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Fullerenes from a Fulgurite

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Peaks at 720 and 840 atomic mass units were identified by mass spectrometry in a sample extracted from a fulgurite, which is a glassy rock that forms where lightning strikes the ground. The peaks are interpreted as arising from C_{60} and C_{70} and the associated peaks as produced from other fullerenes. The intense conditions generated by the lightning not only melted the rock it struck and fused the associated soil but also allowed fullerenes to form, presumably from the organic debris in the soil.

Fullerenes (C_{60} and C_{70}) were first identified in products from laser ablation experiments (*1*). They were subsequently synthesized with the use of carbon arcs (*2, 3*), combustion (*4, 5*), and ion beams (*6*), all under intense conditions that rarely occur in the natural environment. However, fullerenes were recently reported from a geological sample (*7*). In that report, Buseck *et al.* speculated that lightning strikes might provide extreme conditions that could resemble those used for the laboratory synthesis of fullerenes. Therefore, we decided to investigate fulgurites, the geological products of lightning, for the presence of natural fullerenes.

Lightning produces a wide variety of unusual effects, one of which is that the ground area where the lightning strikes tends to melt. The peculiar branching forms produced in this way commonly have dendritic structures reminiscent of the stepped leaders of lightning. The resulting fulgurites typically consist of glass, the result of the intense heat produced by the lightning. They are usually tubular, with hollow interiors and fragile, porous exteriors. The inner diameters of tubular fulgurites are generally in the millimeter to centimeter range, comparable to typical lightning channel diameters (*8*). Fulgurites contain phases that require temperatures exceeding 2000 K (*9–11*), reflecting the extreme conditions that can be produced locally by lightning.

We examined a variety of fulgurites derived from different materials and locations (Table 1). Portions of each sample were pulverized and placed into an extraction thimble that was then loaded into a clean Soxhlet apparatus. The samples were cycled in the Soxhlet system for 24 hours (toluene was used as the solvent) (*12*). All glassware was cleaned and baked after each extraction. Upon completion, the solvent was evaporated, and the extracts were redissolved in ~1 ml of distilled toluene. A droplet of the concentrated sample was placed onto a copper substrate for analysis by time-of-flight (TOF) mass spectrometry. The samples were desorbed from the copper surface by a 355-nm ultraviolet neodymium:yttrium-aluminum-garnet laser with an ~0.9-mJ, 8-ns pulse focused to ~0.5 mm^2. An accelerating voltage of +20 kV produced a TOF mass spectrum of positively charged ion fragments.

The fulgurite found on Sheep Mountain, Colorado, near Wolf Creek Pass (37°29′N, 106°54′W), contained detectable fullerenes; the others did not. The glass of the Sheep Mountain sample is black and vesicular along the outer parts of the tube. Figure 1 shows a portion of the fulgurite tube perched on top of the host rock from which it presumably formed. The fulgurite is fused to that rock, which also contains melted pockets within its bulk, clearly showing that the lightning caused extreme heating but only in highly localized regions. The black glass within the pockets (a few millimeters in diameter) is free of macroscopic vesicles and has the appearance of dense black obsidian. The centers of the larger pockets are hollow and so may indicate the existence of small glass tubes passing through the interior of the rock. They occur up to at least 5 cm from the fulgurite on the rock exterior.

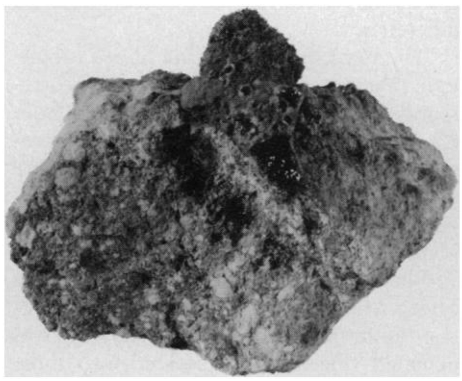

Fig. 1. The fullerene-bearing fulgurite from Sheep Mountain. The tubular, glassy mass on top and the pockets within the rock were produced by lightning (a few millimeters across).

Table 1. Fulgurite samples studied.

Source material	Location	Source	Identification no.	Contains fullerenes?
Ash-flow tuff	Sheep Mountain, CO	Chuck Lewis		Yes
Quartz sand	Florida	U.S. National Museum	74118.0000	No
Quartz sand	Alamosa County, CO	David New		No
Glacial till	Winans Lake, MI	Eric Essene		No
Pseudofulgurite*	Maryland	U.S. National Museum	116544.0000	No

*This sample was produced when a broken high-power line fell to the ground.

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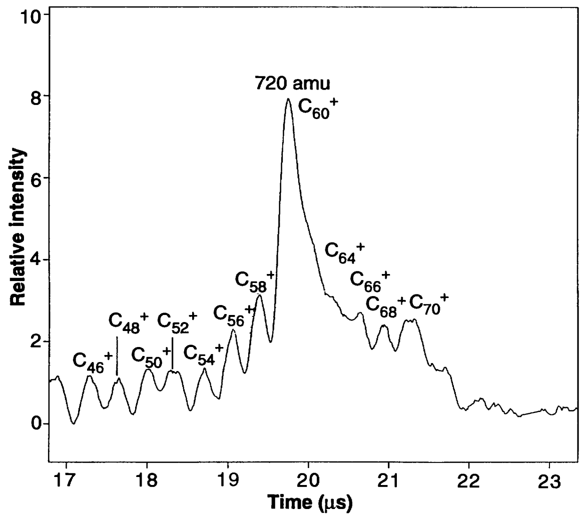

Fig. 2. Positive-ion TOF mass spectrum of the Sheep Mountain sample showing C_{60}^+ at 720 amu, C_{70}^+ at 840 amu, and other fullerenes.

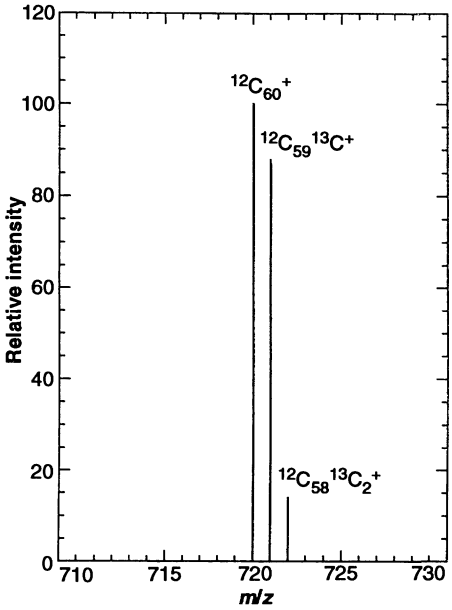

Fig. 3. Positive-ion electron ionization mass spectrum ($m/\Delta m$ = 800) of C_{60}^+ of the Sheep Mountain sample. Although the amount of sample was less than that required for accurate statistical measurements, the relative isotopic abundances of C_{60} are 100% for a mass-to-charge ratio m/z = 720, 88% for m/z = 721, and 14% for m/z = 722.

We subjected a piece of the host rock that was not fused by the lightning to the same solvent extraction and TOF testing as the fulgurite; fullerenes were not detected. Blank and standard C_{60} samples were tested before and after each analysis. We also examined three dozen other geological samples by the previously outlined techniques and, with the exception of a reanalysis of the sample described in (7), detected no fullerenes. We are thus confident that neither contamination nor the instrumental technique is the source of the observed fullerenes.

The mass spectrum of the Sheep Mountain fulgurite (Fig. 2) shows peaks corresponding to C_{60}^+ and C_{70}^+. Peaks from C_{46}^+ to C_{58}^+ and C_{64}^+ to C_{68}^+ at increments of C_{2n}^+ are also present. To remove any concerns that the C_{60} might have been generated by the laser and to confirm the identification, we subsequently tested the 720-amu (atomic mass unit) region of the Sheep Mountain fulgurite extract by electron ionization mass spectrometry; C_{60} was detected (Fig. 3) and resolved into three peaks at 720, 721, and 722 amu (at a mass resolution, $m/\Delta m$, of 800), corresponding, respectively, to $^{12}C_{60}^+$, $^{12}C_{59}\,{}^{13}C^+$, and $^{12}C_{58}\,{}^{13}C_2^+$. The ratios of these peaks are 1:0.88:0.14. However, the spectrum is from a quantity of fullerenes near the detection limits of the mass spectrometer, and so we do not ascribe a high accuracy or significance to this ratio as compared to the expected calculated values of 1:0.67:0.24 for C_{60}.

The flank of Sheep Mountain where the fulgurite was found is covered with rocks from the Masonic Park Tuff (13), which has been described as a phenocryst-rich quartz latite (14). On the basis of its appearance in hand specimen and thin section, the specific sample from which the fullerene-bearing fulgurite formed appears to have been derived from an intermediate to felsic pyroclastic flow. It has a fine-grained ashy matrix and contains abundant shattered, angular crystals and lithic fragments. The major mineral constituents are calcic plagioclase feldspar, oxyhornblende, and pyroxene cemented within a fine-grained matrix. Other minerals include zircon, titanomagnetite, ilmenite, and apatite. There are banded vug fillings that probably consist of clay weathering products.

Latites and related rocks typically are essentially free of carbon; the single analysis of Masonic Park Tuff [table 6 in (14)] totals to 100.14% and indicates <0.05% CO_2, consistent with the above observations. Given the composition of the Sheep Mountain sample, the carbon required to form the fullerenes must have had an external source. The absence of fullerenes in the fulgurites we examined from sand dunes, which are among the most common type, suggests that the carbon did not arise from the air (such as, perhaps, from CO_2). The Sheep Mountain sample was surrounded by pine needles and cones. We hypothesize that they provided the necessary carbon.

We do not know the exact parameters of the lightning that presumably formed the fullerenes, but a consideration of average features can provide insight. We assume that the strike was of the negative cloud-to-ground variety, which is the case for over 90% of all lightning strikes to ground (15). From the cloud, lightning travels toward the ground in the form of a stepped leader (16). The potential difference between the leader tip and the ground can exceed 10 million volts (17).

Promontories on the ground nearest the leader cause the electric field to surpass the breakdown limit of the surrounding air. This breakdown causes a connecting leader to form from the object on the ground, in this case the host rock for our fulgurite, that propagates upward toward the stepped-leader channel. When these two leaders attach, the intense return stroke forms and propagates up the leader channel toward the cloud. This process causes the greatest lightning damage (17). The entire return-stroke process occurs in ~100 μs, delivering peak currents to ground of ~30,000 A (18). The release of return-stroke energies heats the channel to peak temperatures of 30,000 K (19). Channel pressures can reach tens to hundreds of atmospheres and then return to normal atmospheric pressure within microseconds (17). The rate of energy dissipation from a lightning discharge, for a channel radius of ~0.5 mm, peaks at 1.5×10^8 ergs/cm·μs (20). The energies, energy changes, and associated currents, voltages, and temperatures are truly extraordinary and well in excess of those used in the laboratory for fullerene synthesis.

Interesting features of the spectrum of the Sheep Mountain fulgurite are the existence of peaks at increments of 24 amu (C_{2n}^+) from C_{46}^+ to C_{58}^+ and C_{64}^+ to C_{68}^+ (Fig. 2). Although these peaks are possible fragmentation products of C_{60} and C_{70} generated during the laser desorption process (21, 22), lightning does typically occur in multiple, closely spaced strokes. Fragmentation to smaller fullerene species also could have occurred in our sample from secondary lightning return strokes on C_{60} and C_{70} that formed during prior strokes, similar to photodissociation processes described by Lykke *et al.* (*23*). Owing to the lack of an additional sample, further investigation into the origin of the fragments was precluded. Thus, their origin is indeterminate at this time.

The vapor environment in which fullerenes can form and then persist is of interest. The first step in fullerene formation involves vaporization of carbon into atoms, dimers, or both (*24, 25*). In our case, the fullerenes that were contained within the fulgurite formed in the presence of many other gases. These include all atmospheric gases in the lightning channel as well as materials vaporized on the ground by the strike. The techniques used to synthesize fullerenes provide evidence that fullerenes can form while in the presence of other gases. For example, in the combustion process, fullerenes form in the presence of hydrogen and oxygen (*4, 5*). In the laser ablation of polymers as well as of coals, fullerenes form in vapors containing nitrogen, sulfur, hydrogen, and oxygen (*26–28*). Bombardment of a polymer containing fluorine and hydrogen by a $^{127}I^{14+}$-MeV ion beam also produced fullerenes (*6*). Essene and Fisher (*10*) described highly reduced phases in a fulgurite, clearly indicating that the immediate, local region can differ greatly from the surrounding ambient environment. In this case also, the extreme effects of lightning are evident and were apparently conducive to fullerene formation.

Finally, Chibante *et al.* (*29*) indicate that fullerenes have finite lifetimes in the ambient air. The Sheep Mountain sample was collected in about 1980 (by C. F. Lewis) and appeared so fresh and free of breakage and sharp edges that it probably had not experienced the weathering associated with seasonal cycles.

The peculiar association of fullerenes with a fulgurite strongly suggests to us that the lightning was the causative agent for both. The only other fullerenes reported from the terrestrial environment occur in shungite (*7*), a coal-like rock found in Karelia, Russia. An obvious question is whether the formative agent for the shungite material was lightning. Unfortunately, we did not observe the shungite sample in the field, and so we cannot be certain that it is unrelated to a lightning strike. However, the occurrence of fullerenes in thin veinlets and the absence of evidence of localized melting, such as is typical of fulgurites, argue against an origin related to lightning. We thus tentatively conclude that the two samples have distinct geological histories and that their fullerenes are unrelated in origin.

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Buckytubes and Derivatives: Their Growth and Implications for Buckyball Formation

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Transmission electron microscopy (TEM) observations of graphite tubules (buckytubes) and their derivatives have revealed not only the previously reported buckytube geometries but also additional shapes of the buckytube derivatives. Detailed cross-sectional TEM images reveal the cylindrical cross section of buckytubes and the growth pattern of buckytubes as well as their derivatives. These observations of frozen growth stages of buckytubes and derivatives suggest a helical growth mechanism analogous to that of crystal growth via screw dislocations. The helicacy of buckytubes is analyzed by electron diffraction whereas the anisotropy of electronic structure is revealed by momentum transfer resolved electron energy loss spectrometry. Based on the TEM observations, it is proposed that buckytubes act as precursors to closed-shell fullerene (buckyball) formation and the possible steps in buckyball formation are outlined. In arc evaporation experiments in which residue rods (containing various amounts of buckytubes) were used as the starting anode for fullerene production, the amount of buckytubes in the rod was correlated with fullerene yield.

The synthesis, characterization, and properties of various all-carbon molecules, the fullerene family (buckyballs), have been on the research forefront since the large-scale production scheme developed by Krätschmer *et al.* (*1*). Recently, Iijima and co-workers (*2–4*) reported TEM observations of hollow graphitic tubules of nanometer scale (buckytubes). In particular, the large-scale buckytube synthesis method of Ebbesen and Ajayan (*5*) has stirred considerable interest similar to that after the Krätschmer *et al.* (*1*) discovery of large-scale buckyball synthesis.

We have synthesized gram-scale quantities of buckytubes and their derivatives based on an arc method similar to that of Ebbesen and Ajayan (*5, 6*). Most of the TEM observations were made by scraping the transition region between the "black ring" material and the outer shell and then dispersing the powder on a holey carbon TEM grid. Additional experiments were

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