

Biogenic fullerenes?

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Abstract: If the discoveries of C₆₀ and C₇₀ fullerenes in terrestrial hard rocks are real, then some of these may have formed in the solid state by dehydrogenation-driven ‘zip-up’ of C₆₀H_n and C₇₀H_m progenitors. At three sites of such fullerene discoveries the building blocks for these large molecules may have come from algal remains.

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A biological origin with formation in the solid state is proposed here for certain terrestrial fullerenes but with considerable trepidation because it entails formidable hurdles. The first is whether the smaller polycyclic aromatic hydrocarbons (PAHs), that must eventually be fused to the larger C₆₀H_n and C₇₀H_m fullerene progenitors, occur in biological remains. The second is whether these PAHs can be fused in geological formations to proper progenitors by reaction with elemental sulphur at elevated temperatures. The third is whether total dehydrogenation with ‘zip-up’ of these progenitors to fullerenes could have occurred during the process of carbonization and aromatization of the biological remains when the host rocks were metamorphosed under conditions of low oxygen fugacity.

The impetus for our hypothesis came from the discoveries of fullerenes in the carbonaceous rock shungite from Karelia, Russia (Buseck *et al.* 1992), in carbonaceous matter from the Black Member of the Onaping Formation (BMOF) at Sudbury, Canada (Becker *et al.* 1994), and in solid bitumens at Mitov, Czech Republic (Jehlicka *et al.* 2000). Because there was insufficient biota available for ‘global wildfires’ at the Earth’s surface at the time of the Precambrian impact at Sudbury and when the shungite formed, the ‘global wildfire hypothesis’, used by Heymann *et al.* (1994a, b) to explain the occurrence of C₆₀ and C₇₀ fullerenes in the Cretaceous–Tertiary boundary clays of New Zealand does not apply in these cases. In the case of Mitov, fullerenes should also have been found in the rock adjacent to the bitumens and that was not the case.

At Sudbury the putative fullerenes C₆₀ and C₇₀ could have been acquired from the extraterrestrial body, which struck the location some 1.8 Ga (Becker *et al.* 1994), but the two other occurrences have no known terrestrial impact events associated with them. The amounts of C₆₀ reported were

small: 0.2 ppm in the Mitov samples by high-performance liquid chromatography and 6–10 ppm in the Sudbury samples by non-calibrated mass spectrometry. These fullerene occurrences have long been a conundrum. Had the molecules formed inside the rocks or had they been imported from elsewhere? For many years, the simplest hypothesis, formation in the solid state, was never seriously considered perhaps because of the strongly expressed opinions of experts that it was improbable (see Amato 1992). However, fullerene formation in the solid state of charcoal, coal and Shungite carbon, was more recently advocated again but without detailed speculations on the biological sources and their possible evolution to fullerenes (Osawa 1999), which is precisely the issue that we shall examine here.

Fullerenes have been produced in laboratories by laser ablation at low laser power densities of the pyrolyzed algal product coorongite (Rose *et al.* 1993, 1994), laser ablation of extracts from pyrolysed algae-derived oil shales (Fisher *et al.* 1996), and by pyrolysis of (non)-alternant PAHs, such as naphthalene (C₁₀H₈), corannulene (C₂₀H₁₀) and benzo[*k*]fluoranthene (C₂₀H₁₂; Taylor *et al.* 1993; Crowley *et al.* 1996), but presumably always in the gas phase, e.g. in the plume after ablation. The coorongite lost about 40% of its weight and showed great increases of the C_{aromatic}/C_{total} ratio when heated to 400 °C under helium flow prior to the laser ablation. The oil shales lost between 45 and 72.2% of their weight and showed modest increases in their C_i/H atomic ratios after similar treatments. The significance of the PAH pyrolysis to C₆₀ is that ring rearrangements must have occurred to produce the required 12 pentagonal carbon rings of the fullerene molecule from a precursor that contained only hexagonal carbon rings (Sarobe *et al.* 1999a). It has also been shown that the diterpenoid camphor represents a natural source for C₆₀ as the burning of camphor followed

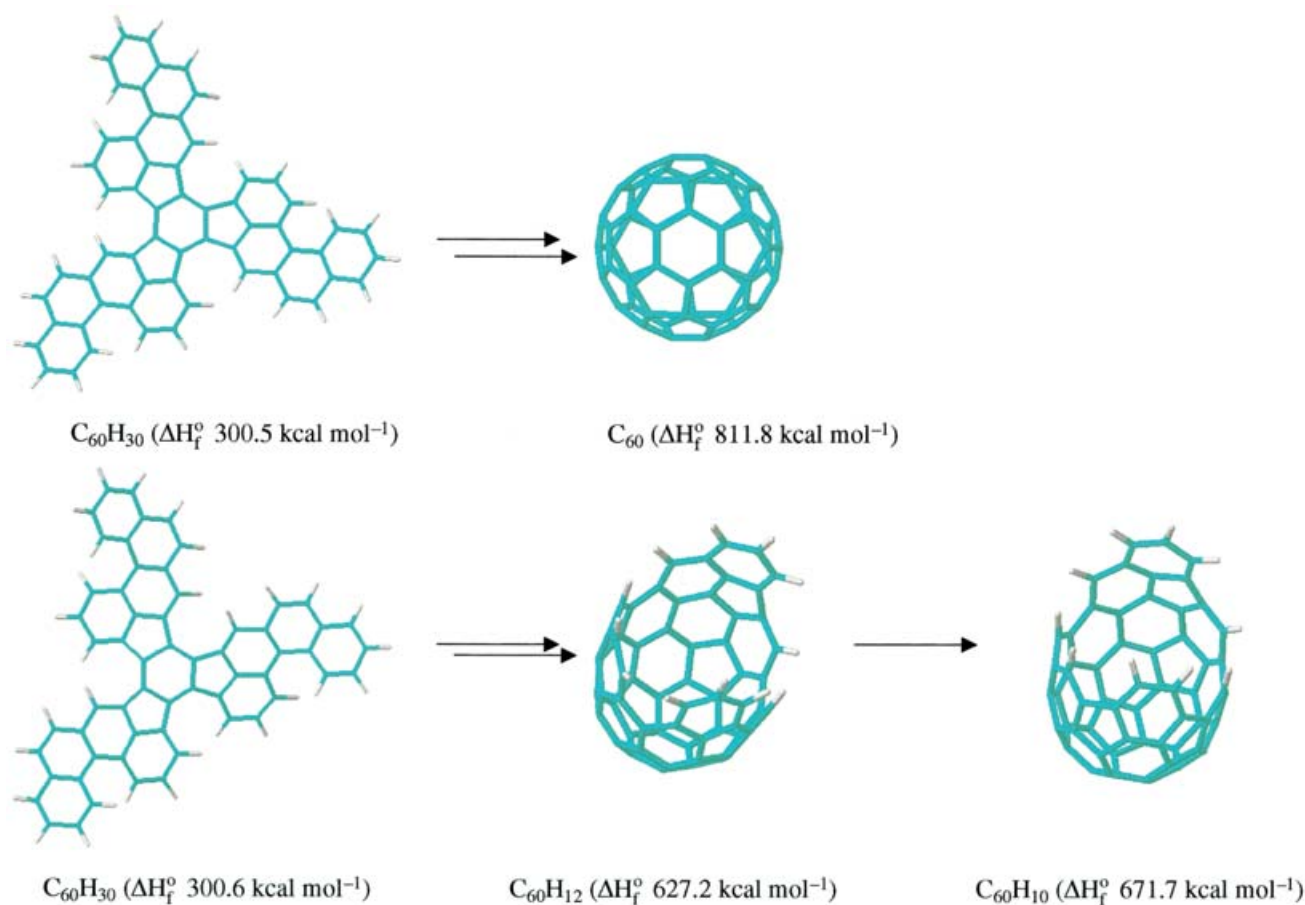


Fig. 1. Top panel: the 'right' C₆₀H₃₀ progenitor of C₆₀, benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]tribenzo[*I*]acephenanthrylene. Bottom panel: its 'wrong' isomer, benzo[1,2-*e*:3,4-*e'*:6,5-*e''*]tribenzo[*I*]acephenanthrylene. The latter gives the curved non-alternant PAHs C₆₀H₁₂ and C₆₀H₁₀ (Sarobe *et al.* 1999b). All structures were optimized using the semi-empirical RHF/PM3 method (MOPAC 7.0).

by hot-filament (600–700 °C) chemical vapour deposition (10⁻¹⁵ torr, substrate temperature 140–150 °C) of the toluene soluble soot extract yielded C₆₀ (Mukhopadhyay *et al.* 1994). Hence, C₆₀ appears to be accessible from biologically important terpenoids (see also Vančik *et al.* 1995). These are interesting results, but they do not involve fullerene formation under natural conditions, and certainly not in the solid state.

PAHs with as many as 60 or more carbon atoms have not been readily identified in nature (Fetzer 2000) but may have escaped detection owing to their anticipated cumbersome analysis due to their exceedingly low solubility in common extraction solvents (Yoshimura *et al.* 2001). This is substantiated by the C₃₆H₁₈ PAH decacyclene, which is readily obtained by S₈-mediated cyclotrimerization of acenaphthene in the melt (210 °C 1 h and 285 °C 4 h, Sarobe *et al.* 1999b). Nevertheless, fullerenes in rocks must have formed primarily from smaller molecules. One may consider formation by lightning strikes, analogous to fullerenes found in fulgurites (Daly *et al.* 1993), but the amounts produced would be extremely small due to the localized nature of the strikes.

Recently, it was demonstrated that three molecules of 4,5-dihydro[*I*]benzacephenanthrylene (C₂₀H₁₄) can be readily

cyclotrimerized to the highly insoluble non-alternant PAH C₆₀H₃₀ by heating the monomer with elemental sulphur (Sarobe *et al.* 1999b). However, under these conditions the cyclotrimerization process gave a mixture of two insoluble C₆₀H₃₀ isomers benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]- and benzo[1,2-*e*:3,4-*e'*:6,5-*e''*]tribenzo[*I*]acephenanthrylene (ratio 1:3) of which only the minor component possesses the proper carbon skeleton of the C₆₀ Schlegel diagram. Notwithstanding, it was shown that under mild MALDI TOF-MS (positive-ion mode, laser power density *ca.* 60 MW cm⁻²) conditions the major C₆₀H₃₀ isomer zipped up to the curved non-alternant PAH C₆₀H₁₀/C₆₀H₁₂ without any rearrangement of its basic carbon skeleton (Fig. 1). Subsequently, MALDI TOF-MS of the independently synthesized proper C₆₀H₃₀ isomer revealed that it indeed can be zipped-up to C₆₀ by 15 successive cyclodehydrogenations, not only 'on computer', but also by 'blasting' at surprisingly low power densities (*ca.* 60 MW cm⁻²) without the occurrence of fragmentation and buildup (Boorum *et al.* 2001; Gómez-Lor *et al.* 2002). Although this specific C₆₀ synthesis is not necessarily the source for fullerenes in rocks, the cyclotrimerization phase suggests that a variety of large fullerene precursors may form in sediments during early metamorphism in the 100–200 °C range (cf. the convenient

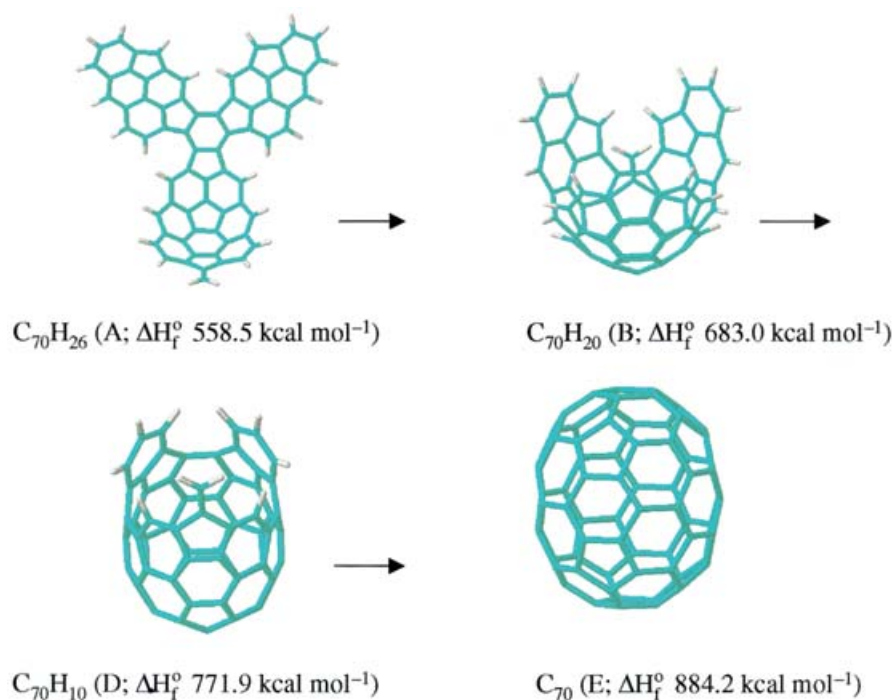


Fig. 2. (A) The hypothetical $C_{70}H_{26}$ progenitor for C_{70} ; (B) $C_{70}H_{20}$, obtained from A by three successive dehydrogenations; (C) $C_{70}H_{10}$, obtained from B by five successive dehydrogenations; and (D) the final product C_{70} . All structures were optimized using the semi-empirical RHF/PM3 method (HyperChem v.5.11).

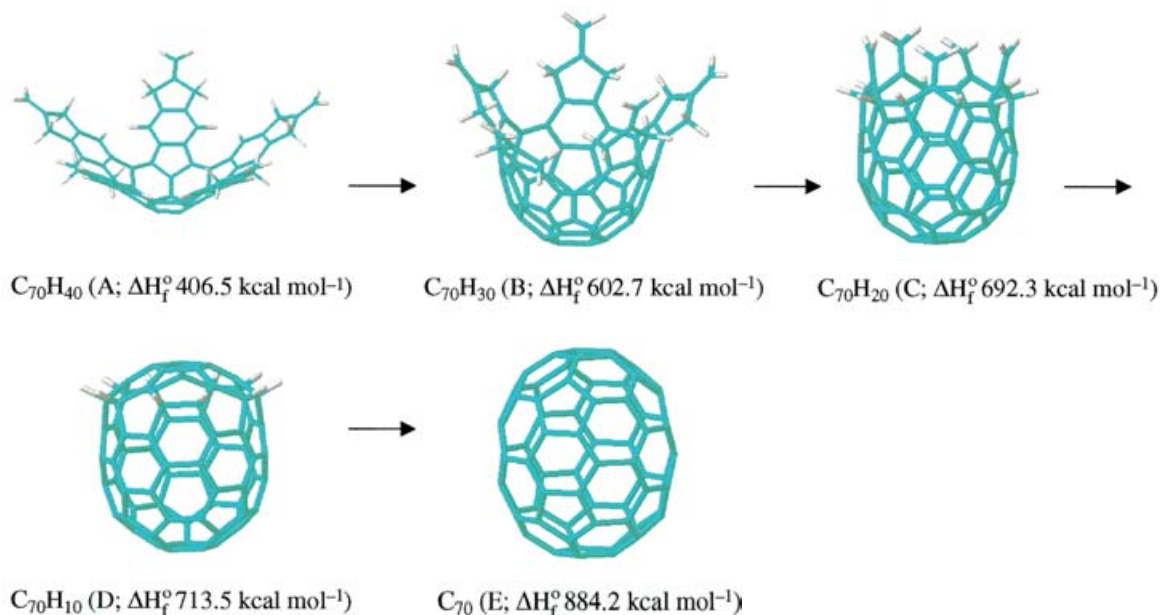


Fig. 3. (A) $C_{70}H_{40}$ another hypothetical progenitor for C_{70} ; (B) $C_{70}H_{30}$ obtained by fivefold dehydrogenations; (C) $C_{70}H_{20}$ obtained by additional fivefold dehydrogenations; (D) $C_{70}H_{10}$ by ring closures; and (E) the final product C_{70} . The $C_{70}H_{40}$ progenitor is derived from a corannulene skeleton. All structures were optimized using the semi-empirical RHF/PM3 method (MOPAC 7.0).

S_8 -mediated cyclotrimerization of acenaphthene ($C_{12}H_{10}$) and 4,5-dihydro[*I*]benzacephenanthrylene ($C_{20}H_{14}$) into decacyclene and benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]- and benzo[1,2-*e*:3,4-*e'*:6,5-*e''*]-tribenzo[*I*]acephenanthrylene, respectively in Sarobe *et al.* (1999b). Since their concentrations could be small, their distribution in inhomogeneous rocks and their

solubility in common (organic) extraction solvent is exceedingly low, they thus may have escaped unequivocal analytical detection. Some of these may be *true unimolecular* trimers, whereas others may have 'arms' of two, or even three different PAHs and represent constitutional analogues. The case for C_{70} is even more complicated because of the fivefold

symmetry of the molecule. Two hypothetical progenitors $C_{70}H_{26}$ and $C_{70}H_{40}$, which were constructed for the present work on the basis of the Schlegel diagram of C_{70} , are shown in Figs 2 and 3. In the case of the $C_{70}H_{26}$ progenitor there are three arms: $C_{22}H_8$ (twice; its pre-fusing formula is $C_{22}H_{12}$) and $C_{26}H_{12}$ (its pre-fusing formula is $C_{26}H_{16}$) with a central hexagon. The progenitor molecule has twofold symmetry; the fivefold symmetry required for C_{70} is hidden but appears in the intermediate structures during the computerized zip-up, two of which are shown in Fig. 2. The $C_{70}H_{40}$ progenitor is derived from corannulene ($C_{20}H_{10}$), which is an identified constituent in fullerene-containing combustion effluents (Lafleur *et al.* 1993).

We assume here that algae provided the carbon for the fullerenes at the three locations of interest. At Shunga and Sudbury there are no fossil remains in the fullerene-bearing rocks (Avermann 1994). In the case of Shunga the opinions on an algal parentage of the carbonaceous matter are divided (Melezhik *et al.* 1999; Kovalevski *et al.* 2001). For Sudbury, the biological origin of the carbon in the BMOF was firmly proven (Heymann *et al.* 1999). Given the Precambrian age of metamorphism of the BMOF host rock, algae was the most likely source for the carbon. There is a general consensus for an algal biogenic source of carbon in black shales, schists and silicified stromatolites in the Mitov area (Pouba & Kribek 1986).

What could be the small molecular building blocks for fullerene precursors that need to come from the diagenesis and subsequent metamorphism of sediments containing dead algae? The overwhelming majority of such molecules contain only hexagonal carbon rings. PAHs with acenaphthylene units such as in $C_{20}H_{14}$ are either very rare in, or absent from sediments, crude oil and oil shales (see Table 109.2 of the Standard Reference Materials Program of the National Institute of Standards and Technology, Gaithersburg, Maryland, USA). Living algae contain hopanoids, steroids and sterols, the structures of which have external pentagonal carbon rings (Miller 1962; Simoneit 1990; Kannenberg & Poralla 1999), but it is not clear how these evolve during diagenesis and metamorphism, especially what happens to their $-CH_3$ and longer side-chains. Pyrolysis of lignitic matter apparently can form molecules similar to $C_{20}H_{14}$ or the molecules used for the zip-up of C_{70} above (Lafleur *et al.* 1996). Perhaps suitable building blocks do form in algal remains during the greenschist facies metamorphism of the rocks at Shunga and Sudbury and during the high emplacement temperatures of the bitumens at Mitov, estimated to have been in the range 800–1000 °C.

Elemental sulphur (S_8) is common in sediments either from bacterial activity or from weathering of sulphides such as pyrrhotite. Hence the formation of large PAHs from the smaller ones should be possible 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 sulphur (see Sarobe *et al.* 1999a, b) or certain oxides play a role in the removal of hydrogen, perhaps dehydrogenation and zip-ups in natural settings are catalytically accelerated by inorganic minerals (Osawa 1999).

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 biological remains in the upper water column and the possible role of unpaired electrons which are abundantly present in kerogens and carbonaceous matter.

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