

Fullerenes: An extraterrestrial carbon carrier phase for noble gases

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In this work, we report on the discovery of naturally occurring fullerenes (C₆₀ to C₄₀₀) in the Allende and Murchison meteorites and some sediment samples from the 65 million-year-old Cretaceous/Tertiary boundary layer (KTB). Unlike the other pure forms of carbon (diamond and graphite), fullerenes are extractable in an organic solvent (e.g., toluene or 1,2,4-trichlorobenzene). The recognition of this unique property led to the detection and isolation of the higher fullerenes in the Kratschmer/Huffmann arc evaporated graphite soot and in the carbon material in the meteorite and impact deposits. By further exploiting the unique ability of the fullerene cage structure to encapsulate and retain noble gases, we have determined that both the Allende and Murchison fullerenes and the KTB fullerenes contain trapped noble gases with ratios that can only be described as extraterrestrial in origin.

Since the synthesis, isolation, and characterization of fullerenes (1–5), there has been considerable interest in ascertaining whether or not this family of carbon molecules occurs naturally on the Earth and in the cosmos (e.g., circumstellar shells, interstellar medium, etc.). For example, it has been suggested that the fullerene molecule, C₆₀, might be widely distributed in the universe, particularly in the outflows of carbon stars, due to its exceptional thermal stability and photochemical properties (6). Despite an intense effort carried out by the scientific community to verify this hypothesis, only a few natural occurrences of fullerenes have been reported. Terrestrial discoveries (7–10) have been limited to the detection of mostly C₆₀ and C₇₀ whereas extraterrestrial evidence is based on trace findings of C₆₀ (11) and a single mass spectrum of a high mass carbon envelope from the Allende meteorite (12).

On the Earth, trace amounts of fullerenes have been reported in some unusual rocks such as “shungite,” a highly metamorphosed coal, and “fulgurite,” a glassy rock, that forms when lightning hits the ground (7, 8). Fullerenes have also been detected in deposits associated with two separate events involving the impact of a large bolide (asteroid or comet) with the Earth. Fullerenes have been extracted from shock-produced breccias (Onaping Formation) associated with the 1.85 billion-year-old Sudbury Impact Crater and in clay sediments within the 65 million-year-old Cretaceous/Tertiary (KTB) boundary (9, 10). Possible scenarios for the presence of fullerenes in the Sudbury and KTB impact deposits are as follows: (i) Fullerenes were synthesized within the impact plume from the carbon contained in the bolide or target rocks; and/or (ii) fullerenes were already present in the bolide and survived the impact event (e.g., Sudbury) based on their unique noble gas isotopic signature (9); or (iii) fullerenes in the KTB clays formed as a result of global wildfires triggered by the impact event (10).

The survival of fullerenes over geologic time (millions to billions of years) and in two very different geological environments raises many interesting questions about the importance of fullerenes on the early Earth and, by implication, on the surfaces of other planets. A potential problem for fullerenes produced in the KTB wildfires is that, although fullerenes have been detected in high-temperature benzene flames (13), fullerenes have not

been detected in modern day wildfires (14). This raises the possibility that the fullerenes found in the KTB clays were either synthesized in the impact plume or that fullerenes were already present in the bolide and somehow survived the impact event. Do fullerenes form as result of an impact event or by the transformation of other carbon compounds in the gas phase? How can we determine the origin of fullerenes in natural samples? One possibility we have explored is to search for trapped noble gases inside the fullerenes.

Noble Gas Atoms Inside Synthetic Fullerenes. Recently, it has been demonstrated that helium (He) can be trapped inside fullerenes prepared by using the Kratschmer/Huffmann procedure (3, 4). The C₆₀ molecule is large enough to enclose all of the noble gases He, neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) (4, 15). Theoretical barriers for He to penetrate the benzene rings of the fullerene molecule have been calculated to be greater than 200 kcal·mol⁻¹ (16). It has also been demonstrated that (i) He is incorporated into C₆₀ during fullerene formation in the Kratschmer/Huffmann arc evaporated soot (3, 4) in a He atmosphere and (ii) noble gases of a specific isotopic composition can be introduced into synthetic fullerenes at high temperatures and pressures. These gases can then be released by the breaking of one or more carbon bonds or a “window mechanism” during step heating under vacuum (refs. 4 and 15; Fig. 1). These results convincingly showed that the helium is trapped inside of the fullerene molecule (He@C₆₀) and there is no exchange with the atmosphere.

To determine the origin of the fullerenes found in the Sudbury carbon-rich breccias, we decided to search for trapped noble gases (15). The Sudbury fullerenes (C₆₀ and C₇₀) were found to contain trapped helium with a ³He/⁴He ratio of 5.5×10^{-4} to 5.9×10^{-4} (9). This ³He/⁴He ratio exceeds the accepted solar wind value by 20–30% and is an order of magnitude higher than the maximum reported mantle value (17, 18). The high He ratios detected in the Sudbury fullerenes is most similar to those found in some interplanetary dust particles (19). The implication is that the He within the Sudbury fullerenes is of extraterrestrial origin. The unique thermal release patterns for He encapsulated within the Sudbury fullerenes are also similar to the patterns for acid-resistant residues of carbonaceous chondrites (20, 21), suggesting that fullerenes could be a carrier of trapped noble gases in meteorites.

In this work, we are reporting definitive evidence of naturally occurring C₆₀, C₇₀, and the higher fullerenes (C₆₀ to C₄₀₀) with

Abbreviations: LDMS, laser desorption (linear) time-of-flight mass spectrometry; TCB, 1,2,4 trichlorobenzene.

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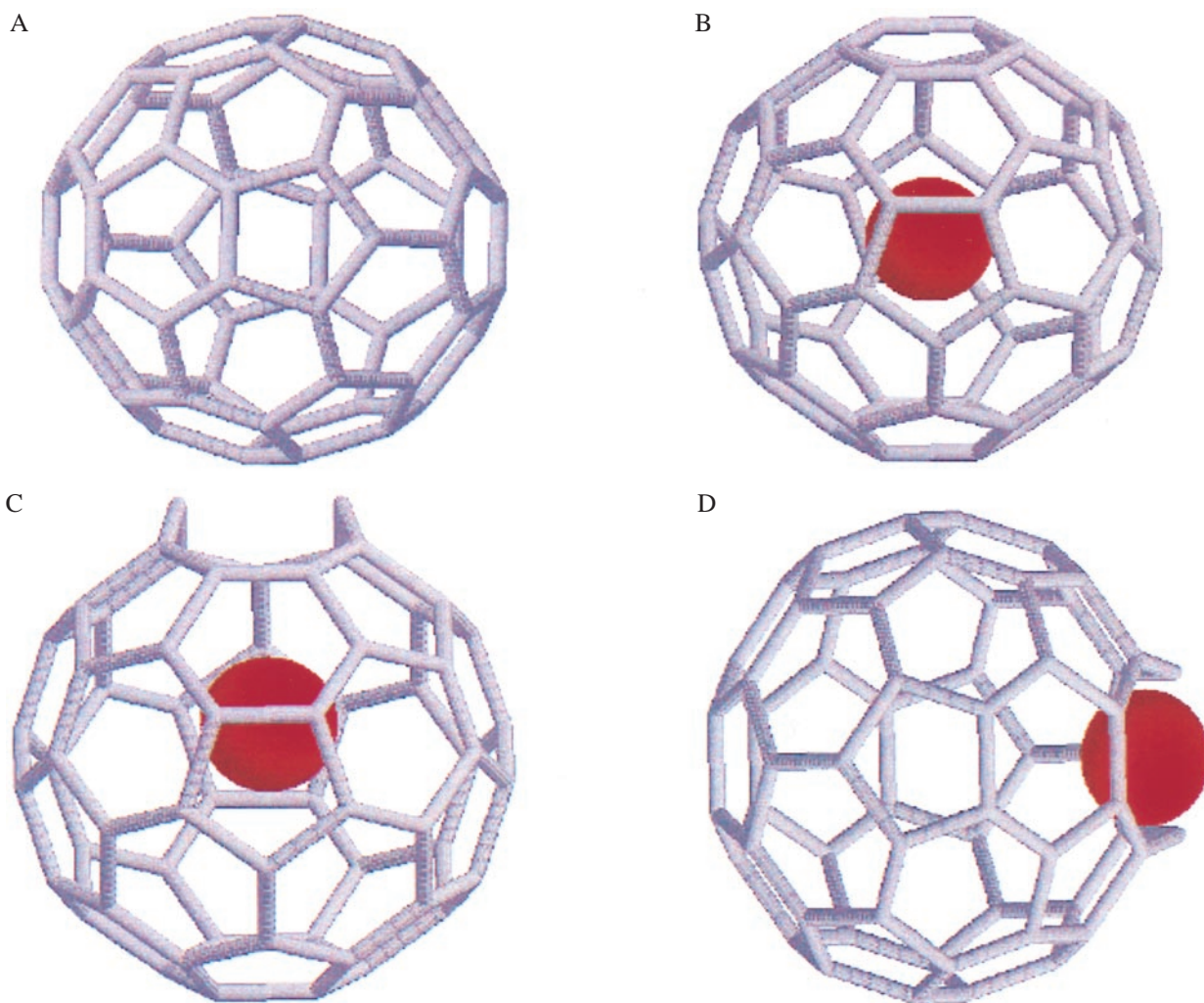


Fig. 1. “Window mechanism” for the encapsulation of atoms inside the fullerene cage. (A) C_{60} or buckminsterfullerene. (B) C_{60} with an atom inside. (C) C_{60} with an atom inside and with a bond broken (open window). (D) Same molecule as in C but with the atom moving out through the window. Figure adapted from ref. 15.

trapped noble gases in two carbonaceous chondrites and in “terrestrial” impact material from some Cretaceous/Tertiary boundary (KTB) sediments. Laser desorption (linear) time-of-flight mass spectrometry (LDMS) was used for the detection of C_{60} , C_{70} and the higher fullerenes present in these residues, and noble gas mass spectrometry was applied to search for trapped noble gases inside the fullerene molecule to determine the origin and to verify that the carbon clusters isolated were indeed fullerene-related (4, 9, 15). We have adopted this approach because, to our knowledge, fullerenes both naturally occurring (9) and man-made (3, 4, 15) are the only known material that can encapsulate a noble gas atom within its cage structure and can also be isolated by extraction in an organic solvent (2, 22, 23) without altering the composition of the noble gas trapped inside.

Materials and Methods

Several grams of ground meteorite or KTB sediment bulk material were demineralized by using procedures outlined by Robl and Davis (24). The demineralized portion of the sample (≈ 1 g) was then placed into a Soxhlet apparatus and refluxed with an organic solvent [e.g., toluene or 1,2,4-trichlorobenzene (TCB)] for a period of 24 hours to extract the fullerenes. Laser desorption (linear) time-of-flight mass spectrometry (LDMS) was used for the detection of fullerenes and higher carbon

clusters in the meteorite and KTB sediment solvent-extracted residues (9). Microgram quantities of the fullerene-enriched residues were loaded into a metal tube furnace within a glove box and were flushed with nitrogen in preparation for noble gas analyses. After heating the samples in vacuum for 3 days at 100°C to completely remove any residual solvent, the fullerene residue (≈ 200 μg of fullerene per aliquot) was incrementally heated to release the trapped noble gases (4, 9, 12).

Results and Discussion

LDMS Spectra. LDMS analyses of the Murchison carbon residue extracted with toluene yielded a predominately “kerogen-like” carbon component and revealed only trace amounts of C_{60} (< 1 μg per 60 g of meteorite). This toluene extract also contained no helium above the blank levels. Subsequent extraction of the same residue with TCB revealed a small peak for C_{60}^+ and a much more prominent high-mass envelope that dominates the spectrum between C_{70}^+ and C_{250}^+ (Fig. 2A). Analyses of the Allende carbon residue extracted with TCB revealed a much more prominent peak for C_{60}^+ and C_{70}^+ and some of the higher fullerenes (C_{76}^+ to C_{96}^+) and a similar high-mass envelope (C_{100} to C_{250}) to the Murchison TCB extract.

A toluene extract for the continental KTB Raton Basin, Colorado fullerene residue showed a strong peak at a mass-to-

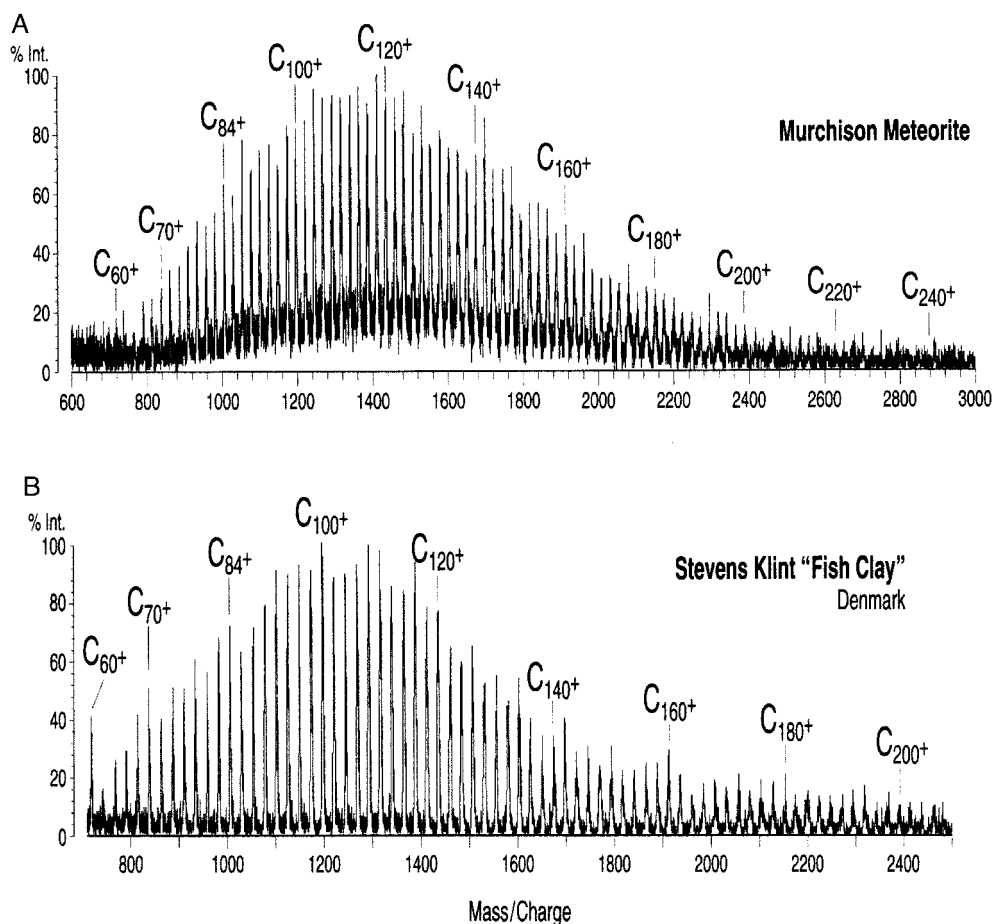


Fig. 2. Laser desorption mass spectrometry (LDMS) of the Murchison carbonaceous chondrite and the 65 million-year-old Cretaceous/Tertiary boundary layer from Stevens Klint, Denmark. The mass spectra show a remarkably stable high-mass envelope, C_{60} - C_{250} , with individual peaks separated by a C_2^+ that are interpreted as individual closed-caged structures.

charge ratio (m/z) of 720 atomic mass units, which corresponds to C_{60}^+ , and a peak at 840 atomic mass units, which corresponds to C_{70}^+ . The KTB Stevens Klint, Denmark fullerene residue extracted with 1,2,3,5-tetramethylbenzene showed a small peak for C_{60}^+ and a much more prominent high-mass envelope that dominates the spectrum between C_{84}^+ and C_{200}^+ (Fig. 2B). The higher fullerenes appear to be the major extraterrestrial fullerene component in the Murchison, Allende and the KTB Stevens Klint fullerene residues.

Noble Gas Measurements. Measurements of He in the Murchison residue (1.1×10^{-8} cm³/g of fullerene; Fig. 3) revealed $^3\text{He}/^4\text{He}$ ratios of 2.1×10^{-4} or $\approx 150\times$ greater than the air ratio, a value similar to that estimated for the early solar system (25). The $^3\text{He}/^4\text{He}$ ratios are most likely attributed to a “He-A” component often regarded as the prototype for the “planetary noble gas” component (17, 21). Previous measurements of helium reported by Weiler *et al.* (20, 21) for a CSSE (Closed System Stepped Etching with nitric acid) of the bulk Murchison acid residue produced similar helium isotopic ratios. The procedure used (20, 21) to oxidize a carbonaceous residue with nitric acid would likely destroy fullerenes and release the encapsulated noble gases. Unlike other carrier phases, fullerenes are the only identifiable and “extractable” carrier that would react with nitric acid (as opposed to inert phases such as SiC and diamond). Our measured helium concentrations for the higher fullerene fraction is much lower than that measured for the CSSE extract

of Weiler *et al.* (20, 21). Preliminary measurements of the remaining bulk residue after extraction with solvents also demonstrated that there is still a large fraction of ^3He (1.5×10^{-8} cm³/g) in our acid residue. This suggests that we are either not completely successful at extracting the fullerenes from the meteorite carbon residues or other caged carbon carriers (e.g., giant fullerenes) exist that are readily oxidized by nitric acid, but are not very soluble in TCB. Additional extractions with higher boiling solvents (1-methylnaphthalene) may lead to the isolation of even larger fullerene cages.

The high temperature release steps for Murchison also yielded argon with a non-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ of 35. After correction for an atmospheric blank, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio dropped to 10, clearly reflecting the formation of the Murchison fullerenes in an extraterrestrial environment (versus 295 for the Earth’s atmosphere). We should expect the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in this extraterrestrial component to be less than 1; however, the use of an organic solvent such as TCB has effectively trapped some atmospheric gases, which is indicated by the corrected argon ratio.

The isotopic composition of the He contained within the Allende fullerene extract is more than one order of magnitude greater than the values found in Murchison. This unexpected result contrasts with the He observed by Weiler *et al.* (20, 21) in the CSSE experiments on Allende but is similar to the helium found in other meteorites, which has been interpreted as “implanted” or He produced by “spallation” processes (ref. 9 and references therein). Due to the high temperatures and partial pressures of He needed

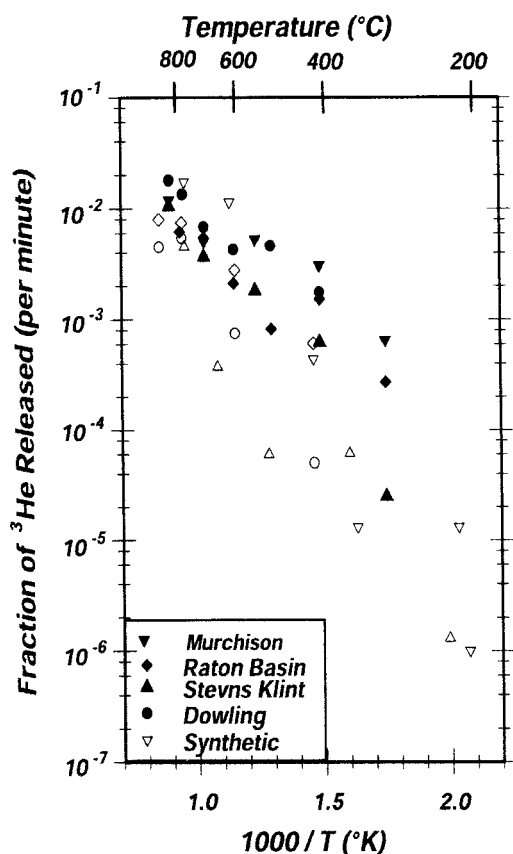


Fig. 3. Temperature (T)-dependent ^3He release for the Murchison Meteorite, K/T Boundary sediments and the Sudbury Dowling samples. The open symbols are the release rates for the synthetic fullerenes (C_{60} and C_{70}) taken from ref. 4.

[1,000 atm (1 atm = 101.3 kPa) at 1,000°C] for incorporation into the fullerene caged molecule, it seems unlikely that the ratios measured in the Allende fullerenes could have originated from implantation or spallation processes. Measurements of other noble gases (such as Ne and Xe) should reveal the source of this unique signature. The Allende extracts also contained argon with a mixture of an atmospheric and non-atmospheric component that was higher than that observed for the Murchison fullerene residue ($^{40}\text{Ar}/^{36}\text{Ar} \approx 150$), but clearly below the atmospheric value and consistent with the formation of the fullerene carrier in an extraterrestrial environment.

Measurements of He in a toluene residue from the continental KT boundary clay (KTB) at Raton Basin, Colorado, revealed a clear extraterrestrial helium signal with $^3\text{He}/^4\text{He}$ ratios $\approx 100\times$ the air ratio in the highest temperature steps ($1.3 \times 10^{-7} \text{ cm}^3/\text{g}$ of fullerene). The marine KTB Stevns Klint residue (extracted with 1,2,3,5 tetramethylbenzene) consists of mostly higher fullerenes ($>\text{C}_{100}$) and has $^3\text{He}/^4\text{He}$ ratios of $>4 \times 10^{-3}$ ($4 \times 10^{-7} \text{ cm}^3/\text{g}$ of fullerene) in the high temperature fraction. The ratio is similar to the $^3\text{He}/^4\text{He}$ ratios measured in the Allende fullerene residue. According to the rigid sphere model (4), the ^3He partial pressure for the Stevns Klint fullerenes at the time of formation is estimated to have been ≈ 0.5 torr (versus 10^{-10} torr in the present-day atmosphere) (1 torr = 133 Pa), suggesting that a mechanism other than a terrestrial synthesis is needed. This $^3\text{He}/^4\text{He}$ ratio is more than $10\times$ higher than any bulk meteoritic reservoir (planetary or solar) and may be produced by a combination of implantation and cosmic ray-induced (spallogenic) bombardment as observed in some meteorites and interplanetary dust particles. However, experimental results indicate that nuclear reaction implantation is not

a very effective mechanism for trapping He inside the fullerenes (26), suggesting that the high $^3\text{He}/^4\text{He}$ ratios found in both the KTB Stevns Klint and Allende fullerene residues may be a unique, previously unidentified He component. Future measurements of the heavy noble gases trapped in the fullerene carrier phase should allow us to determine the origin of this unusual He signature.

The very high $^3\text{He}/^4\text{He}$ ratio makes it unlikely that the fullerenes were produced during the impact because it is inconceivable that the atmosphere of the Earth, even in close proximity to the bolide, would have contained helium with such an anomalous isotopic signature (i.e., the Earth's atmosphere has a much larger fraction of ^4He). The concentration of helium (per microgram of fullerene) in Stevns Klint ($4 \times 10^{-7} \text{ cm}^3/\text{g}$ of fullerene) indicates that the ^3He concentration is some $4\times$ higher than that found in the Sudbury fullerenes (9) ($1.1 \times 10^{-7} \text{ cm}^3/\text{g}$ of fullerene). We attribute the anomalously high $^3\text{He}/^4\text{He}$ ratios and high ^3He concentration for the Stevns Klint sample to the abundance and stability of higher fullerenes extracted from the residue.

Conclusions

The higher fullerenes (C_{100} to C_{400}), which are barely soluble and are firmly embedded in the poorly graphitized carbon matrix of the meteorite, can be extracted by efficiently demineralizing the bulk meteorite material and refluxing in high boiling solvents (2, 22, 23). The anomalous $^3\text{He}/^4\text{He}$ ratios in both Murchison and Allende coupled with a non-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio clearly indicate that the fullerene component is extraterrestrial in origin. Moreover, the high $^3\text{He}/^4\text{He}$ ratios measured in the KTB deposits also rule out the possibility that the fullerenes were formed on impact or were the result of biomass burning triggered by the impact event (9, 10). The presence of these extraterrestrial noble gases in the meteorite and KTB fullerene extracts further demonstrates the remarkable properties of these carbon molecules and supports our interpretation that the high-mass envelope observed in our LDMS mass spectra represent individual close caged molecules rather than some other polymer or carbon compound.

Thus, by exploiting the unique properties of the fullerene molecule, we have identified a carrier phase for noble gases associated with impact (asteroidal or cometary) and meteoritic carbon. The recognition of the fullerene carrier phase with an extraterrestrial noble gas signature in carbonaceous chondrites provides pathways for the origin and evolution of planetary atmospheres and/or presolar (circumstellar or interstellar) environments. The survival of ^3He in fullerenes associated with two impact events that span the geologic record (≈ 2 billion to 65 million years ago) suggests that fullerenes, volatiles, and perhaps other organic compounds were being exogenously delivered to the early Earth and other planets throughout time (9, 12). In support of this suggestion, abiotic amino acids, α -aminoisobutyric and isovaline, have been reported in some Stevns Klint KTB and DSDP 577 sediments (27) and, more recently, in some continental KTB deposits (Art Webber, personal communication). The survivability of fullerenes with trapped noble gases and α -aminoisobutyric in KTB sediments from Stevns Klint is indeed unexpected and suggests that exogenous delivery of "intact" organic material to the surfaces of planets may be more favorable than has been previously assumed (28). Future searches for fullerene and ^3He as a tracer of the flux of extraterrestrial material in sediments throughout the geologic record, and its possible association with changes observed in climate and the biostratigraphic record, could have broad implications for the evolution of life on the Earth.

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