

Geological fullerenes: review and analysis

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Abstract

Fullerenes have been reported from numerous terrestrial and meteoritic sources, but only at low concentrations. The occurrences are associated with localized energetic events such as lightning, impacts of extraterrestrial objects, and wildfires. Great interest has also been generated by a series of papers that report noble gases with anomalous isotopic compositions encapsulated within fullerenes. In spite of all of the published work, many unresolved questions remain about the identity and formation of fullerenes in geological environments.

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1. Introduction

The 1985 synthesis of a new form of carbon [1] electrified the scientific world. In addition to the well-known graphite and diamond (and its lonsdaleite variety), there was now a series of closed-cage molecules of pure carbon (Fig. 1). As a group these high-symmetry, geodesic molecules were called fullerenes and they immediately formed the basis of high-intensity research in leading academic, industrial, and government lab-

oratories worldwide in an effort to find new theoretical and applied uses for this unexpected form of this most familiar of elements. The 1996 Nobel Prize for Chemistry was awarded to R.F. Curl, H.W. Kroto and R.E. Smalley for their spectacular discovery of fullerenes.

The graphite structure consists of planar sheets (called graphene) of carbon atoms in six-membered rings. However, carbon can maintain its four-coordinated valency even if there are only five atoms in a ring; in this case the sheet is forced to curve slightly, which is normally an unstable configuration and thus rare. A dramatic change occurs if 12 pentagonal rings occur in a sheet because then it can curl sufficiently to form a closed structure, and this shape turns out to be extremely stable. Such a network of hexagonal and pentagonal rings underlies the principle of the geodesic dome, made famous by architect Buckminster Fuller, after whom the fullerene mol-

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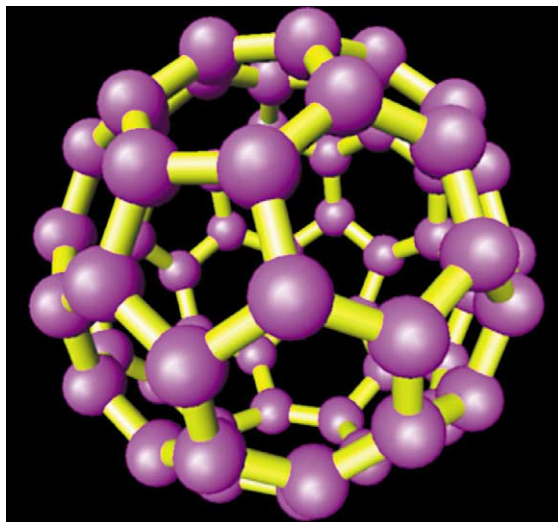


Fig. 1. C_{60} molecule. The purple spheres represent carbon atoms. They are organized into the hexagonal (aromatic) rings characteristic of graphite and many other C compounds, and 12 pentagonal rings that produce the curvature that makes this form a roughly spherical molecule.

ecules were named. The most stable common fullerene molecule is C_{60} , with 60 carbon atoms (and the appearance of a soccer ball), followed by C_{70} . These are also the fullerenes that turned out to be geologically most abundant.

As if the discovery of the fullerene family of molecules were not enough, a fascinating relative was discovered in 1991. In a beautiful example of the power of high-resolution transmission electron microscopy (HRTEM), Sumio Iijima reported the occurrence of single (sometimes more) graphene sheets rolled into long cylinders called nanotubes [2]. As for fullerenes, nanotube formation requires high energies, like those in plasmas, to overcome the strong tendency for carbon atoms to form graphite. They were immediately the focus of intense interest because of their electronic potential (e.g. <http://www.pa.msu.edu/cmp/csc/nanotube.html>). However, I know of no confirmed natural occurrences of such carbon nanotubes and so shall not discuss them further.

In 1992 several colleagues and I reported the discovery of fullerenes in a geological sample, an unusual carbon-rich rock from Russia [3]. The paper appeared at a time when fullerenes were on the center stage of scientific attention and

therefore attracted much interest. In addition to the intrinsic fascination with the geological occurrence of fullerenes in rocks roughly two billion years old, the discovery raised the possibility that a solid-state process might exist to produce fullerenes. At the time, and even to the present, all fullerene syntheses had been by relatively costly, high-energy, vapor-phase processes (e.g. evaporation of carbon by resistive heating, AC or DC arc discharge, sooting flames, laser ablation, and high-frequency inductive heating in plasmas [4]). Moreover, these high-temperature methods allowed little control over the final product, so that the prospect of a potentially more efficient mechanism had great allure. It also held the promise of new insights into the formation of these intriguing molecules. For geology the possibility existed that the various fullerene molecules might each have their own unique fields of stability and thus provide a sensitive new set of geothermometers and environmental indicators.

We found the natural fullerenes in shungite (Fig. 2), a carbon-rich rock that occurs in Karelia, a province in western Russia. Most shungite rocks are Lower Proterozoic (2.0–2.1 Ga) metasediments, but they also include rocks of volcanic and metasomatic origin [5]. Shungite is possibly unique among rock types, but it occurs in vast amounts (estimated at 25×10^{10} tons in the region of Lake Onega – see [5] and references therein – although the glassy variety of shungite in which the fullerenes were discovered is far less abundant). There thus seemed to be the possibility of a gigantic natural resource for fullerenes at a time when their economic potential was being actively explored in leading laboratories across the globe. The available literature on shungite, although extensive in Russian publications and in-house reports, was sparse in Western journals, causing great uncertainty about its nature.

Buseck et al. [3] reported that the fullerenes occur in thin films within fractures in shungite. We did not know how widespread or unusual these fracture fillings were, nor did we speculate on the subject. Amidst the publicity and excitement, an impression seems to have grown that they were common in these largely unfamiliar rocks. Although initial hopes for abundant natu-

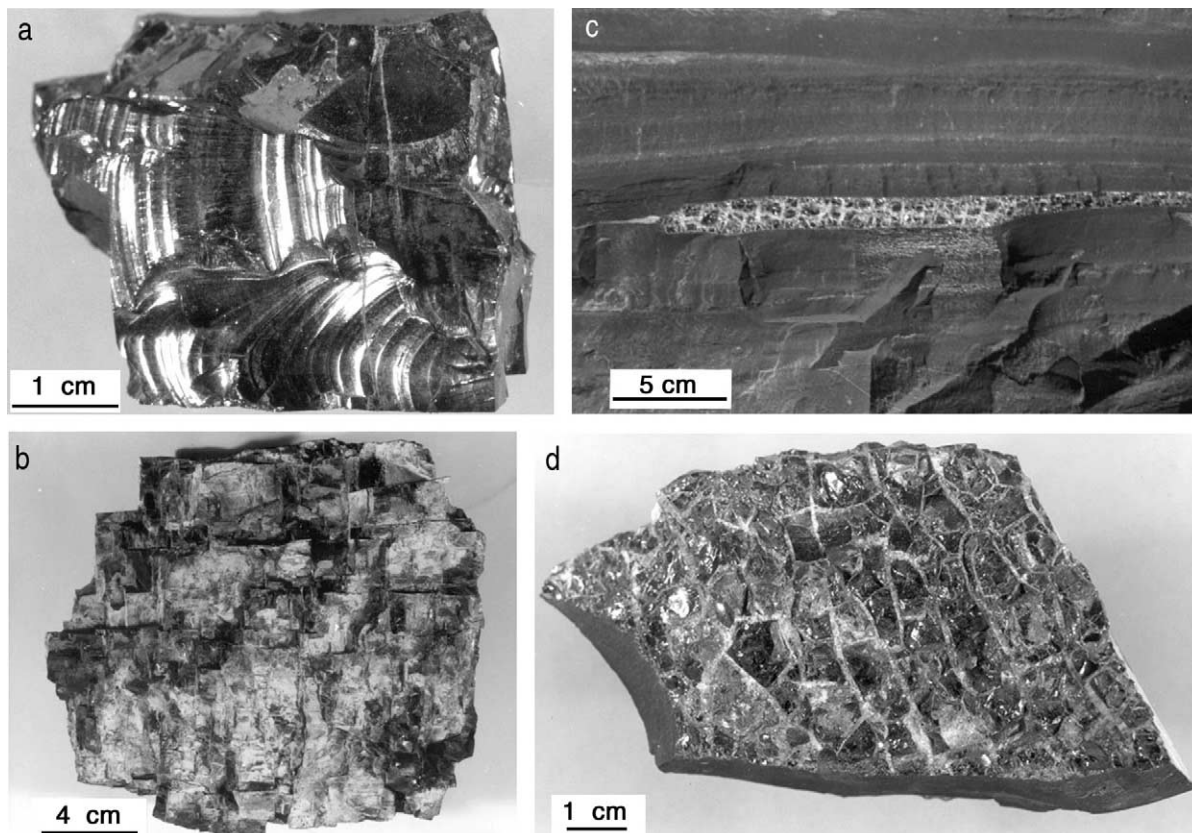


Fig. 2. Various types of shungite rock. (a) Glassy shungite of the type in which fullerenes were found, (b) blocky shungite with some of the characteristics of coal cleating, (c,d) a lens and surface view of brecciated glassy shungite. The shungite rocks in (a,b) are from Shunga and those in (c,d) are from Nigozero, all in Karelia, Russia.

ral fullerenes were not realized, much attention was generated by subsequent reports of fullerenes from different geological occurrences such as the impact structure at Sudbury, Ontario, and the Cretaceous–Tertiary (K–T) and Permian–Triassic (P–T) stratigraphic boundaries that contain encapsulated noble gases having non-terrestrial isotopic ratios.

A decade has passed since fullerenes were discovered in nature. However, conflicting claims in the literature about their occurrence and significance have resulted in skepticism by many geochemists. The purpose of this note is to review and analyze the existing literature regarding the possible origins and geological significance of natural fullerenes, both in shungite and in other natural environments, including those reported to have encapsulated noble gases.

2. Fullerenes in shungite and other terrestrial rocks

Shungite samples have been difficult to obtain. They were of military interest in the former USSR, apparently because of their conducting, refractory character, and for a time information about shungite was restricted for national security reasons. The areas where shungite occurs are remote and samples are relatively rare outside Russia.

Following our initial report, many groups, including mine, searched for and were disappointed not to find plentiful fullerenes in shungite and other carbon-rich rocks. With the exception of their occurrence in a fulgurite, the fused product of a lightning strike [6], and in our original shungite sample, we found no other reproducible occurrences of fullerenes. There are, however, abun-

dant reports of minor amounts of fullerenes in Karelian shungite [7–15].

Ebbesen et al. [16] pointed out the scarcity of fullerenes in shungite and suggested that they likely resulted from lightning strikes. Buseck and Tsipursky [17] disagreed with that interpretation because of the lack of supporting evidence other than their occurrence in thin fracture coatings. Subsequent work confirmed the scarcity of fullerenes in shungite; it seems likely that Buseck et al. [3] studied an unusual sample. Given the extent of the shungite deposits, their presumably significant exposure ages and their reducing character, which would protect fullerenes from destruction through oxidation, a lightning origin is plausible. However, no subsequent evidence has become available to either support or refute such an origin, and the explanation is not readily compatible with the other reports of shungite fullerenes unless they reflect residues of multiple lightning strikes over time. Further work will be required before the issue is settled.

Fullerenes have also been reported from a rich variety of other sources that include pillow lavas that cut across black shales [18], coal [19,20]², fossil dinosaur eggs [21], a carbonaceous impact breccia from the Canadian Sudbury structure [22–25], and the thin strata separating rocks formed at the major K–T [24,26,27] and P–T [28,29] stratigraphic boundaries. Many of the published results are summarized in Table 1.

3. Extraterrestrial fullerenes and fullerenes from impact structures

The possibility that fullerenes may occur as components of interstellar dust [1,30] stimulated immediate interest in searching for fullerenes in primitive meteorites. Also, meteorites contain noble gases with intriguing anomalous isotopic com-

positions and their host phase has long been puzzling. Several groups recognized that fullerenes are potentially the long-sought carriers because they have the capability of encapsulating gas atoms within their cages. Indeed, Saunders et al. [31,32] and DiCamillo et al. [33] demonstrated that fullerenes could trap noble gases (Figs. 3 and 4). A result of all this interest is that the literature on extraterrestrial fullerenes may be even more extensive than that on terrestrial samples. Several of these reports appeared in high-impact journals and received wide attention.

There is an extensive literature on searches for fullerenes in interstellar space, but there are no positive reports. However, a sampling mission had success. The Long Duration Exposure Facility (LDEF) spacecraft was flown to collect interplanetary and interstellar particles prior to their likely destruction when entering Earth's atmosphere. [34] used laser-ionization mass spectrometry and Raman spectroscopy to determine the presence of fullerenes in the residue of one of the impact craters on the LDEF collectors.

The history of finding fullerenes in meteorites by standard extraction and analytical methods is more mixed. There are many reports of unsuccessful attempts to locate fullerenes in meteorites. However, Becker and co-workers, in contrast, successfully located fullerenes in several meteorites [35–38]. They also reported both terrestrial and meteoritic fullerene molecules that contain trapped He and Ar [23,24,29,38]. These fullerenes are from various types of samples: breccias from the impact crater at Sudbury, Ontario; the rocks at the K–T boundary in several widely separated localities; the P–T boundary in three other widely separated localities; and in the Allende, Murchison, and Tagish Lake meteorites.

An unanswered question is why all research groups (ours included) other than that of Becker have been unsuccessful in locating fullerenes in meteorites. The answer may lie in the delicate measurements required to detect such low concentrations of these materials. The combination of careful fullerene extraction, analyses near the limits of sensitivity, and exquisite care to avoid contamination at extremely low concentration levels make these challenging measurements.

² In his paper, Osawa [20] reported fullerenes in a heavy crude oil from Czechoslovakia, but he wrote me (email of 7/2/00) that he now believes that report as well as the one by Jehlicka et al. [18] should be confirmed by independent mass spectrometry.

Table 1
Fullerenes in nature: reported occurrences and methods of analysis

Source	Identification methods	Possible fullerene origin	Reference
Shungite, a carbon-rich rock; Shunga, Karelia, Russia		Unknown	
Shungite	HRTEM; LD-FTMS; EC-TD-MS		[3]
Shungite	HPLC; FTIR		[9]
Shungite	HPLC; MS		[10]
Shungite	Raman and IR spectroscopy		[14]
Shungite	EI-MS; powder XRD; ¹³ C NMR		[15]
Cretaceous–Tertiary boundary		Cataclysmic impact; possibly extensive wildfires	
Woodside Creek, NZ	HPLC/UV-Vis		[26]
Flaxbourne River, NZ	HPLC/UV-Vis		[26]
Caravaca, Spain	HPLC/UV-Vis		[27]
Sumbar and Malyi Balkhan, Turkmenistan	HPLC/UV-Vis		[27]
Stevns Klint, Denmark	HPLC/UV-Vis		[27]
Stevns Klint, Denmark	LD-TOFMS		[24]
Raton Basin, CO	LD-TOFMS		[24]
Permian–Triassic boundary		Cataclysmic impact	
Inuyama, Japan	HPLC/UV-Vis		[28]
Meishan, China	LD-TOFMS		[29]
Sasayama, Japan	LD-TOFMS		[29]
Extraterrestrial samples		Unknown	
Allende carbonaceous chondrite	LD-TOFMS		[35]
Allende carbonaceous chondrite	LD-TOFMS		[36]
Allende carbonaceous chondrite	LD-TOFMS		[37]
Allende carbonaceous chondrite	LD-TOFMS		[24]
Murchison carbonaceous chondrite	LD-TOFMS		[24]
Tagish Lake carbonaceous chondrite	LD-TOFMS		[38]
Carbonaceous residue; crater on the LDEF spacecraft	Laser ionization MS; Raman spectroscopy	Chondritic impactor	[34]
Miscellaneous			
Fulgurite, Sheep Mtn., CO	EI-TD-MS	Vaporization of carbon by lightning strike	[6]
Solid bitumen, Mitov, Bohemia	HPLC	Formed by pillow lavas cutting black shales	[18]
Coals, Yunnan, China	HPLC	Unknown	[19]
Dinosaur egg, Xixia, China	TOFMS; HPLC	Unknown	[21]
Shock-produced breccias; Onaping Formation, Sudbury, Ontario, Canada	LD-TOFMS	Carbon-rich impactor; pyrolysis of organic matter	[22]
	LD-TOFMS; HPLC/UV-Vis		[23]
	HPLC/UV-Vis		[26]

EC – electron capture; EI – electron ionization; FTIR – Fourier-transform infrared spectrometry; FTMS – Fourier-transform mass spectrometry; HPLC/UV-Vis – high-performance liquid chromatography plus ultraviolet-visible spectral analysis; HRTEM – high-resolution transmission electron microscopy; LD – laser desorption; MS – mass spectrometry; NMR – nuclear magnetic resonance spectroscopy; TD – thermal desorption; TOFMS – time-of-flight mass spectrometry; XRD – X-ray diffraction.

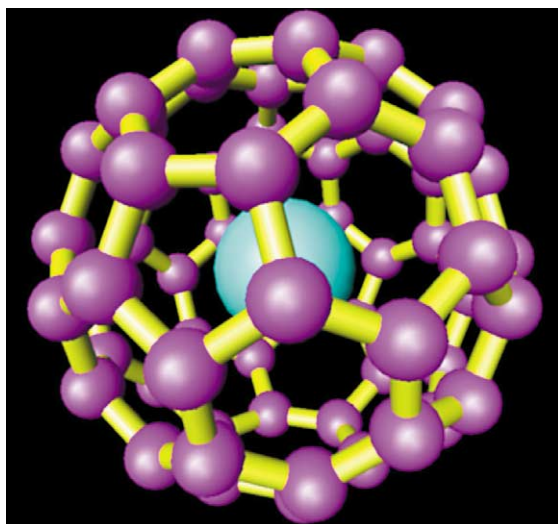


Fig. 3. C_{60} molecule with trapped foreign atom in its center.

4. Fullerene analyses

A wide range of analytical measurements has been used to detect and measure fullerenes in natural samples (Table 1). Mass spectrometry is the most widely used method because of its ability to determine the fullerene identities at the molecular level. Although [3] measured fullerenes directly from solid, untreated, rock chips, most and perhaps all subsequent analyses have been of concentrates made by dissolving samples in any of a variety of solvents. The concentrate is then commonly placed onto a stainless steel probe tip and irradiated with a focused CO_2 laser beam, which results in simultaneous desorption and ionization of the sample into the mass spectrometer. Both positive and negative ions can be generated by such laser-desorption mass spectrometry (LD-MS), and either type can be measured. Although LD-MS is powerful for characterizing fullerenes, there is a risk of generating them from carbon-rich material that was free of fullerenes before laser radiation (laser ablation was the method first used by Kroto et al. to synthesize fullerenes from graphite [1]). This complication depends, among other things, on the laser power density and is more pronounced in the positive-ion than in the negative-ion mode [39]. Details of fullerene gener-

ation by a CO_2 laser are given by Kasuya et al. [40].

Although most published fullerene analyses use LD-MS, the original report of Buseck et al. [3] utilized both it and thermal desorption mass spectrometry (TD-MS), a non-pulsed technique that eliminates the potential problem of fullerene generation. The sample is also placed on a probe tip, but this time the probe is heated to between 200 and 500°C to desorb neutral fullerene molecules. Rather than using photons such as in LD-MS, these molecules are then ionized by electrons to yield either positive or negative ions. Such mass spectrometry overcomes the potential problem of creating fullerenes in samples that were initially free of them, thus providing an important check on the LD-MS experiments.

Instead of using mass spectrometry, Heymann et al. [41] selected high-performance liquid chromatography (HPLC) in combination with UV-visible spectroscopy to detect fullerenes, as have others (e.g. [21,28,37]). The work of Heymann established HPLC as a sensitive and reliable analytical method for measuring fullerenes at low concentrations. However, Taylor and Abdul-Sada [42] challenged HPLC analyses because of both the risk of interferences at the same retention times as fullerenes and the problem of contami-

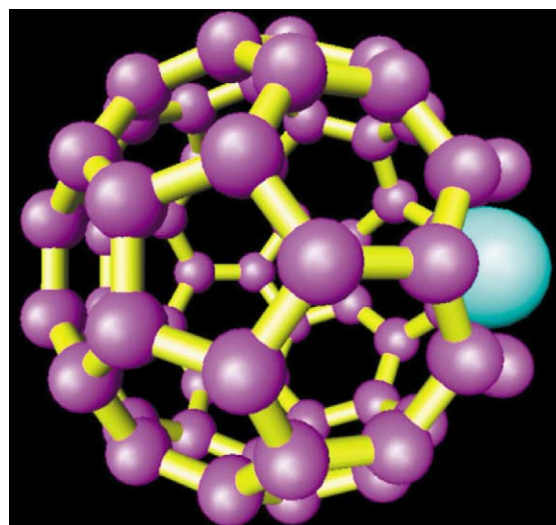


Fig. 4. Schematic diagram of a C_{60} molecule trapping a foreign atom (cf. [31]).

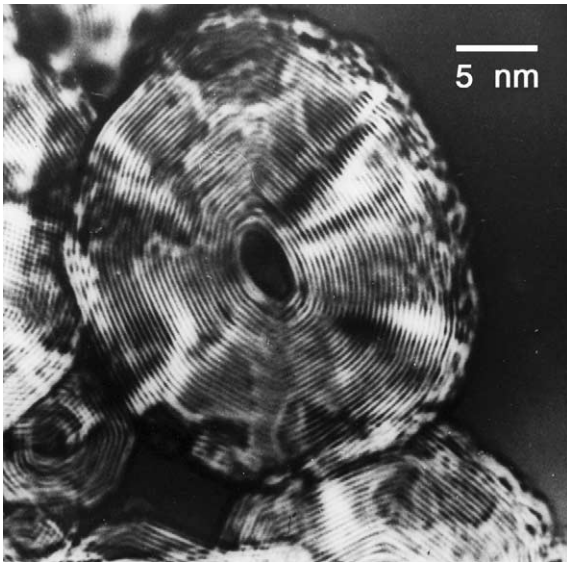


Fig. 5. Carbon 'onions' from the Allende meteorite (cf. [43]).

nation. They state that fullerenes can form thin films on flasks and other glass surfaces and can remain there 'tenaciously' in spite of vigorous cleaning efforts.

Becker and colleagues, who primarily detected fullerenes through the use of LD-MS, reported many of the natural occurrences of fullerenes; they confirmed some of their results using HPLC and Raman spectroscopy. Other techniques that produced positive results include HRTEM, powder X-ray diffraction, and ^{13}C nuclear magnetic resonance spectroscopy (Table 1).

Natural fullerenes only appear to occur at close to the lower analytical detection limits, but they have been detected by a variety of analytical techniques, all of which also resulted in negative values on blank samples. Nonetheless, the record is such that reports of geological fullerenes must be viewed with care. Many occurrences are 'once only' reports and validations of specific measurements by independent observers are needed. Some, like the LDEF fullerenes [34], might have been generated by particle impact on the collector in the same way as can occur through LD-MS, while others, such as fullerenes in a fossil dinosaur egg [21], seem sufficiently improbable and lacking of explanation that uncritical acceptance is risky.

Use of C_{78} or C_{84} , both of which are available commercially, as internal standard 'spikes' would increase confidence in LD-MS analyses.

5. Giant fullerenes

The discovery of fullerenes and much of the initial work focused on the most abundant varieties, C_{60} and C_{70} . There are, however, also reports of larger natural fullerenes, sometimes called 'giant' fullerenes. Our HRTEM images of acid-residue concentrates from the Allende carbonaceous chondrite [43] (Fig. 5) were recognized by Becker et al. [44] as probably the first recording of extraterrestrial fullerenes. These are large and closely resemble the concentric carbon layers in the 'carbon onions' that are presumed to be related to fullerenes [45,46]. An uncertainty arises because similar images have not subsequently been reported from Allende, raising the possibility that these images are of artifacts produced during sample preparation or transmission electron microscopy (TEM) observation³. We subsequently used HRTEM for imaging fullerite [49], the name given to crystalline fullerenes, and Harris et al. [50] imaged features that could be individual giant fullerenes. In spite of the formidable problems with locating specific targets such as fullerenes if present in only tiny amounts, TEM may be the best available technique for locating such large molecules in meteorites.

The low solubilities of the large fullerenes (A. Smith, personal communication, February 2001) make it difficult to extract them from solid samples, and low volatilities limit the effectiveness of TD-MS measurements. LD-MS can be conducted on unprocessed solid samples, but it is prone to two types of problems: (1) as discussed above, the LD-MS process can itself generate fullerenes;

³ Allende contains other such 'once-only' mineral sightings, e.g. cordierite [47] and a sodalite chondrule (Brian Mason, personal communication, April 10, 2001). On the other hand, Zwanger et al. [48] found that concentrically layered carbon shells are 'dissipative structures' that are thermodynamically unstable.

although negative ions can reduce this complication, the large fullerenes have low electron affinities, making it problematic to detect these species in such an LD-MS experiment. (2) The high masses of the large fullerenes, combined with the natural isotopic distribution of carbon, makes accurate mass measurements of such species difficult if one desires to measure the fullerene molecules with their trapped contents intact.

As an example of the above problem, the mass spectrum of a sample of pure C_{200} consists of several peaks with mass-to-charge (m/z) ratios between 2400 and 2407 as a result of both ^{12}C and ^{13}C in the sample, with $m/z=2402$ as the most abundant species (Fig. 6). Such multiple peaks could mask signals from light atoms, such as hydrogen or helium, trapped within some of the fullerene cages or attached to the molecules as ligands; the trapped atoms would be hard to detect unless accurate isotope-ratio measurements were performed or a high-mass-resolution instrument were used. For example, the mass resolving power required to separate $^{12}C_{200}He$ from $^{12}C_{196}^{13}C_4$ is greater than 200 000 and requires accurate isotope-ratio measurements or a high-mass-resolution instrument. Most LD-MS instruments cannot make such accurate isotope-ratio measurements, nor do they have sufficient resolution to distinguish these closely spaced peaks. Obviously,

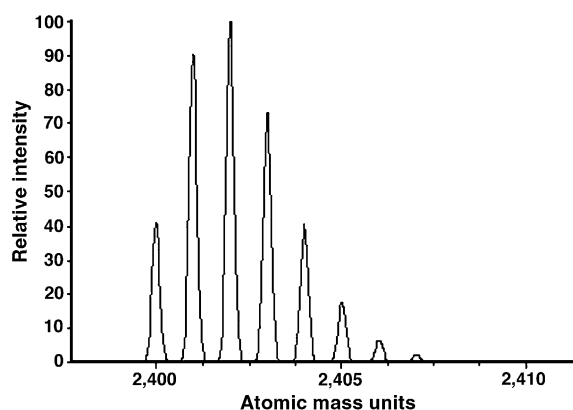


Fig. 6. Calculated mass spectrum of C_{200} at a mass resolution of 10 000 (full width at half maximum), assuming a natural isotopic distribution of ^{12}C and ^{13}C atoms (courtesy, R.L. Hettich).

under such conditions it can be difficult to determine the exact identity of the species or even the presence of hydrogen or helium atoms, significantly complicating the unambiguous mass identification of large fullerenes. For all of these reasons, the analysis of large fullerenes remains problematic.

Becker et al. [24,29] lessened some of the concentration problems by using solvents with higher boiling points than are normally used for concentrating fullerenes. Their published LD-MS measurements of the concentrates show peaks characteristic of fullerenes, and they report molecules as large as C_{800} from the Allende and Murchison meteorites. These molecules are far larger than other natural fullerenes reported through mass spectrometry.

6. Discussion; trapping of noble-gas atoms

The occurrence of natural fullerenes remains both intriguing and puzzling. Becker et al. [29] state that fullerenes are ‘highly resistant to metamorphism’ and are ‘a robust tracer in the geological environment’, but their scarcity, high reactivity [51,52] and low abundances suggest the opposite. Serious analytical problems provide potential pitfalls: (a) sample contamination at low levels, including on glassware, is a major concern; (b) interferences in retention times for HPLC is a potential problem, especially when complex natural mixtures are examined; (c) fullerenes can be generated from carbon-rich materials by the LD process. None of these problems is insurmountable, but analytical care is clearly required.

The natural fullerenes apparently have origins that vary with their type of host rocks. Those in carbonaceous meteorites conceivably formed during chondrule formation or other early high-temperature events. Fullerenes are known to form in flames, and those reported from rocks from along major stratigraphic boundaries (K–T, P–T) possibly formed through wildfires set by impacts or were introduced by the impactor. The fullerenes from the Sudbury impact structure remain problematic because there were apparently not enough fullerenes in the impactor, and formation from

local carbon is problematic because there was not much local source carbon or carbonate [53]. The origin of the fullerenes in shungite and some of the other occurrences listed in Table 1 is not known.

The reports of noble gases encapsulated within natural fullerenes [23,24,29] are probably the most intriguing aspect of these molecules. There are, however, important unresolved questions. Farley and Mukhopadhyay [54], Isozaki [55] and Braun et al. [56] took issue with some of the results of [29]; although many of these concerns were answered by [57], it would be desirable to have independent confirming results. It is unclear how fullerenes could have survived the high temperatures of the impacts that are inferred to have brought them to Earth during the K–T, P–T, and Sudbury events, and it is equally surprising that they retained their noble-gas contents through these highly energetic episodes. Mukhopadhyay et al. [58] examined samples from the Sudbury Onaping formation and detected a ^3He content compatible with that implied by the fullerene data of Becker et al. [23]. However, Mukhopadhyay et al. found neither evidence for an extraterrestrial He component nor indications that fullerene hosts the ^3He in this rock. In addition, B. French has pointed out (personal communication, March 2001) that the short-duration, experimental He-loss data for fullerenes presented by Becker et al. ([23], Fig. 2) imply that virtually all encapsulated He would be lost from natural fullerenes in periods $\ll 1$ Ma, even under geologically benign conditions. The Sudbury fullerene results appear contradictory.

The conclusion that noble gases are encapsulated in natural fullerenes is presented with confidence by Becker et al. [23,24,29]. However, the measurements require high sensitivities and the results are based on sample splits analyzed on separate instruments at different times and places. Low gas contents plus overlaps with peaks that result from the natural abundance of ^{13}C (1.1% of total carbon) make it difficult to obtain direct mass-spectrometric measurements of noble gases within fullerenes on a single instrument. Such spectra were published for He in natural fullerene [23] as well as for Ar [33], Kr and Xe [59] in

synthetic fullerene. Although the occurrence of the noble gases in the fullerene products of solvent extraction is presumably diagnostic, it is also possible that minor amounts of other gas carriers might have survived extraction. It would be more satisfying if the same mass spectra that show the natural fullerenes would also provide evidence of the encapsulated noble gases.

7. Summary and outlook

Much work has been done on geological fullerenes, and there are numerous intriguing reports of their occurrence. However, important open issues remain. These include:

- Why do fullerenes only occur in low abundance in geological samples?
- Is there a solid-state mechanism that produced the geological fullerenes or did they all form through an energetic event sufficient to generate a plasma (although a plasma origin seems incompatible with some of the geological occurrences)?
- Their rarity and low abundance seem to suggest geological instability and yet they occur in extremely old rocks. How or why did they survive?
- Why have so many attempts to detect fullerenes in meteorites been unsuccessful and why are the successful measurements of extraterrestrial fullerenes restricted to only three of the many meteorites analyzed?
- What effects, if any, would ‘spikes’ of C_{78} or C_{84} as analytical internal standards have on the reported fullerene abundances and types?
- Will direct measurements, rather than on separate aliquots, confirm that the noble gases are actually enclosed within the cages of natural fullerenes?

It remains for the future to see how these questions resolve. In spite of the many reports of natural fullerenes, their origin and occurrence remain elusive. I encourage more investigators to become involved with the problem, using a wider range of analytical methods, so that the distribution of fullerenes and encapsulated gases in geological samples can be confidently established, or dis-

proved, by additional multidisciplinary investigations, preferably on similar or identical samples. Many of the materials studied to date are rare or difficult to obtain, but the Onaping Formation, the impact breccia from which both fullerenes and encapsulated noble gases have been reported, is widely available and can be easily obtained in kilogram quantities for study. The verification of fullerene occurrences in this unit, and the determination of their horizontal and vertical distribution within the Sudbury impact structure, would be important steps in understanding the formation of fullerenes through unusual extraterrestrial events.

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