of the event is now determined as 65 Ma ago. Whereas the target rocks at Sudbury were mostly igneous and metamorphic with very little limestone, the target at Chicxulub was a thick carbonate platform with seams of sulfates. At Chicxulub there also were no thick elemental carbon-rich rocks.

The search for fullerenes in KTB materials was undertaken because it had been reported that these were rich in soot due to global wildfires following the impact,[138–143] and because it was known that fullerenes form in oxygen-starved sooting flames.[144–146] The disaggregated and powdered samples were extracted with toluene and the filtered solutions were analyzed by HPLC. Because most of these samples were also rich in organic compounds, including PAHs, the fullerene peaks in HPLC were riding on the tails of large organic peaks. This problem was significantly alleviated by the pre-separation of organics and fullerenes with a large semi-preparative HPLC column (Heymann et al., 1995). The identification of fullerenes was made on the basis of retention times and UV-VIS spectra. The presence of C_{70} in some chromatograms was especially important because it seemed unlikely that false positives would be obtained for two fullerenes.

The first hint that C_{60} was present in a small sample from the KTB at Woodside Creek, New Zealand was presented at the conference on New Developments Regarding the KT Event and Other Catastrophes in Earth History, 1993.[147] No fullerenes were found in the massive limestones above and below the KTB clay at Woodside Creek. Subsequently, fullerenes were studied in much larger samples and were found to be present or absent at 13 different KTB sites around the world.[58,74,148–154] One of the discoveries was reported in note 13 of Becker et al.[117] The location of the site was not given, but it is at Gubbio, Italy (Dr. L. Becker and Dr. T. Bunch, personal communication, 1994). All results are presented in Table 3. The C_{60} contents range from essentially zero to 16 ppb. C_{70}, when present was typically between 0.2 and 0.3 times C_{60}.

It was suggested that the fullerenes at the KTB had formed by oxygen-starved wildfires following the event. Since most of the KTB clays studies are relatively shallow water deposits formed near landmasses, it was also suggested that the fullerenes were co-deposited with the soot particles on which they were absorbed. It was also suggested that the fullerenes came from local fires and not from a worldwide deposit. It is not understood why fullerenes were not present at some locations. The most logical explanation is that the local conditions were unfavorable for fullerene-producing wildfires.

Table 3.   Fullerenes in samples from Cretaceous Tertiary Boundary sites.

Site Name	Country	C_{60} (ppm)	Reference
Woodside Creek[a]	New Zealand	2.17	[157]
Woodside Creek	New Zealand	2.74	[157]
Woodside Creek	New Zealand	2.5	[157]
Woodside Creek	New Zealand	4.7	[157]
Woodside Creek	New Zealand	5.4	[157]
Woodside Creek[b]	New Zealand	0.325	[157]
Woodside Creek[c]	New Zealand	2.48	[157]
Flaxbourne River[d]	New Zealand	0.556	[157]
Flaxbourne River	New Zealand	1.14	[157]
Flaxbourne River	New Zealand	0.0058	[157]
Flaxbourne River	New Zealand	2.3	[157]
Flaxbourne River	New Zealand	1.84	[157]
Flaxbourne River[c]	New Zealand	15.7	[148,149]
Flaxbourne River	New Zealand	11.9	[148,149]
Caravaca	Spain	11.9	[74,151,152]
Caravaca[c]	Spain	2.7	[74,151,152]
Sumbar-4	Turkmenistan	4.0	[74,151,152]
Sumbar-5	Turkmenistan	1.2	[74,151,152]
Stevns Klint	Denmark	2.17	[74,151,152]
Stevns Klint	Denmark	0.9	[74,151,152]
Elendgraben	Austria	0	[74,151,152]
Tetri Tskaro	Georgia	0	[74,151,152]
Brazos River[e]	Texas, USA	0	[153,154]
Gubbio[f]	Italy	detected	[117]
Raton Basin	Colorado, USA	detected	[117]
Stevns Klint[g]	Denmark	detected	[126]
Woodside Creek	New Zealand	0	[126]

[a]This material came from high on a hillside at Woodside Creek at which no sampling had ever been done before.
[b]This sample came from the southern bank of the creek, at river level.
[c]Demineralized samples.
[d]This material came from a location at Flaxbourne River at which no sampling had ever been done before.
[e]No fullerenes were found in 55 samples studied.
[f]Reference # 13 in Becker et al.[117]
[g]Also higher fullerenes reported.

841 These results and discussions were questioned on the grounds that the
842 oxygen content of the atmosphere at the time of the Chicxulub event was too
843 high and that no fullerenes were found in a sample from burned wood
844 associated with the 1993 Malibu Fires.[155] However, oxygen is needed to
845 remove hydrogen from the fullerene precursors in flame-produced fullerenes.
846 The "burned wood argument" overlooks the deduction that the KTB fires
847 started only after the combustible biota had become dry.[138–143] The wood
848 burned by the Malibu Fires was green. Stronger evidence against the wildfire
849 hypothesis was provided when it was found that preterrestrial isotopically
850 anomalous He associated with fullerenes occurs in the Raton and Stevns Klint
851 samples.[155] A fullerene molecule cannot be both terrestrial and preterrestrial.
852 One problem with this argument is that there is no direct evidence that the
853 helium atoms are actually inside these C_{60} molecules.

854 A quite serious objection was raised in a paper with the grossly misleading
855 title "There are no fullerenes in the K-T boundary layer".[156] The authors
856 reported no traces of C_{60} or C_{70} in a single sample from the Woodside Creek
857 site. They suggested that earlier HPLC results measured only "a mixture of
858 hydrocarbons". However, there are questions about this study also. While the
859 large number of positive results both by HPLC and later by LDMS of Table 3
860 are no guarantee that fullerenes actually occur in KTB clays, a single measure-
861 ment on a 20 g sample from the riverside location at Woodside Creek is not very
862 convincing evidence for "no fullerenes in the K-T boundary layer". It was not
863 explained by the critique why the so-called "false" C_{60} peak in the HPLC
864 chromatograms of the positive results sticks out from the tail of "a mixture of
865 hydrocarbons".[148] The probable explanation is simply that C_{60} has an
866 exceptionally large molar extinction at 336 nm, much larger than that of
867 hydrocarbons. It was not explained either by the critique why several of the
868 KTB extracts show not only C_{60} at the expected retention time and with its
869 known UV-VIS spectrum but also C_{70} at the expected retention time and with its
870 known UV-VIS spectrum. This seems too much of a coincidence to be
871 explained away with mixtures of hydrocarbons. The authors of the critique
872 are also concerned about the "known high oxidative instability of fullerenes".
873 That is a puzzling statement because nobody has yet shown that C_{60} in the
874 ground state reacts detectably with molecular oxygen in the ground state.

875
876
877 3.5.2.   Permian-Triassic Boundary
878

879 It has long been known that the extinctions that define the PTB boundary
880 251 Ma ago killed more than 90% of all marine species, about 70% of terrestrial
881 vertebrate genera and most land plants. Until recently there was no direct
882 evidence that these catastrophic extinctions had been caused by the aftermath of

883 a large meteorite impact on Earth. There is no significant global iridium anomaly
884 at the PTB and evidence for shocked minerals is weak. However, if C_{60} and C_{70}
885 fullerenes with encapsulated isotopically anomalous helium were found, the
886 case for an impact-caused PTB extinction could be compared with that of the
887 KTB event at Chicxulub. In 1999, Chijiwa et al. reported the occurrence 10–
888 20 ppt of these fullerenes in a PTB sediment from Inuyama, Japan.[157]
889 Subsequently Becker and coworkers[158] studied fullerenes and their possible
890 encapsulated noble gases from PTB sites at Meishan (China), Sasayama (Japan),
891 and Bálvány (Hungary). The analysis of extracts by LDMS showed peaks at
892 720 amu (C_{60}^{+}) and 840 amu (C_{70}^{+}) for the Meishan and Sasayama samples. No
893 ions due to C_{60} or C_{70} were detected in the Bálvány sample, which, however,
894 produced peaks in the range 780–2400 amu. Concentrations of the fullerenes
895 were not reported. Isotopically anomalous He was reported in the Meishan and
896 Sasayama samples. No evidence was presented that the helium atoms were
897 actually inside the fullerene molecules.

898   These conclusions were soon questioned. Braun et al.[159] criticized the
899 absence of sampling descriptions from the stratigraphic layers, sample amounts
900 and homogeneity, and the huge discrepancy between the ppb amounts of
901 fullerenes found by Becker et al. at Sasayama as against the ppt amounts
902 reported by Chijiwa at the Inuyama site. At the time of writing of this review,
903 there was no reply available from the Becker team. Farley and Mukhopadhyay
904 found no extraterrestrial He in fifteen aliquots from a sample from Bed 25 at
905 Meishan and six such samples from an equivalent bed at Shangsi, China.[160]
906 Isozaki pointed out that the PTB horizon is missing at the Sasayama section and
907 that the ^{3}He-enriched sample of Becker et al. has actually come from at least
908 0.8 m below the PTB.[161] Becker and Poreda replied that Farley and Mukho-
909 padhyay used a faulty experimental technique and that their own interpretation
910 of where the PTB at Sasayama is differs from that of Isozaki.[162] Perhaps both
911 answers are valid, but it remains worrisome that only one research group has
912 been able thus far to find isotopically anomalous helium in samples from
913 meteorites, and from the Sudbury, Chicxulub and end-Permian events.

914
915
916   **4. ODDBALLS**
917
918   **4.1. Fulgurite**
919
920   Fulgurites are glassy rocks that form from inorganic minerals when lightning
921 strikes the ground. In five fulgurite samples studied, one contained C_{60} and C_{70} as
922 determined by laser-desorption mass spectrometry.[163] Presumably, carbon for
923 the fullerenes was from biologic remains in the ground. The conditions of
924 temperature and pressure during the lightning stroke are extreme and hugely

outside any laboratory conditions of fullerene synthesis. It is therefore impossible to reconstruct how the fullerenes in the one fulgurite formed.

4.2. Chinese Ink Sticks

Chinese ink sticks, used for calligraphy, are made from soot obtained by the slow burning of oils, mixed with animal glue, and then dried. Because fullerenes had been shown to form in flames, a search for C_{60} and C_{70} in such materials was undertaken by solvent extraction and HPLC.[164,165] The amounts reported were up to 0.1 (weight) %. Two subsequent studies found much less fullerenes (3 ppm at most), which also suggested that the C_{60} content of older sticks was less than that of younger sticks.

4.3. Dinosaur Eggs

C_{60} but not C_{70} was reportedly found in a 70 mA old fossilized dinosaur egg from Xixia, China.[166]

4.4. Tree Char

Char collected from a Norway spruce struck by lightning was studied for the presence of fullerenes but none were found.[167] Because of the presence of much water the conditions during the formation of tree char are very different from those of fulgurite formation. Temperatures and pressures are much lower because much of the lightning's energy is converted to steam.

5. BIOGENIC FULLERENES?

We have pointed out in an earlier section that one of the fundamental issues about naturally occurring fullerenes is whether these could form in the solid state. We have also noted that fullerenes can form by the "zip-up" of PAHs and that algal remains were the most likely source for the carbons at Shunga, Sudbury, and Mitov. Here we will briefly comment on the biological aspects of the hypothesis of fullerene formation in the solid state.

PAHs with as many as sixty or more carbon atoms are not known to occur in nature[168] but may have escaped detection owing to their anticipated cumbersome analysis[169] due to their exceedingly low solubility in common extraction solvents. Nevertheless, fullerenes in rocks must have formed primarily from smaller molecules.

967   Fullerenes have been produced in laboratories by laser ablation at low laser
968 power densities of the pyrolized algal product coorongite,[170,171] laser ablation
969 of extracts from pyrolyzed algae-derived oil shales,[172] and by pyrolysis of
970 (non)-alternant PAH, such as naphthalene ($C_{10}H_8$; Ref.[63]), corannulene
971 ($C_{20}H_{10}$), and benzo[k]fluoranthene ($C_{20}H_{12}$, Ref.[173]), but presumably always
972 in the gas phase, e. g. in the plume after ablation. The coorongite lost about
973 40% of its weight and showed great increases of the $C_{aromatic}/C_{total}$ ratio when
974 heated to 400°C under helium flow prior to the laser ablation. The oil shales
975 lost between 45% and 72.2% of weight and showed modest increases in their
976 C/H atomic ratios after similar treatments. The significance of the PAH
977 pyrolysis to C_{60} is that ring rearrangements must have occurred to produce
978 the required 12 pentagonal carbon rings of the fullerene molecule from a
979 precursor that contained only hexagonal carbon rings.[174] It has also been
980 shown that the diterpenoid camphor represents a natural source for C_{60} as the
981 burning of camphor followed by hot (600–700°C) filament CVD (10^{-15} Torr,
982 substrate temperature 140–150°C) of the toluene soluble soot extract yielded
983 C_{60}.[175] Hence, C_{60} appears to be accessible from biologically important
984 terpenoids. These are interesting results, but they do not involve fullerene
985 formation under natural conditions, and certainly not in the solid state.
986   We assume that algae provided the carbon for the fullerenes at the three
987 locations of interest. At Shunga and Sudbury there are no fossil remains in the
988 fullerene-bearing rocks.[176] In the case of Shunga the opinions on an algal
989 parentage of the carbonaceous matter are divided[108,177]. For Sudbury, the
990 biologic origin of the carbon in the BMOF was firmly proven.[127] Given
991 the Precambrian age of metamorphism of the BMOF host rock, algae were the
992 carbon's most likely source. There is a general consensus for an algal biogenic
993 source of carbon in black shales, schist's and silicified stromatolites in the
994 Mitov area.[178]
995   What could be the small molecular building blocks for fullerene precursors
996 that need to come from the diagenesis and subsequent metamorphism of
997 sediments containing dead algae? The overwhelming majority of such mole-
998 cules contain only hexagonal carbon rings. PAHs with acenaphtylenic units such
999 as in $C_{20}H_{14}$ are either very rare in, or absent from sediments, crude oil, and oil
1000 shales (Standard Reference Materials Program). Living algae contain hopa-
1001 noids, steroids, and sterols whose structures have external pentagonal carbon
1002 rings[179–181] but it is not clear how these evolve during diagenesis and
1003 metamorphism, especially what happens to their —CH_3 and larger side-chains.
1004 Pyrolysis of lignitic matter apparently can form molecules similar to $C_{20}H_{14}$ or
1005 the molecules used for the zip-up of C_{60} above. Perhaps suitable building blocks
1006 do form in algal remains during the greenschist facies metamorphism of the
1007 rocks at Shunga and Sudbury and during the high emplacement temperatures of
1008 the bitumens at Mitov, estimated to have been in the range 800–1000°C.

Elemental sulfur (S_8) is common in sediments either from bacterial activity or from weathering of sulfides such as pyrrhotite. Hence the formation of large PAHs from the smaller ones should be possible to occur at relatively low temperatures during early metamorphism. The serious enigma is how fullerenes might form from these larger precursors under conditions that are a far cry from the laser-ablation zip-ups in the laboratories. Substantial dehydrogenation and aromatization of biological remains during rock metamorphism is well established, but is it sufficient for zip-ups of precursors to fullerenes? Perhaps elemental sulfur or certain oxides play a role in the removal of hydrogen, and dehydrogenation and zip-ups in natural settings are perhaps catalytically accelerated by inorganic minerals.[182]

Obviously the journey from algae to fullerenes is replete with pitfalls and perhaps detours but it is important to remember that the reported amounts of C_{60} in the Mitov bitumens of 200 ppb is some five to six orders of magnitude smaller than the fullerene concentrations routinely achieved by carbon condensation and in soot from controlled hydrocarbon burning. Much also needs to be learned about the photochemistry of biologic remains in the upper water column and a possible role of unpaired electrons, which are abundantly present in kerogens and carbonaceous matter, has to be established.

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