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Extraterrestrial Helium Trapped in Fullerenes in the Sudbury Impact Structure

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Fullerenes (C_{60} and C_{70}) in the Sudbury impact structure contain trapped helium with a $^3He/^4He$ ratio of 5.5×10^{-4} to 5.9×10^{-4}. The $^3He/^4He$ ratio exceeds the accepted solar wind value by 20 to 30 percent and is higher by an order of magnitude than the maximum reported mantle value. Terrestrial nuclear reactions or cosmic-ray bombardment are not sufficient to generate such a high ratio. The $^3He/^4He$ ratios in the Sudbury fullerenes are similar to those found in meteorites and in some interplanetary dust particles. The implication is that the helium within the C_{60} molecules at Sudbury is of extraterrestrial origin.

Fullerenes (C_{60} and C_{70}) have recently been identified in a shock-produced breccia (Onaping Formation) associated with the 1.85-billion-year-old Sudbury impact structure (*1*). The presence of 1 to 10 parts per million (ppm) (*1*) of fullerenes in these samples from the Onaping Formation raises questions about the origin of fullerenes and about the potential for delivery of intact organic material to Earth by a large bolide (for example, an asteroid or comet). Because the Sudbury target rocks are poor in carbon (C), we have suggested that the fullerene C was extraterrestrial in origin (*1*). There are two possible scenarios for the presence of fullerenes in the Sudbury impact deposits: (i) that fullerenes are synthesized within the impact plume from the C contained in the bolide (*1*), or (ii) that fullerenes were already present in the bolide and survived the impact event. We examine here these possible sources of the Sudbury fullerenes by searching for noble gases trapped inside the fullerene molecule.

The correlation of C and trapped noble gas atoms in meteorites is well established (*2*). Primitive meteorites contain several trapped noble gas components that have anomalous isotopic compositions. For example, Black and Pepin (*3*) found anomalous Ne values in several primitive unmetamorphosed meteorites, and Anders and co-workers (*4*) reported Kr and Xe values in the Murchison and Allende meteorites that are indicative of a presolar origin. Several C-bearing phases have been recognized as carriers of trapped noble gases, including SiC, graphite, and diamond (*5*). Fullerenes have been suggested as a carrier of noble gas components in carbonaceous chondrites (*6*); however, so far, the identification of fullerenes (C_{60} and C_{70}) is limited to a single occurrence in the Allende meteorite (*7*).

The C_{60} molecule is large enough to enclose the noble gases He, Ne, Ar, Kr, and Xe but is too small to contain diatomic gases such as N_2 or triatomic gases such as CO_2. Recent experimental work has demonstrated that (i) He is incorporated into C_{60} during fullerene formation 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 C–C bonds during step-heating under vacuum (*8*). The unique thermal release patterns for He encapsulated within the C_{60} molecule ($He@C_{60}$) are similar to the patterns for acid-resistant residues of carbonaceous chondrites (*9*), suggesting that fullerenes could be a carrier of trapped noble gases in meteorites.

To determine the noble gas abundances and isotopic ratios for the fullerenes, we undertook a systematic study of acid-resistant residues generated from samples collected at the Dowling and Capreol townships within the C-rich layer (Black Member) of the Onaping Formation (*10*). If the fullerenes were formed in the impact plume, then the isotopic ratios of the trapped gases would reflect the composition of Earth's atmosphere (that is, terrestrial) at the time of the impact. If, on the other hand, the fullerenes were present in the bolide before impact, then the isotopic ratios of the trapped gases would have an extraterrestrial signature (*3*, *4*, *11*).

We demineralized samples using HF-BO_3, and the carbonaceous residue was refluxed with toluene to extract fullerenes (*1*, *12*, *13*). An ultraviolet-visible absorption spectrum of the toluene fractions revealed a peak at 330 nm indicative of C_{60} (*14*). The toluene fractions were then analyzed by laser desorption (linear and reflectron) time-of-flight mass spectrometry (*1*, *15*). All of the toluene fractions showed a strong peak at mass-to-charge ratio (m/z) of 720 atomic mass units (amu), which corresponds to $C_{60}{}^+$, and a peak at 840 amu, which corresponds to $C_{70}{}^+$ (Fig. 1A). In addition, the mass spectrum of the Capreol toluene fraction (Fig. 1B) showed a strong peak at 720 amu corresponding to $C_{60}{}^+$ and a peak at 724 amu corresponding to $^4He@C_{60}{}^+$. The mass spectrum (Fig. 1B) of this sample indicates that not only are fullerenes present in the Sudbury deposits, but they contain trapped He (*16*).

Synthetic $He@C_{60}$ molecules release He upon heating (*8*). We evaporated a separate toluene fraction from Sudbury (containing fullerenes) to dryness, heated the residues incrementally, and measured the ^3He and ^4He concentrations (Table 1) using a mass spectrometer (*17*, *18*). The He concentrations in the Dowling sample correspond to 67 atoms of ^4He per 10^7 fullerene molecules and 37 atoms of ^3He per 10^{10} fullerenes. The ^3He release pattern for the Capreol sample (Fig. 2) is similar to the release pattern determined for synthetic fullerenes (*8*). The release of ^3He from the Dowling sample (Fig. 2) is somewhat greater at lower temperatures and is attributed to the preferential release of He from C_{70}. These measurements suggest that the He was released from fullerenes because no other acid-resistant He carrier phase, such as carbides or microdiamonds (*19*), was observed in our samples nor would such phases produce the release pattern characteristic of $He@C_{60}$ that we found upon heating.

The $^3He/^4He$ ratio (sum of all heating steps) was 5.88×10^{-4} for Capreol and 5.46×10^{-4} for Dowling. These ratios are higher than the accepted solar wind value of 4.4×10^{-4} (*20*) and higher by an order of magnitude than the maximum mantle value of 4.4×10^{-5} (*21*). Some meteorites have been reported to contain He with a higher $^3He/^4He$ ratio, produced by a combination of implantation and cosmic-ray bombardment (*20*). The $^3He/^4He$ ratios measured for the Sudbury fullerenes are higher than the 3.0×10^{-4} value reported for interplanetary dust particles collected in the stratosphere and in deep-sea sediments (*22*). The implication of the $^3He/^4He$ results for the Sudbury fullerenes is that the He within the

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C_{60} molecule is also of extraterrestrial origin. In order to retain extraterrestrial He, fullerenes must have survived the impact that produced the Sudbury crater (*23*).

Table 1. Concentration of the He released during step-heating (*17*). The $^3He/^4He$ ratio (R) is compared to the average value for terrestrial air (R_{air}).

Temperature (°C)	^3He (10^{-9} cm³/g)	^4He (10^{-6} cm³/g)	$^3He/^4He$ (R/R_{air})	Fraction of ^3He released per minute
		Dowling 1		
400	7.51	22.06	245	0.0018
500	31.17	51.93	432	0.0046
600	22.43	34.79	464	0.0043
700	27.59	41.36	480	0.0069
800	22.77	48.86	335	0.0138
850	3.56	10.25	250	0.0167
Total	115	209	393	
		Capreol 2		
350	0.51	0.61	601	0.00012
450	3.32	7.66	312	0.00082
550	9.20	15.98	414	0.00239
650	9.11	15.75	416	0.00276
750	25.62	40.88	450	0.00932
800	18.88	32.10	423	0.01557
850	1.33	2.67	358	
Total	68.0	115.6	423	

If the fullerenes had formed as a result of the impact event, it seems likely that the $^3He/^4He$ ratio would reflect some contribution from Earth's atmosphere, resulting in a $^3He/^4He$ ratio lower than solar wind values. The rigid-sphere incorporation model developed for the synthetic fullerenes (*8*) suggests that the probability that a noble gas atom will be trapped within a fullerene molecule during formation is a function of the size of the fullerene cavity and the density of the gas. According to this model (*8*), the ^3He partial pressure for the Sudbury fullerenes at the time of formation is estimated to have been 0.5 torr (versus 10^{-10} torr in the present-day atmosphere), suggesting that a mechanism other than a terrestrial synthesis is needed. The ratios of the C_{60} isotopic mass peaks for the fullerenes (*1*) show a possible enrichment in ^{13}C, which would also indicate an extraterrestrial source of C.

Other possible terrestrial production mechanisms for the ^3He, such as cosmic-ray bombardment on Earth, may account for only a tiny fraction of the total ^3He in the C_{60} because surface exposure of the Sudbury rocks for more than 5×10^9 years would be necessary to generate the measured amount (*24*). Nuclear reactions in the terrestrial environment over geologic time are also capable of generating high $^3He/^4He$ ratios, and this process has been invoked to explain the high $^3He/^4He$ ratios determined in some diamonds (*25*). The dominant production mechanism is $^6Li + n \rightarrow {}^3He + {}^4He$ (^3H decays to ^3He). However, in typical crustal rocks, the $^3He/^4He$ ratio of this nucleogenic component is 10^{-8}, or 10^{-4} times that observed for Sudbury fullerenes. Experimental results (*26*) indicate that, even under ideal conditions in which the Li atom is attached to the C_{60} molecule and then irradiated with a low thermal neutron flux (10^{14} neutrons per square centimeter), only four ^3H atoms were incorporated per 10^{10} C_{60} molecules. The irradiation also destroyed a large portion of the fullerenes. The experimental yield is only 11% of the concentration (37 ^3He atoms per 10^{10} C_{60}) observed, demonstrating that nuclear reaction implantation is not an effective mechanism for getting He into fullerenes.

The presence of extraterrestrial He@C_{60} in the Sudbury impact deposits suggests that fullerenes may indeed be present in some meteorites or comets and that fullerenes may also be a unique carrier of noble gases in certain extraterrestrial environments. In addition, on the basis of the He release and temperature-pressure stability estimates for

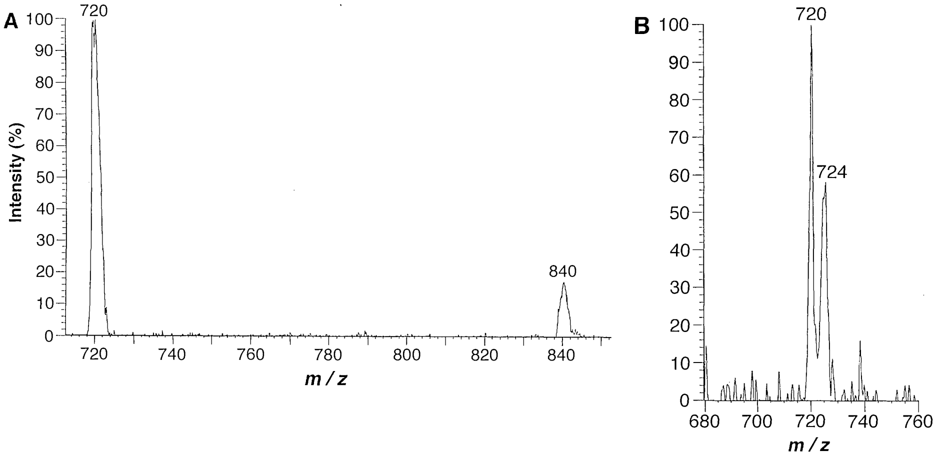

Fig. 1. (**A**) Laser desorption (reflectron) mass spectrum (LDMS) of the Dowling sample showing peaks at *m/z* of 720 and 840 amu. Intensity is given in arbitrary units. The Dowling sample had significantly more C_{70}^+ (804 amu) than the Capreol sample (the C_{70}^+ peak for Capreol was barely above background). (**B**) The LDMS of the Capreol sample. By carefully calibrating the mass spectrometer at an acceleration voltage of 5 keV, we were able to observe a mass spectrum that included C_{60}^+ and $C_{60}He^+$ at 724 amu (a peak for 724 amu was not observed in any of the authentic fullerene standards). This analysis maximizes the detection for C_{60}^+ and $C_{60}He^+$, and thus the peak intensities shown are exaggerated and do not reflect the absolute abundances of the ions. Under the LDMS conditions, it is unlikely that $C_{60}He^+$ would survive if He were bound to the exterior of the C_{60}^+ molecule. These results suggest that He is in the interior of the Sudbury C_{60}^+ molecule, indicating an endohedral complex (*16*).

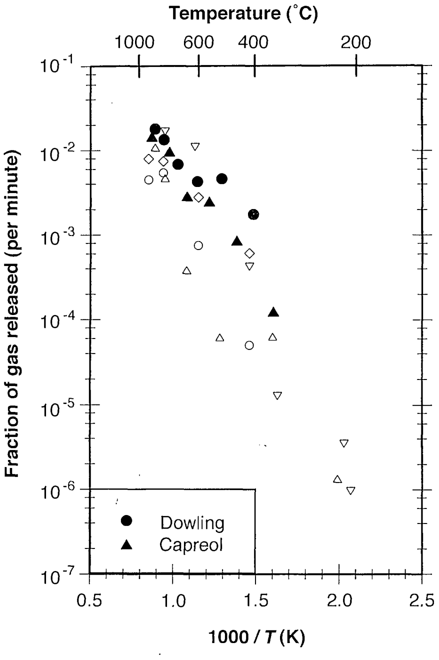

Fig. 2. Temperature (T)-dependent ^3He release for the Capreol (▲) and Dowling (●) samples. Open symbols are the release rates for the synthetic fullerenes (C_{60} and C_{70}) taken from (*8*): (▽ and △) ^3He, (○) ^4He, and (◇) Ne.

He@C_{60} [see Fig. 2 and (*8*)], some portion of the Sudbury bolide must have remained well below the He@C_{60} stability temperature (1000°C). The survival of He@C_{60} during a bolide impact such as the one that created the Sudbury crater is unexpected (*27*) and suggests that the exogenous delivery of organic material to the early Earth may be more favorable than has been previously assumed. The extensive fragmentation of a bolide during passage through Earth's atmosphere may be one way of preserving some of the extraterrestrial organic material during an impact event.

An important remaining consideration is the type of environment that would favor fullerene formation. The diffuse interstellar medium (ISM) is a hostile environment, and several processes may act to destroy fullerenes (for example, sputtering or shocks). However, there is evidence for the existence of a solid form of C that is of the size of a large molecule or a small particle, having survival characteristics against ultraviolet photodissociation and destructive shocks (*28*). Whether this material is in the form of polycyclic aromatic hydrocarbons (*28, 29*) or is related to fullerene molecules (*30*) remains an intriguing question.

Because the Sudbury fullerenes exhibit $^3He/^4He$ ratios that exceed those associated with the solar wind and because of the high He pressure of incorporation (~1000 torr at 1000°C), we favor a scenario in which He is trapped in the Sudbury fullerenes before the condensation of the solar nebula (*30*). However, alternative mechanisms occurring in the ISM, such as spallation reactions and selective He implantation, may also be responsible for the higher than solar $^3He/^4He$ ratios. The paucity of H appears to be necessary to promote the C shell closure required for fullerene formation (*31*). Environments in which the formation and preservation of fullerenes may be favorable (*30, 31*) include those for which the H concentrations are much lower than the mean cosmic abundance ($H/He < 10^{-9}$), the C/He ratio is ~0.004, and the C/O ratio is >1. These conditions are similar to the outflows from Wolf Rayet and R Coronae Borealis stars (*30–33*). Confirmation of a presolar origin for the Sudbury fullerenes will require the identification of anomalous isotopic compositions of Ne, Kr, and Xe [for example, the pure ^{22}Ne component (*5*)] that may be contained within the fullerene molecule (*34*) and precise determination of the Sudbury fullerene C isotopic ratio.

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11. We have considered the possibility that some of the Sudbury fullerenes may have opened up as a result of metamorphism (temperatures of 300° to 400°C at pressures of 3 to 5 kbar in the Onaping rocks). If exchange of He took place, atmospheric He ($^3He/^4He \sim 1.4 \times 10^{-6}$) or radiogenic ($^3He/^4He \sim 10^{-8}$) components typical for crustal rocks would have been added to the fullerene molecule.
12. The common approach for the demineralization of meteorites is to use HF-HCl acids to concentrate and isolate organic matter and C. This procedure often leads to the formation of fluoride salts, which are insoluble and could potentially trap organics and carbonaceous materials. Here we selectively dissolved neoformed fluorides in a two-step process by reaction with BF_3, a water-soluble gas, generated by the reaction of H_3BO_3 with HF and water. Then BF_3 reacts with fluoride salts to form water-soluble fluoroborates. The demineralized portion (typically 80 to 100 g of powdered bulk rock treated with acid yields ~1 g of carbonaceous residue) of the Onaping rock was then put into an extraction thimble, placed into a Soxhlet apparatus, and refluxed with toluene for 24 hours. The excess toluene was evaporated to dryness, leaving a small amount (microgram quantities) of residue. This residue was then redissolved in toluene and concentrated to ~1 ml, yielding a bright reddish solution.
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17. The toluene extracts containing the Sudbury fullerenes were loaded into a metal tube furnace within a glove box under a N_2 atmosphere in preparation for noble gas analyses. After heating the samples in vacuum for 3 days at 100°C, which completely removed any residual toluene, we then incrementally heated (60 min per step) the microgram quantities (about 200 μg of C_{60} per aliquot) of fullerene residues to release the trapped noble gases (*8*). Noble gases He, Ne, and Ar were cryogenically separated and then sequentially measured with a VG 5400 noble gas mass spectrometer fitted with a Johnston electron multiplier with pulse counting electronics on the axial collector [R. J. Poreda and K. A. Farley, *Earth Planet. Sci. Lett.* **113**, 129 (1992)]. A resolution of 550 ($m/\Delta m$) achieved complete baseline separation of $^3He^+$ and HD^+. Absolute abundances of ^3He, ^4He, ^{36}Ar, ^{40}Ar, and ^{22}Ne were calculated by peak height comparison to a standard of known size (0.101 cm^3 of air at standard temperature and pressure) with an accuracy of ±3%. The small amount of ^{22}Ne and ^{36}Ar at all temperatures (10^{-11} and 10^{-10} cm^3, respectively) was equivalent to the average blank. Average blank levels were 1×10^{-10} cm^3 for ^4He and 2×10^{-16} cm^3 for ^3He. The contribution of adsorbed atmospheric He can be estimated from the measured ^{22}Ne and the $^4He/^{22}Ne$ ratio in air of ~3.1. In all of the temperature steps above 200°C, this contribution was negligible (<1% of ^4He and <0.01% of ^3He). In comparison to the fullerene toluene fractions, heating 10 mg of the bulk acid residue to 800°C released ^3He and ^4He at levels about three times the extraction blank.
18. Atmospheric isotopic ratios of Ne and Ar were measured for the Dowling and Capreol samples in all temperature fractions. The measured gas indicates that the presence of an adsorbed atmospheric component or that a certain percentage of the fullerene molecules has opened up over geologic time, allowing atmospheric gases to be incorporated. Blank levels of ^{22}Ne were about 10^5 times the blank levels for ^3He (~10^{-11} cm^3 for Ne versus ~10^{-16} cm^3 for He). If the anomalous gas component has a solar $^3He/^{22}Ne$ ratio of 1.3 [M. Ozima and F. Podosek, in *Noble Gas Geochemistry* (Cambridge Univ. Press, Cambridge, 1983)], then we need to achieve a factor of 10 reduction in our ^{22}Ne background to observe any anomalous Ne isotopic ratios.
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34. Recent calculated equilibrium constants for the incorporation of noble gas atoms inside the C_{60} molecule (two different models were used to calculate the potential between the noble gas atom and each C atom) indicate that the potentials agree for encapsulation of He and Ne but disagree strongly for encapsulation of Kr and Xe. If this is the case, then the C_{60} molecule may preferentially incorporate the lighter noble gases over the heavier noble gases (H. A. Jiménez-Vásquez and R. J. Cross, *J. Chem. Phys.*, in press).
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Orientation-On-Demand Thin Films: Curing of Liquid Crystalline Networks in ac Electric Fields

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Electric fields have been used in the processing of thin film, liquid crystal thermosets to produce cured network structures selectively oriented either parallel or perpendicular to a film substrate. Orientation, which depends on both the liquid crystal nature of the thermosets and their dielectric anisotropy, is selected by varying the frequency of the alternating electric field and is locked into a robust network structure by a cross-linking reaction that takes place concurrent with orientation. Structural changes and orientation during the curing reaction were measured in real time with synchrotron x-ray diffraction. Diffraction studies show that, before curing in a modest electric field of 1 volt per micrometer, reorientation can be induced by changing, for example, from a high-frequency (>1000 hertz) to a low-frequency (<50 hertz) electric field, which causes a 90-degree flip in the molecular orientation.

The ability to control organization at the molecular level is revolutionizing the design of materials and leading to new structures, which range from self-assembled monolayers (*1*) to mesoporous inorganics (*2*). The molecular assemblies used in the formation of these complex compositions are usually built from aliphatic compounds with long alkyl segments that produce spontaneous organization similar to surfactants. Layer-by-layer assembly, which makes use of ionic and hydrogen-bond formation between alternate layers of polymers, has also been used to form stable, lamellar structures useful for applications such as light-emitting diodes (*3*). Liquid crystals (LCs), however, have similar self-assembly characteristics for forming complex phases and provide additional features, such as their remarkable ability to respond to applied fields.

When aligned with external fields, LCs can be used in a wide range of applications, including optical filters, displays, and data storage. By locking-in the anisotropic properties of LCs (*4*, *5*) through the formation of covalently bonded networks, controlled-order materials can be created. The development of LC thermosets (small-molecule LC precursors that can link up to form such networks) has been motivated by their potential use in structural applications where the need for more versatile polymeric materials with tunable strength and stiffness and well-controlled mechanical anisotropy exists (*6*).

Our goal in this study was to create a molecular system in which one could not only align the components in external fields to form anisotropic networks but also selectively control and lock-in the direction of alignment by network formation. Such materials have physical and chemical properties that are very different along each orientation, and one can conceive of using photochemistry, for example, to form films with order and orientation set in specified regions. By establishing orientation in a controlled fashion, one can vary the properties of such a film on demand before cross-linking with a single chemical precursor to form materials with tunable transport, optical, and mechanical properties. Orientation, which occurs in seconds in the uncross-linked thermoset under modest electric fields of $E = 1$ V/μm, is retained at temperatures more than 100°C above the glass transition because of the presence of the network.

Studies carried out previously in our laboratories on LC cyclic siloxanes in an E field showed frequency-addressable switching, that is, frequency-dependent orientation selection either parallel or perpendicular to an applied ac electric field (*7*). Our experience with the processing of these low–molecular weight mesomorphic compounds suggested that we could orient LC

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